



## Applications of Light Stable Isotopes (C, O, H) in the Study of Sandstone Diagenesis: A Review

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**Abstract:** This article reviews the applications of light stable isotope, including carbon, oxygen and hydrogen, in the studies on origin and formation temperature of authigenic carbonate, quartz and clay minerals. Theoretical knowledge and analytical methods for major light stable isotopes are introduced in detail. Negative and positive  $\delta^{13}\text{C}$  values indicate significant differences on the origin of carbonate cements. The  $\delta^{18}\text{O}$  value is an effective palaeotemperature scale for authigenic minerals formation. Various fractionation equations between  $\delta^{18}\text{O}$  and temperature are proposed for carbonate cements, quartz cements and clay minerals, whose merit and demerit, applicable conditions are clarified clearly. Clumped isotope analysis can reconstruct the temperature of carbonate precipitation with no requirement on the  $\delta^{18}\text{O}$  of initial waters, which makes temperature calculation of carbonate cements formation more convenient and accurate. Hydrogen and oxygen isotopes mainly reflect the origin of diagenetic fluid for clay mineral formation, providing reliable evidence for diagenetic environment analysis. This work aims at helping researchers for better understanding the applications of light stable isotope in sandstone diagenesis.

**Key words:** light stable isotopes, carbonate cements, quartz cements, clay minerals, sandstone diagenesis

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### 1 Introduction

Isotopes can be divided into two fundamental kinds, namely stable and radioactive species. So far, more than 1500 isotopes have been discovered, but only 20% are stable ones (Hoefs, 2009). Radioactive isotopes can be classified as being either artificial or natural. Natural ones are more interested by geologist, since they are the basis for radiometric dating method (Rasmussen, 2005; Bui et al., 2016; Zhang et al., 2017). The foundations of stable isotope geochemistry are the thermodynamic properties of isotopic substances (Urey, 1947). Most of the elements are mixtures of at least two isotopes, whose relative abundance may vary substantially (Eiler and Schauble, 2004). Isotope fractionation is pronounced when the mass differences between the isotopes of a specific element are large relative to the mass of the element (Friedman and O'Neil, 1977). For the light elements, one isotope is predominant, the others being present only in trace amounts. Thus, isotope fractionations are especially large for the light elements, which can provide valuable information for understanding diagenetic processes (Ziegler et al., 1994; Bristow et al., 2011; Horita et al., 2014; Denny et al., 2017). Carbonate cements, quartz overgrowth and authigenic clay minerals are the major

diagenetic minerals in sandstone reservoirs (Lynch et al., 1997; Bjørlykke, 1998). Diagenetic minerals have been studied extensively in recent years, whose origins, time and distributions, in principle, are the main issues (Lander and Bonnell, 2010; Lehmann, et al., 2011). Isotopic composition is mainly determined by the physicochemical environment in which the rocks formed, and molecules bearing the light isotope will react slightly more readily than those with the heavy isotope during a chemical reaction (Hoefs, 2009). In order to better clarifying the origins, time and distributions of diagenetic minerals, light stable isotope geochemistry, especially carbon, oxygen and hydrogen isotopes, have been widely used in sandstone diagenesis studies (Santos Jr., 2007; Mansour et al., 2014; Sample et al., 2017; Denny et al., 2017). However, applicable conditions in the use of light stable isotope reflecting sandstone diagenesis, especially suitable temperature range for isotope fractionation equations between  $\delta^{18}\text{O}$  and temperature, are always ignored by some researchers (Horita et al., 2014). In response to this, a systematic review is made on application of light stable isotope (C, H, O) in sandstone diagenesis including isotope analytical methods, origin and formation time of diagenetic minerals, which will be very useful for researchers in better understanding these issues and improving the applicability in future studies.

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### 1.1 Overview on major light stable isotopes used in sandstone diagenesis

Among the various light stable isotopes, carbon ( $^{12}\text{C}$  and  $^{13}\text{C}$ ), oxygen ( $^{16}\text{O}$  and  $^{18}\text{O}$ ) and hydrogen isotopes ( $^1\text{H}$  and  $^2\text{H}$ ) are the most common ones applied to the analysis on sandstone diagenesis (Hoefs, 2009). Previous studies showed that the difference in absolute isotope ratios between two substances is sufficient for most geochemical purposes (Friedman and O'Neil, 1977). The absolute isotope ratios  $R$  refers to the relative abundance ratio of two isotopes of a specific element, which is always written as the ratio of the heavy (rare) isotope to the light (common) isotope, such as  $R=^{13}\text{C}/^{12}\text{C}$ ,  $R=^{18}\text{O}/^{16}\text{O}$  and  $R=\text{D}/\text{H}$ . In order to show the stable isotope abundances and variations far more precisely during geological processes,  $\delta$  value is used almost exclusively isotope geochemistry studies, which can be expressed as follows (Friedman and O'Neil, 1977):

$$\delta(\text{‰}) = \left( \frac{R_S - R_{\text{STD}}}{R_{\text{STD}}} \right) \times 1000 \quad (1)$$

where  $R_S$  is the ratio of two isotopes in the studied sample, i.e.  $R_S = (^{13}\text{C}/^{12}\text{C})_S$ ,  $(^{18}\text{O}/^{16}\text{O})_S$ ,  $(\text{D}/\text{H})_S$ , and  $R_{\text{STD}}$  is the corresponding ratio in a standard sample. Negative  $\delta$  values indicate that the sample is depleted heavy isotopes by that amount relative to the standard. On the contrary, positive  $\delta$  values reveal that the samples are enrichment in heavy isotopes relative to the standard.

In general, analysis results of oxygen isotope in liquid samples are reported in comparison with SMOW standard, while the PDB standard was used for minerals. As a result, interconversion between two standards is necessary in some cases, such as sandstone diagenesis. The classic transformation equations were proposed by Coplen (1983) to make the conversion:

$$\delta^{18}\text{O}_{\text{V-SMOW}} = 1.03091 \delta^{18}\text{O}_{\text{PDB}} + 30.91 \quad (2)$$

$$\delta^{18}\text{O}_{\text{PDB}} = 0.970020 \delta^{18}\text{O}_{\text{V-SMOW}} - 29.98 \quad (3)$$

The SMOW standard is also used for reporting hydrogen isotope compositions (Craig, 1961). The standard for reporting carbon isotope compositions is PDB. In order to make the application more convenient, some typical international and China standards for carbon, oxygen and hydrogen isotopes are summarized in the Table 1 as follow.

Isotope fractionation is the basis for application of light stable isotopes in sandstone diagenesis (Ziegler et al.,

1994). The isotope fractionation factor between two substances, A and B, is defined as (Hoefs, 2009):

$$\alpha_{\text{A-B}} = R_{\text{A}}/R_{\text{B}} \quad (4)$$

Combined with equation (1) and (4), the isotope fractionation factor  $\alpha_{\text{A-B}}$  can be expressed as:

$$\alpha_{\text{A-B}} = \frac{1000 + \delta_{\text{A}}}{1000 + \delta_{\text{B}}} \quad (5)$$

The equation (5) can be further transformed to the form:

$$\ln \alpha_{\text{A-B}} = \ln(1000 + \delta_{\text{A}}) - \ln(1000 + \delta_{\text{B}}) \quad (6)$$

This logarithm function has added theoretical and experimental significance (Friedman and O'Neil, 1977). For perfect gases,  $\ln \alpha$  varies as  $1/T^2$  and  $1/T$  in the high- and low-temperature limits, respectively (Bigeleisen and Mayer, 1947). Additionally, it shows a well linear relationship between  $1000 \ln \alpha$  and  $1/T^2$  in mineral pairs or mineral-water pairs (Friedman and O'Neil, 1977). The isotope fractionation factor  $\alpha$  is related to equilibrium constant ( $K$ ) for isotope exchange reactions in the following way:

$$\alpha = K^{1/n} \quad (7)$$

where  $n$  is the number of atoms exchanged. For simplicity, isotope exchange reactions are usually written such that only one isotope is exchanged. Thus, the equilibrium constant can be approximately equal to the fractionation factor.

### 1.2 Carbonate clumped isotope used in sandstone diagenesis

Carbonate clumped isotope thermometry is a newly developed technique, which allows independent access to both temperature and water  $\delta^{18}\text{O}$  values based on measurements of the degree of ordering of  $^{13}\text{C}$  and  $^{18}\text{O}$  into bonds with each other (making the  $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$  ion group) in lattices of carbonate minerals (Ghosh et al., 2006; Eiler, 2007; Eiler, 2011; Mangenot et al., 2017). Carbonate minerals contains 20 different isotopologues, or isotopic variants of the carbonate ion group (Ghosh et al., 2006). Among them,  $^{12}\text{C}^{16}\text{O}_3^{2-}$  that contains no rare isotopes is the most abundance one with 98.2%, followed by  $^{13}\text{C}^{18}\text{O}_3^{2-}$  with about 1.1%,  $^{12}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$  with about 0.6% and  $^{12}\text{C}^{17}\text{O}^{16}\text{O}_2^{2-}$  with about 0.11% (Ghosh et al., 2006). In a carbonate crystal at thermodynamic equilibrium, the relative abundances of the various carbonate ion isotopologues can be exemplified as (Ghosh et al., 2006; Eiler, 2011):

$$^{13}\text{C}^{16}\text{O}_3^{2-} + ^{12}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-} = ^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-} + ^{12}\text{C}^{16}\text{O}_3^{2-} \quad (8)$$

This reaction involves ordering or clumping of  $^{13}\text{C}$  and  $^{18}\text{O}$  into bonds with each other making the doubly substituted isotopologue  $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2^{2-}$  ion group (Fig. 1), which can be easily measured due to high relative abundance. Most importantly, this reaction has a temperature dependent equilibrium constant, since proportions of  $^{13}\text{C}$ - $^{18}\text{O}$  bonds in carbonate minerals are sensitive to their growth temperatures, independent of bulk isotopic composition (Schauble et al., 2006; Ghosh et al., 2006; Eiler, 2007; Guo et al., 2009; Eiler, 2011; Mangenot et al., 2017). Thus, clumped isotope analysis of carbonates can be used to reconstruct the temperature of carbonate precipitation that requires no assumptions about

**Table 1 Some typical international and China isotope standards after (Wang, 2000; Friedman and O'Neil, 1977)**

Element	Standard	Source
Hydrogen	V-SMOW	Standard mean ocean water; $\delta\text{D}=0.00\text{‰}$
	Peking University	Well water from Peking University; $\delta\text{D}=0.00\text{‰}$
Carbon	PDB	Peedee belemnite; $\delta^{13}\text{C}=0.00\text{‰}$
	NBS-19	White marble; $\delta^{13}\text{C}=1.95\text{‰}$
	NBS-20	Solenhofen limestone; $\delta^{13}\text{C}=-1.06\text{‰}$
	NBS-21	spectrographic graphite; $\delta^{13}\text{C}=-27.79\text{‰}$
	TTB-1	Limestone from Zhoukoudian, Beijing; $\delta^{13}\text{C}=0.58\text{‰}$
Oxygen	V-SMOW	Peedee belemnite; $\delta^{18}\text{O}=30.91\text{‰}$
	NBS-19	White marble; $\delta^{18}\text{O}=-2.20\text{‰}$ (PDB)
	TTB-1	Limestone from Zhoukoudian, Beijing; $\delta^{18}\text{O}=-8.49\text{‰}$ (PDB)

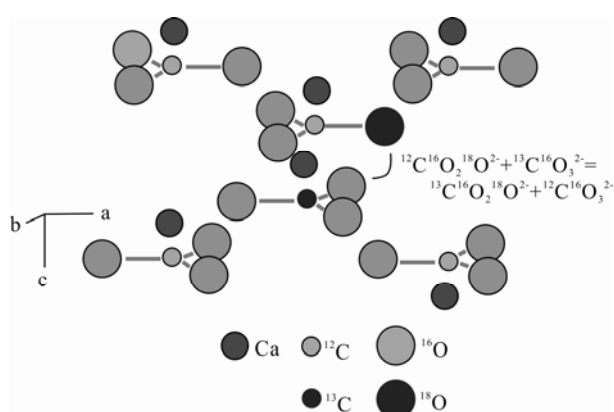


Fig. 1. Atomic structure of the calcite lattice, illustrating the homogeneous isotope exchange reaction between carbonate ion units on which carbonate clumped isotope thermometry is based (modified from Eiler, 2011).

the  $\delta^{18}\text{O}$  of waters from which analyzed carbonates grew (Eiler, 2007; Bristow et al., 2011; Jay et al., 2013; Hill et al., 2014).

The degree of clumping, expressed as  $\Delta_{47}$  in units of ‰, shows a systematic dependence on temperature (Ghosh et al., 2006; Came et al., 2007; Guo et al., 2009; Bristow et al., 2011; Mangelot et al., 2017).  $\Delta_{47}$  is defined as the difference in between the measured  $R_{47}$  value of the sample and the  $R_{47}$  value expected for that sample if its stable carbon and oxygen isotopes were randomly distributed among all isotopologues (Came et al., 2007). The  $\Delta_{47}$  value of  $\text{CO}_2$  can be calculated by (Eiler and Schauble, 2004; Eiler, 2007; Huntington et al., 2009):

where  $R_{47}$ ,  $R_{46}$ ,  $R_{45}$  are abundance ratios of masses 47,

$$\Delta_{47} = \left[ \left( \frac{R_{47}}{R_{47*}} - 1 \right) - \left( \frac{R_{46}}{R_{46*}} - 1 \right) - \left( \frac{R_{45}}{R_{45*}} - 1 \right) \right] \times 1000 \quad (9)$$

46 and 45 relative to mass 44, i.e.,  $R_{47} = (\text{mass}47)/(\text{mass}44)$ .  $R_{47*}$ ,  $R_{46*}$ ,  $R_{45*}$  are the corresponding ratios that would occur in the sample if it had a stochastic distribution.

The isotopologues with mass number of 44, 45, 46 and 47 can be shown as:

$$\begin{aligned} [44]^* &= [^{12}\text{C}][^{16}\text{O}][^{16}\text{O}] \\ [45]^* &= [^{13}\text{C}][^{16}\text{O}][^{16}\text{O}] + 2[^{12}\text{C}][^{16}\text{O}][^{17}\text{O}] \\ [46]^* &= 2[^{12}\text{C}][^{18}\text{O}][^{16}\text{O}] + 2[^{13}\text{C}][^{17}\text{O}][^{16}\text{O}] + [^{12}\text{C}][^{17}\text{O}][^{17}\text{O}] \\ [47]^* &= 2[^{13}\text{C}][^{18}\text{O}][^{16}\text{O}] + 2[^{12}\text{C}][^{17}\text{O}][^{18}\text{O}] + [^{13}\text{C}][^{17}\text{O}][^{17}\text{O}] \end{aligned}$$

where 2 is a symmetry number (Huntington et al., 2009).

Accordingly,  $R_{47*}$ ,  $R_{46*}$ ,  $R_{45*}$  can be expressed as:

$$\begin{aligned} R_{45*} &= R^{13} + 2R^{17} \\ R_{46*} &= 2R^{18} + 2R^{13}R^{17} + (R^{17})^2 \\ R_{47*} &= 2R^{13}R^{18} + 2R^{17}R^{18} + R^{13}(R^{17})^2 \end{aligned}$$

Finally, the equation (9) can be further transformed to the form as:

$$\Delta_{47} = \left[ \frac{R_{47}}{2R_{13} \times R_{18} + 2R_{17} \times R_{18} + R_{13} \times (R_{17})^2} - \frac{R_{46}}{2R_{18} + 2R_{13} \times R_{17} + (R_{17})^2} - \frac{R_{45}}{R_{13} + 2R_{17}} + 1 \right] \times 1000 \quad (10)$$

The numerator terms  $R_{47}$ ,  $R_{46}$  and  $R_{45}$  in equation (10) are derived from measured  $\delta_{47}$ ,  $\delta_{46}$  and  $\delta_{45}$  for the sample referenced to a working gas standard of nominally known isotopic composition (Huntington et al., 2009). The denominator terms  $R_{13}$  and  $R_{18}$  are derived from the measured  $\delta^{13}\text{C}$  (PDB) and  $\delta^{18}\text{O}$  (SMOW) values of the sample, while  $R_{17}$  is derived from  $R_{18}$  assuming a specific mass-dependent fractionation between  $R_{17}$  and  $R_{18}$  (Eiler, 2007; Huntington et al., 2009).

## 2 Methods of Light Stable Isotope Analysis

### 2.1 McCrea method for carbonate cement

#### 2.1.1 Bulk analysis

McCrea method is commonly used in carbon and oxygen isotope analysis of carbonate cements (McCrea, 1950). For bulk analysis, 5–20 mg carbonate powder in less than 200 meshes is used generally. The amount of samples can be increased to about 200 mg if carbonate content of the samples is too low. Detailed procedure of this method can be summarized as: (1) break the samples without detrital carbonate grains into less than 200 meshes; (2) put powder samples into main reaction tube and phosphoric acid (100%) into reaction branch and dewater in vacuum for one to two hours, then let phosphoric acid into main reaction tube at 25°C for 20 min; (3) collect  $\text{CO}_2$  gas and measure the carbon and oxygen isotopes using MAT-253 mass spectrometer. In general, carbon and oxygen isotope of  $\text{CO}_2$  gas collected at 25°C represent for calcite and 50°C for dolomite or ankerite (Morad et al., 1990). This method, however, cannot separate the different types of carbonate very effectively. Thus, the results of isotope analysis are then unable to reflect the accurate diagenetic information for the samples with mixed carbonate cements.

#### 2.2.1 Micro-drilling analysis

Micro-drilling is an effective way to improve the analysis accuracy of carbon and oxygen isotope, especially in the samples with different types of carbonate cements (Wang, 2000). Firstly, the samples should be polished as a thick thin section. Then, the drilling area and carbonate types are determined by polarizing microscope and cathode luminescence (CL). Afterwards, the carbonate cements are drilled from thin section by micro drill bit made by diamond plated mandrels (Siebel et al., 2005). Finally, the carbon and oxygen isotope of drilled carbonate cements are analyzed by the McCrea method. The demands for sample amount cannot be satisfied under the some condition due to the size limitation of drill bit ranging in diameter from 0.25 to 0.51 mm (Davidson et al., 1998), which constrains the use of this method.

#### 2.2 Oxygen isotope analysis in quartz cement

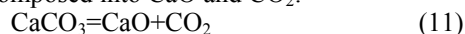
Physical separation of quartz cements is the key technique in measuring of oxygen isotope before in situ isotopic analysis method developed. Firstly, sandstones are disaggregated and soaked into the solution of 0.3 mol Na-citrate, 1.0 mol  $\text{NaHCO}_3$  and sodium dithionite to remove iron oxides. Then, the residues are separated into 7 fractions according to grain size, that is <20, 20–50, 50–

85, 85–160, 160–250, 250–500 and >500  $\mu\text{m}$ . Among them, 160–250  $\mu\text{m}$  grain size fraction is assumed to contain abundant quartz minerals with overgrowth (Brint et al., 1991). Accordingly, this fraction can be used to separate quartz overgrowth with follow procedure: (1) the 160–250  $\mu\text{m}$  fraction are solved in  $\text{NaHSO}_4$  and processed by  $\text{H}_2\text{SiF}_6$  (30%) for 3 days at 15–20°C to deplete feldspars; and the purity of quartz is identified by XRD (Brint et al., 1991); (2) corrode quartz with well-developed overgrowth and dust-rims with dilute HF (8%) for 14 to 48 h, then break them using ultrasonic agitation; (3) sieve the broken samples into four size fractions, including 30–53, 53–85, 85–160, 160–250  $\mu\text{m}$ , and quartz overgrowths are assumed to center in the finest size fraction (30–53  $\mu\text{m}$ ); (4) measure oxygen isotope of the separated quartz overgrowth according to the method proposed by Borthwickb and Harmon (1982), which can be summarized as reaction between quartz and  $\text{ClF}_3$  to generate  $\text{O}_2$ , and then transform  $\text{O}_2$  to  $\text{CO}_2$  by using the platinized carbon rod; (5) finally, oxygen isotope is measured by mass spectrometer like carbonate cements. This method, however, has significant limitations in oxygen isotope analysis of quartz cements and not satisfied in present studies, since the physical separation is not very accurate and some detrital quartz may be mixed into quartz overgrowth.

### 2.3 Laser microprobe analysis in carbonate and quartz cements

Laser microprobe analysis refers to using high-power laser beam (about 10–20  $\mu\text{m}$ ) to ablate a small area on the sample, and this process happened in a glass-topped vacuum chamber (Smalley et al., 1989). Firstly, the samples are made into slabs with the thickness of 0.03–0.1 mm. Then, the slabs are heated at 400°C in a nitrogen atmosphere or in a low-temperature oxygen plasma to remove the organic matters. Afterwards, the slab samples are placed on the glass slide without epoxy adhesives and put in the vacuum chamber. Finally, the analyzed cements and areas are selected and ablated by high-power laser beam. The laser can be operated in two modes: continuous and Q-switched (pulse) (Smalley et al., 1989).

For carbonate cements, after ablation, the minerals are decomposed into metallic oxide and  $\text{CO}_2$ . For example, calcites are decomposed into  $\text{CaO}$  and  $\text{CO}_2$ :



Then, the  $\text{CO}_2$  product is purified by passing through two cryogenic traps. Finally, carbon and oxygen isotopes of  $\text{CO}_2$  are measured in mass spectrometer (Smalley et al., 1989).

For quartz cements, the samples are vacuumized and fluorinated to remove residual moisture firstly. Then, the selected area is ablated by laser beam and  $\text{BrF}_5$  is injected into the vacuum chamber simultaneously. At high temperature, the  $\text{O}_2$  is generated from the reaction between  $\text{SiO}_2$  and  $\text{BrF}_5$ :



The generated  $\text{O}_2$  is purified and transformed to  $\text{CO}_2$  by using the platinized carbon rod. Finally, the oxygen of  $\text{CO}_2$  can be measured in mass spectrometer (Kelly et al., 2007).

Although this method can analysis carbon and oxygen isotope in situ, high temperature (800–1400°C) caused by laser ablation can result in fractionation of oxygen isotopes, especially in carbonate cements. Smalley et al (1989) suggested that there was slight difference in  $\delta^{13}\text{C}$  compared to McCrea method, while  $\delta^{18}\text{O}$  showed significant difference. This is one of the important reasons to explain why this technology is not widely used.

### 2.4 Nano Secondary Ion Mass Spectrometry (Nano SIMS) in carbonate and quartz cements

Secondary ion mass spectrometry (SIMS) or Nano secondary ion mass spectrometry (Nano-SIMS) are the effective methods for in situ oxygen isotope analysis of carbonate or quartz cements, which are characterized by high-precision, high-accuracy, high-spatial resolution in isotope analysis (Harwood et al., 2013; Śliwiński et al., 2016). When using this method for isotope analysis, the samples are prepared as thin sections firstly. Then, quartz standard UWQ-1 (12.33±0.07‰) (Kelly et al., 2007) and carbonate standard NBS-18 (23.2±0.1‰) or IAEA-CO-8 (22.7±0.2‰) (Yang et al., 2015; Śliwiński et al., 2016) are performed on oxygen isotope analysis. Carbonate and quartz samples are polished for a smooth, flat, low-relief surface and gold or carbon is plated on sample surface in preparation for ion microprobe analysis (Kelly et al., 2007). Cameca IMS-1280HR is the newest equipment for Secondary Ion Mass Spectrometry analysis. For quartz cement, the 3 nA  $^{133}\text{Cs}^+$  primary ion beam and 20 keV total accelerating voltage are focused on the target zones (Kelly et al., 2007), while the  $^{133}\text{Cs}^+$  primary ion beam changes to 2 nA for calcite and 30 pA for dolomite and ankerite, the accelerating voltage decreases to 10 keV for carbonate (Liu et al., 2015; Śliwiński et al., 2015). As to the areas within 6–10  $\mu\text{m}$ , the secondary  $^{18}\text{O}^-$  and  $^{16}\text{O}^-$  ions are accelerated by –10 keV (Śliwiński et al., 2015). Finally, two Faraday cups equipped with different resistors ( $1 \times 10^{10} \Omega$  and  $1 \times 10^{11} \Omega$ , respectively) are used to measure  $^{18}\text{O}^-$  and  $^{16}\text{O}^-$  isotopes simultaneously (Kelly et al., 2007). Although, this method can still induce some extent of fractionation, it is obviously better than laser microprobe analysis (Liu et al., 2015). Thus, NanoSIMS is more and more common to use in isotope analysis at present studies.

### 2.5 Clumped isotope analysis in carbonate cements

Clumped isotope analysis needs more samples and more accurate equipment, since the minor amount of doubly substituted isotopologue ( $^{13}\text{C}^{18}\text{O}^{16}\text{O}_2$ ) exists in carbonate minerals (mainly less than 100ppm) (Eiler and Schauble, 2004; Ghosh et al., 2006). The detailed analysis procedures can be summarized as: (1) 5 to 12 mg carbonate powder is selected to soak into the  $\text{H}_2\text{O}_2$  for 12 h to deplete the organic matter (Zheng et al., 2017); (2) the samples react with phosphoric acid (100%) at 90°C for 10 min, generating  $\text{CO}_2$  gas; (3) the  $\text{CO}_2$  gas is collected in cryogenic trap filled with liquid nitrogen and purified by He carrier gas; (4) the cryogenic trap with  $\text{CO}_2$  is warmed to –77.8°C to release  $\text{CO}_2$  gas; (5) the  $\text{CO}_2$  gas is allowed to pass through the gas chromatograph at –20°C for 15 min; (6) the further purified  $\text{CO}_2$  is then collected by

cryogenic traps and delivered into mass spectrometer (Ghosh et al., 2006; Huntington et al., 2009; Bristow et al., 2011). In mass spectrometer, three Faraday cups registered through  $3 \times 10^8$ ,  $3 \times 10^{10}$  and  $3 \times 10^{11} \Omega$  resistors to collect the  $\text{CO}_2$  with  $M/Z$  of 44, 45 and 46; and another three Faraday cups registered through  $1 \times 10^{12} \Omega$  resistors to collect the  $\text{CO}_2$  with  $M/Z$  of 47, 48 and 49 (Ghosh et al., 2006; Huntington et al., 2009). Analyzed results are standardized by comparison with reference gas whose bulk composition had been previously calibrated against  $\text{CO}_2$  from the reaction of standard samples and phosphoric acid, and whose abundance of mass-47 isotopologues was established by comparison with  $\text{CO}_2$  that had been heated to  $1000^\circ\text{C}$  to achieve the stochastic distribution (Ghosh et al., 2006).

## 2.6 Hydrogen and oxygen isotope analysis in clay minerals

Separation and purification of clay minerals from sandstones are the most important and difficult steps in hydrogen and oxygen isotope analysis. Previous studies showed that freezing and heating in repetitive ways is an effective method to separate clay minerals from coarse sand and silt size grains (Liewig et al., 1987). Hydrogen and oxygen isotope analysis in clay minerals can be made as follows: (1) select samples and determine the clay mineral type through XRD and SEM; (2) freeze and heat the sandstone samples from  $-10$  to  $15^\circ\text{C}$  again and again until the rocks are completely broken; (3) centrifugalize the crushed samples into 5 fractions, i.e.  $<0.1$ ,  $<0.2$ ,  $<0.5$ ,  $<1$  and  $<2 \mu\text{m}$ ; (4) check purity of the studied samples

under XRD or SEM, and select the purest samples for isotope analysis; (5) dry the pure samples in muffle at  $170^\circ\text{C}$  for 24 h to remove residual water; (6) generate  $\text{O}_2$  through the reaction of clay mineral with  $\text{BrF}_5$ , and then transform it to  $\text{CO}_2$  by using of platinized carbon rod; (7) prepare  $\text{H}_2$  through uranium reduction method; (8) deliver the  $\text{CO}_2$  and  $\text{H}_2$  into mass spectrometer to analysis hydrogen and oxygen isotopes.

## 3 Application of Light Stable Isotope in Carbonate Cement

### 3.1 Carbon sources of carbonate cements

Carbonate cements in the sandstone reservoirs have various carbon sources. Light stable isotopes  $\delta^{13}\text{C}$  can provide sensitive records of carbon cycling during calcite cements formation processes (Woo and Khim, 2006; Mansour et al., 2014; Denny et al., 2017). Curtis et al. (1972) found that carbonate derived from the marine reservoirs was richer in  $^{13}\text{C}$  than generally found in freshwater situations, which inspired the researchers to work on the carbon sources of the carbonate cements in subsequent studies. Afterwards, Irwin et al. (1977) proposed a classical model for marine sedimentary sequence with organic and carbonate rich, showing that generation of carbon dioxide distinctly different with variation of depth zones (Fig. 2). These studies surely suggested that carbonate cements in the sandstones could form from various carbon source distinguished by  $\delta^{13}\text{C}$  values. On this basis, a large amount of works have been done on carbon source of carbonate cement in the last few

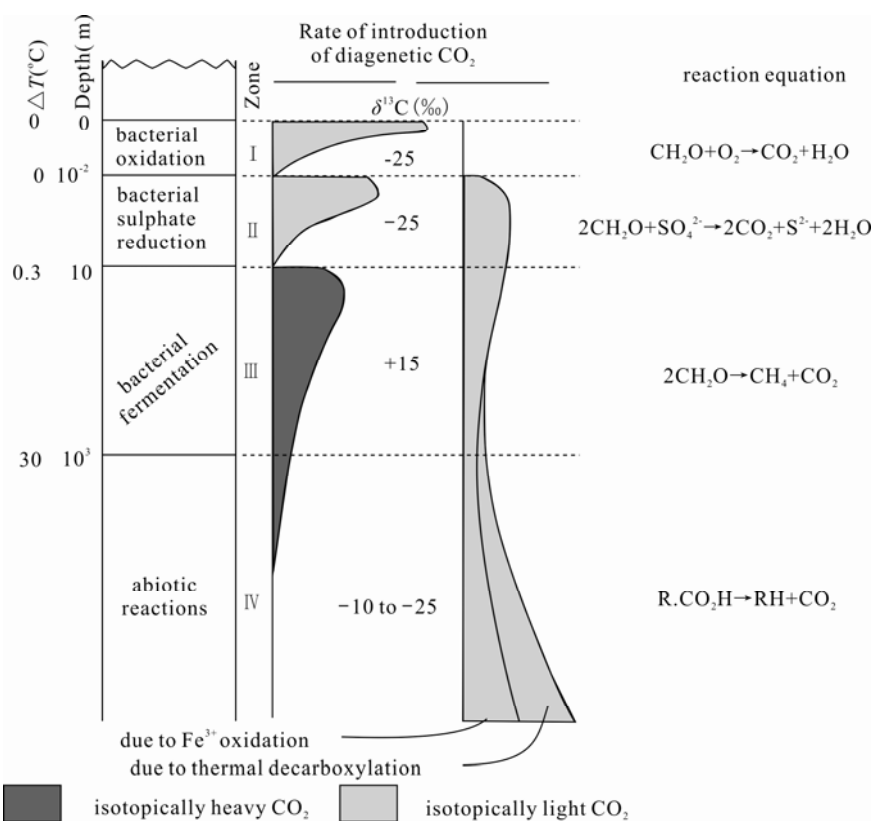


Fig. 2. Classical model of diagenetic  $\text{CO}_2$  within different depth zones (modified from Irwin et al., 1977).

decades. The ranges of  $\delta^{13}\text{C}$  value for each carbon source can be summarized in Fig. 3. Specifically, the positive  $\delta^{13}\text{C}$  values for calcite cements suggest that carbon sources are derivation of dissolved carbon from sea water ( $-4\text{‰}$ – $4\text{‰}$ ) (Bath et al., 1987), dissolved carbon from lacustrine water ( $2.9\text{‰}$ – $9.3\text{‰}$ ) (Cao et al., 2007; Lyu et al., 2018; Tian et al., 2018) or microbial fermentation of organic matter ( $8\text{‰}$ – $23\text{‰}$ ) (Macaulay et al., 2000; Head et al., 2003). While, the negative  $\delta^{13}\text{C}$  values for the calcite cements indicate that carbon sources include meteoric water influence ( $-7\text{‰}$ – $-3.5\text{‰}$ ) (Schmid et al., 2004), magmatic influence ( $-8\text{‰}$ – $-4\text{‰}$ ) (Hoefs, 1973; Xi et al., 2016; Zhu et al., 2017), decarboxylation of organic matter ( $-10\text{‰}$ – $-25\text{‰}$ ) (Irwin et al., 1977), bacterial oxidation ( $-13\text{‰}$ – $-25\text{‰}$ ) (Irwin et al., 1977; Bath et al., 1987), bacterial sulphate reduction ( $-30\text{‰}$ – $-25\text{‰}$ ) (Irwin et al., 1977; Suess and Whiticar, 1989; Jiang et al., 2017), hydrothermal induced methanogenesis oxidation ( $-36\text{‰}$ – $-27\text{‰}$ ) (Bristow et al., 2011; Bian et al., 2013) and biogenic induced methanogenesis oxidation ( $-66\text{‰}$ – $-35\text{‰}$ ) (Suess and Whiticar, 1989; Bristow et al., 2011).

### 3.2 Environments of carbonate cements precipitation

#### 3.2.1 Paleosalinity of pore water

Carbon and oxygen isotope may also serve, in some instances, to characterize a particular diagenetic environment. Keith and Weber (1964) proposed a Z-value to discriminate the carbonate sourced from marine or fresh water, which was given by the equation:

$$Z = a(\delta^{13}\text{C} + 50) + b(\delta^{18}\text{O} + 50) \quad (13)$$

where a and b are constants with 2.048 and 0.498, respectively. Notably, this equation only can be used in the Jurassic or younger than Jurassic. For the samples older than Jurassic, Z-value cannot reflect the paleosalinity of pore water effectively. According to large number of samples analysis, carbonate is classified as marine sources when Z-value is above 120 (Keith and Weber, 1964). On the contrary, carbonate is regarded as fresh water types

when Z-value is below 120 (Keith and Weber, 1964). For Z-value approximate to 120, carbonate cement was formed from a mixture of marine and fresh waters (Keith and Weber, 1964).

#### 3.2.2 Formation temperature based on oxygen isotopes

Oxygen isotope can act as a geological thermometer measuring the formation temperature of authigenic minerals in sandstone reservoirs (Clayton, 1972). The  $\delta^{18}\text{O}$  values of bulk carbonate samples generally decrease with increasing temperature, reflecting thermodynamically-controlled mineral-water isotope fractionation during carbonate precipitation (Schmidt et al., 2005). On this basis, several temperature calculation models have been proposed to calcite- $\text{H}_2\text{O}$  and dolomite- $\text{H}_2\text{O}$  systems at various temperature ranges in the last few decades (Clayton et al., 1968; Fritz and Smith, 1970; Northrop and Clayton, 1966; Matthews and Katz, 1977; Friedman and O'Neil, 1977; Vasconcelos et al., 2005; Schmidt et al., 2005; Schauble et al., 2006; Chacko and Deines, 2008). The model for calcite- $\text{H}_2\text{O}$  was relatively simple, and Friedman and O'Neil (1977) provided the paleotemperature calculation for calcite- $\text{H}_2\text{O}$  as:

$$1000\ln\alpha_{\text{calcite-H}_2\text{O}} = 2.78 \times 10^6/T^2 - 2.89 \quad (14)$$

where  $1000\ln\alpha_{\text{calcite-water}} = \delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}$ . Generally, this model can be appropriate for the temperature from 0 to  $500^\circ\text{C}$  (Friedman and O'Neil, 1977). By contrast, the model for dolomite- $\text{H}_2\text{O}$  is much more complicated than calcite- $\text{H}_2\text{O}$ . Various paleotemperature calculation models were proposed to dolomite- $\text{H}_2\text{O}$  based on theoretical and experimental studies at different temperature ranges. Horita (2014) summarized and made a detailed comparison of each model by considering different temperature ranges (Figs. 4a, 4b). It shows that calcite- $\text{H}_2\text{O}$  exhibits a very linear correlation with slightly smaller coefficient for the  $1/T^2$  term in different temperature ranges, while the dolomite- $\text{H}_2\text{O}$  varies in a complex way with increasing temperature (Figs. 4a, 4b). Additionally,

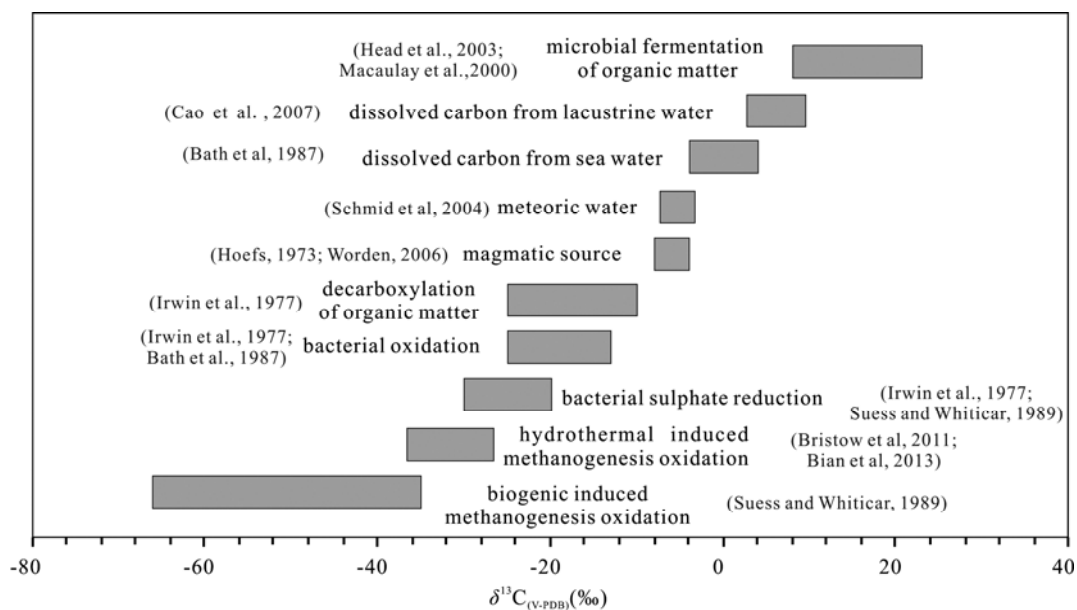


Fig. 3. Ranges of  $\delta^{13}\text{C}$  value for each carbon source to form carbonate cements in sandstones.

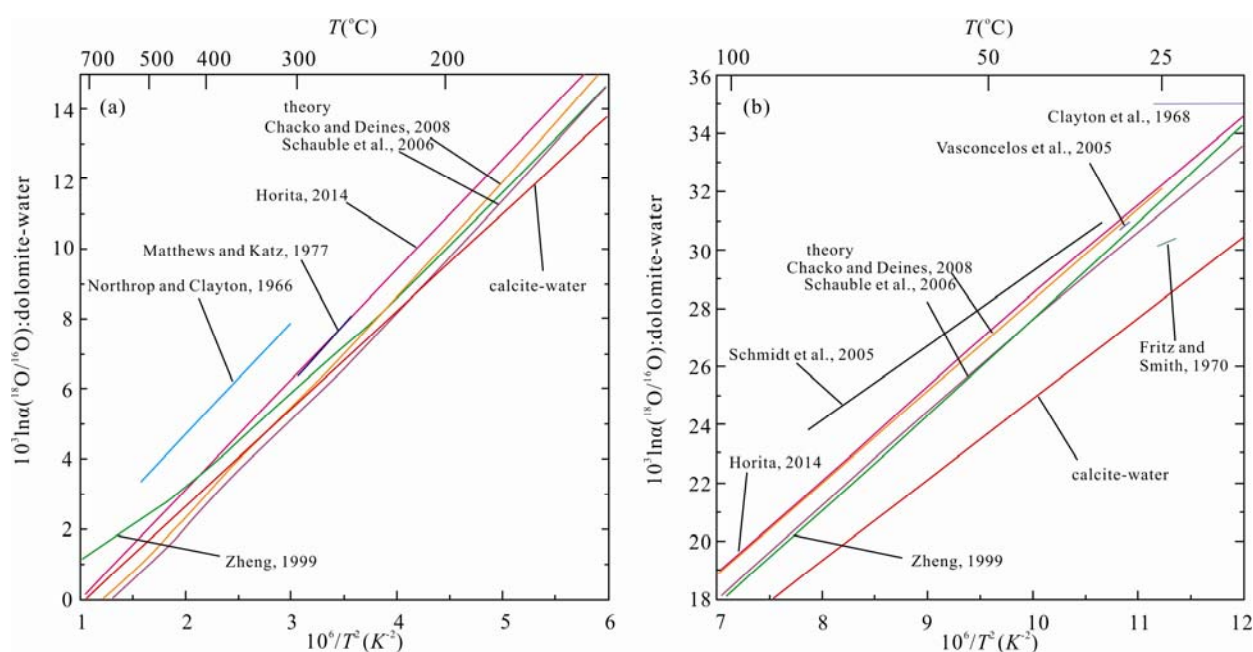


Fig. 4. Relationships between  $\delta^{18}\text{O}$  values and temperature summarized from experimental and theoretical studies. (a) relationships at high temperature; (b) relationships at low temperature (from Horita, 2014).

there is a significant difference between calcite-H<sub>2</sub>O and dolomite-H<sub>2</sub>O systems at low temperatures (Fig. 4b), whereas this difference is not so marked at high temperature ranges (Fig. 4a). Combined with the previous studies, the models for paleotemperature calculation are improved and perfected in recent years. For sandstone reservoir diagenesis studies, the ideal models are chosen as follows. When the temperature ranges from 25 to 80°C, the model for dolomite-H<sub>2</sub>O can be expressed as (Schmidt et al., 2005):

$$1000 \ln \alpha_{\text{dolomite-H}_2\text{O}} = 2.63 \times 10^6/T^2 + 3.12 \quad (15)$$

where  $1000 \ln \alpha_{\text{dolomite-water}} = \delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{water}}$ . At high temperatures from 80 to 350°C, however, the model for dolomite-H<sub>2</sub>O can be expressed as (Horita, 2014):

$$1000 \ln \alpha_{\text{dolomite-H}_2\text{O}} = 3.14(\pm 0.022) \times 10^6/T^2 - 3.14(\pm 0.11) \quad (16)$$

where  $1000 \ln \alpha_{\text{dolomite-water}} = \delta^{18}\text{O}_{\text{dolomite}} - \delta^{18}\text{O}_{\text{water}}$ . In the equations above,  $\delta^{18}\text{O}$  values for calcite and dolomite can be measured easily using various analytical methods mentioned above, such as McCrea method, laser microprobe analysis and NanoSIMS analysis. The values of  $\delta^{18}\text{O}$  for initial waters, however, are unknown, which severely constrains temperature calculations in diagenesis studies (Mangenot et al., 2017). At present, the most common way used for obtaining  $\delta^{18}\text{O}$  of initial water is reverse calculation according to fluid inclusion thermometry (Mangenot et al., 2017; Mernagh, 2015). Other methods include empirical statistics from previous references or using of standard sea water or fresh water  $\delta^{18}\text{O}$  values based on Z-value distinction (Xi et al., 2015). Although these methods can provide a relative temperature to show timing sequence of diagenetic minerals, it is difficult to get accurate temperature and forming time for authigenic minerals.

### 3.2.3 Formation temperature based on clumped isotope

The recently developed carbonate clumped isotope (or  $\Delta_{47}$ ) paleothermometry is based on an internal equilibrium inside the carbonate lattice, which allows to independently access to both temperature and initial water  $\delta^{18}\text{O}$  value (Ghosh et al., 2006; Eiler, 2007). This means that the experimentally determined  $\Delta_{47}$ - $T$  calibrations could successfully unravel precise and accurate crystallization temperatures for a variety of natural carbonate precipitation conditions without influence of carbonate mineralogy or composition (Bonifacie et al., 2017), pH and the salinity of the carbonate parent fluids (Hill et al., 2014). Thus, problems caused by lacking of initial waters  $\delta^{18}\text{O}$  values in paleotemperature calculation based on oxygen isotope were effectively resolved. Firstly, Ghosh et al. (2006) provide a relationship between  $\Delta_{47}$  and  $10^6/T^2$  in the studies of coral formation, which was widely used in calculation of calcite precipitation temperature over a period of time. This relationship can be described as the equation:

$$\Delta_{47} = 0.0592 \times 10^6/T^2 - 0.02 \quad (17)$$

where  $T$  is the temperature in Kelvin and phosphoric acid digestions of calcite are at 25°C. On this basis, the predicted temperature calibration lines for different carbonate clumped isotope thermometers, including aragonite, calcite, dolomite and magnesite were established (Guo et al., 2009) (Fig. 5). However, these functions could only be appropriate for the low temperatures from 0 to 50°C (Ghosh et al., 2006) but unsuitable for deep burial diagenetic calcite cements. In order to further studies on high temperature diagenesis, Guo et al. (2009) developed the predicted calibration lines for calcite, aragonite, dolomite, and magnesite representing the temperature range 260–1500 K, which can be described as follows:



$$\text{Calcite } \Delta_{47} = -\frac{3.33040 \times 10^9}{T^4} + \frac{2.32415 \times 10^7}{T^3} - \frac{2.91282 \times 10^3}{T^2} - \frac{5.54042}{T} + 0.23252 \quad (18)$$

$$\text{Aragonite } \Delta_{47} = -\frac{3.43068 \times 10^9}{T^4} + \frac{2.35766 \times 10^7}{T^3} - \frac{8.06003 \times 10^3}{T^2} - \frac{6.09300}{T} + 0.22893 \quad (19)$$

$$\text{Dolomite } \Delta_{47} = -\frac{3.31647 \times 10^9}{T^4} + \frac{2.29414 \times 10^7}{T^3} - \frac{2.38375 \times 10^3}{T^2} - \frac{5.71692}{T} + 0.21502 \quad (20)$$

$$\text{Magnesite } \Delta_{47} = -\frac{3.31658 \times 10^9}{T^4} + \frac{2.19871 \times 10^7}{T^3} - \frac{2.83346 \times 10^3}{T^2} - \frac{8.39513}{T} + 0.19897 \quad (21)$$

where  $T$  is the temperature in Kelvin and phosphoric acid digestions of carbonate minerals are assumed to be at 25°C. Recently, Bonifacie et al. (2017) reported a  $\Delta_{47}$

calibration for dolomite samples that were precipitated at known temperatures from 25 to 350°C, which aimed to provide more accurate, precise and standardized temperature estimates than current models based on  $\Delta_{47}$  measurements, particularly for temperatures above 50°C. The linear regression between  $\Delta_{47}$  and  $1/T^2$  for describing all dolomite samples is expressed as (Bonifacie et al., 2017):

$$\Delta_{47} = 0.0428 (\pm 0.0033) \times 10^6 / T^2 + 0.1174 (\pm 0.0248) (r^2 = 0.997) \quad (22)$$

Notably, the equation (22) was calculated for  $\Delta_{47}$  data averaged by growth temperatures and weighed from the well-known standard deviation on carbonate reference materials corrected with the t-distribution factor for the 95% confidence interval (Bonifacie et al., 2017; Fig. 6). For the carbonate minerals with statistically indistinguishable compositions, the linear regression between  $\Delta_{47}$  and  $1/T^2$  can be described as (Bonifacie et al., 2017):

$$\Delta_{47} = 0.0422 (\pm 0.0019) \times 10^6 / T^2 + 0.1262 (\pm 0.0207) (r^2 = 0.985) \quad (23)$$

where  $T$  is the temperature in Kelvin and phosphoric acid digestions of carbonate minerals are at 90°C. Thus, the use of the  $\Delta_{47}$  thermometry to study diagenesis and low-grade metamorphism of carbonates with precision on

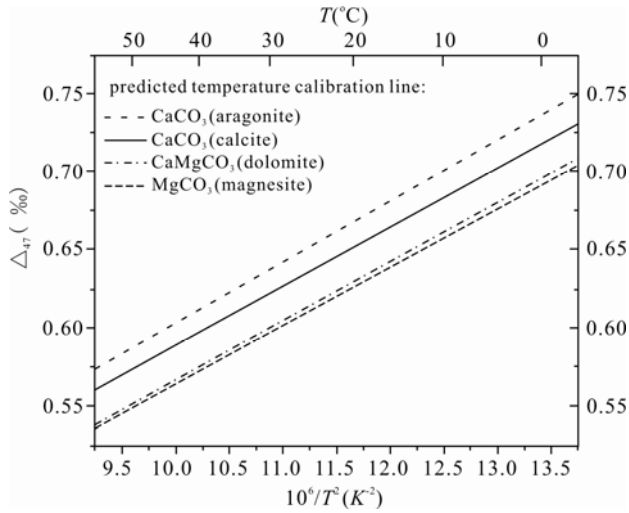


Fig. 5. Predicted temperature calibration lines for different carbonate clumped isotope thermometers, including aragonite, calcite, dolomite and magnesite (from Guo et al., 2009).

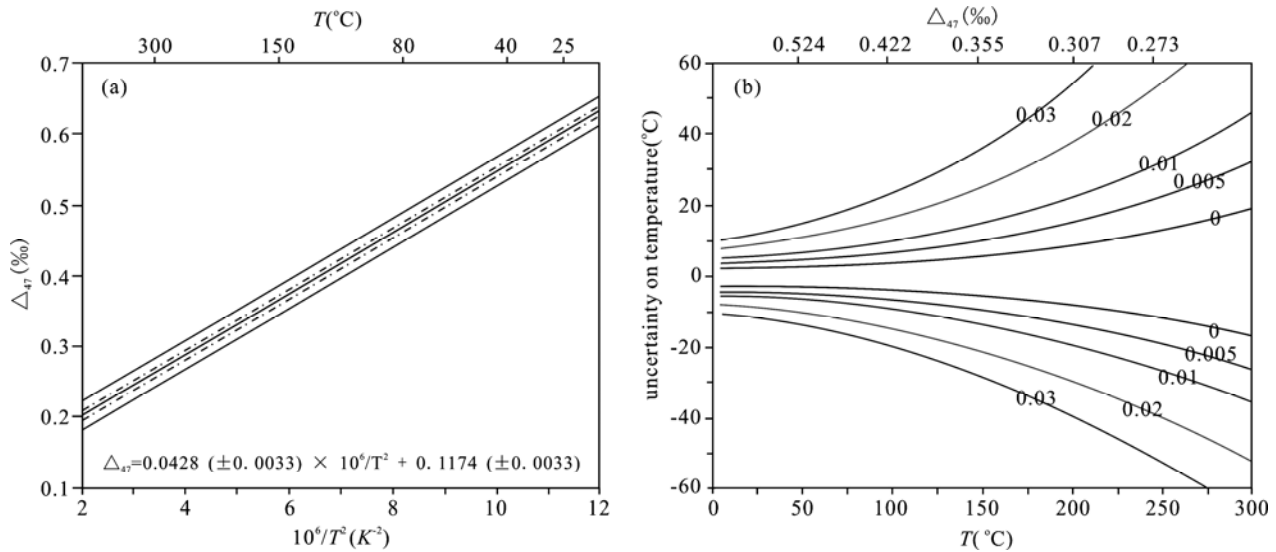


Fig. 6. The linear regression between  $\Delta_{47}$  and  $1/T^2$  for describing all dolomite minerals.

(a) Dolomite  $\Delta_{47}$ - $T$  calibration referring to  $\text{CO}_2$  extracted by phosphoric acid digestion at 90°C; (b) Graphical summary of 95% confidence domain of uncertainty on temperature estimates based on  $\Delta_{47}$  data (from Bonifacie et al., 2017).



temperature estimates based on  $\Delta_{47}$  measurements were further extended.

#### 4 Application of Light Stable Isotope in Quartz Cement

Quartz is of special interest in oxygen isotope geochemistry (Clayton et al., 1972; Tran et al., 2016). In general, oxygen isotopes can provide the valuable information for origin, temperature and time of authigenic quartz during diagenetic processes (Aplin and Warren, 1994; Williams et al., 1997; Girard et al., 2001; Kelly et al., 2007). Like carbonate cements, quartz-water isotopic fractionation curves are widely used in paleothermometric reconstructions, acting as the most important aspect for application of oxygen isotope in sandstone diagenesis studies (Alexandre et al., 2004). Clayton et al. (1972) measured the equilibrium constants for oxygen isotope exchange between quartz and water from 195°C (1000ln $\alpha$ =12) to 750°C (1000ln $\alpha$ =0.4), and proposed the behavior of fractionation with temperature in 200–500°C and 500–750°C respectively, which could be expressed as:

$$200\text{--}500^{\circ}\text{C}: 1000\ln\alpha_{\text{quartz-H}_2\text{O}} = 3.38 \times 10^6/T^2 - 3.4 \quad (24)$$

$$500\text{--}750^{\circ}\text{C}: 1000\ln\alpha_{\text{quartz-H}_2\text{O}} = 2.51 \times 10^6/T^2 - 1.96 \quad (25)$$

where  $1000\ln\alpha_{\text{quartz-water}} = \delta^{18}\text{O}_{\text{quartz}} - \delta^{18}\text{O}_{\text{water}}$ . Although these models have been used in sandstone diagenesis studies by some researchers, these temperatures are too high for sedimentary rocks more specifically unsuitable for sandstone reservoir diagenesis analyses. Later, Méheut et al. (2007) determined more accurate functions between 1000ln $\alpha$  and  $T$  in different temperature ranges, which are showed as equation (26) and (27):

$$1000\ln\alpha_{\text{quartz-water}} = -9.6341 + 4.848 \times 10^6/T^2 - 0.0382 \times (10^6/T^2)^2 + 0.000397 \times (10^6/T^2)^3 \quad (26)$$

$$1000\ln\alpha_{\text{quartz-water}} = -2.9548 + 1.342 \times 10^6/T^2 + 0.6062 \times (10^6/T^2)^2 - 0.040638 \times (10^6/T^2)^3 \quad (27)$$

Where  $1000\ln\alpha_{\text{quartz-water}} = \delta^{18}\text{O}_{\text{quartz}} - \delta^{18}\text{O}_{\text{water}}$ . The equation (26) is appropriate for the temperature from 0 to 130°C, while the equation (27) is suitable for the temperature from 130 to 400°C. These two models, especially the one for temperature range of 0–130°C, are effective to sandstone diagenesis studies. As mentioned in carbonate cements studies, the values of  $\delta^{18}\text{O}$  for initial water are unknown as well (Harwood et al., 2013). Therefore, combined use of fluid inclusion thermometry and oxygen isotope data is the most common way for the determination of the origin and timing of the quartz cements (Girard et al., 2001).

#### 5 Application of Light Stable Isotope in Clay Minerals

Clay minerals play an important role on sandstone reservoir properties (Morad et al., 2003). Their origin, timing and genetic mechanisms, however, are still not completely understood. Light stable isotopes, i.e.,  $\delta\text{D}$  and  $\delta^{18}\text{O}$ , are widely applied to the environmental conditions prevailing during formation of clay minerals, including the origin of fluids, the precipitation temperature and genetic types of clay minerals (Savin and Epstein, 1970; Morad et al., 2003; Santos Jr et al., 2007).

#### 5.1 Origin of diagenetic fluids involved in clay minerals formation

Diagenetic fluid evolution is a complicated issue in sedimentary basins, generating several types of pore water in different sandstone reservoirs (Xi et al., 2016a). Generally, different types of pore waters can influence the hydrogen and oxygen isotopes composition of clay minerals (Morad et al., 2003; Ketzer, et al., 2003; Middleton et al., 2015; Xi et al., 2016b; Xiao et al., 2017). The diagenetic fluid in the sandstone reservoirs mainly includes connate water, sea water, meteoric water, organic water, metamorphic water, igneous water. Morad et al. (2003) summarized the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of each type of diagenetic fluid, contributing to the origin of clay minerals in sandstone reservoirs. Specifically, connate waters, presented within sediments at the time of deposition, are largely a theoretical concept because of the complicated changes caused by various geological processes (Morad et al., 2003). Sea water is the standard used for oxygen and hydrogen stable isotopes (Savin and Epstein, 1970; Morad et al., 2003), which has the  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of 0‰ for the standard V-SMOW (Fig. 7). The  $\delta\text{D}$  and  $\delta^{18}\text{O}$  values of meteoric water change with the latitudes or altitudes, with the values decreasing at higher latitudes or altitudes (Fig. 7). Evaporated sea water achieves elevated  $\delta^{18}\text{O}$  and  $\delta\text{D}$  values up to the point where the water has about four times the original salinity, followed by a decrease in  $\delta^{18}\text{O}$  and  $\delta\text{D}$  (Fig. 7). Organic waters can be generated from kerogen maturation, microbial fermentation of organic matter, decomposition of compounds associated with petroleum and redox processes including petroleum fluids and oxidized species in minerals (Worden et al., 1996; Morad et al., 2003). In such waters, the  $\delta\text{D}$  values range from about –150‰ to –90‰ V-SMOW, and  $\delta^{18}\text{O}$  values vary from about –7‰ to 20‰ V-SMOW (Fig. 7). Metamorphic and igneous waters were enriched in  $\delta^{18}\text{O}$  but depleted in  $\delta\text{D}$  values (Fig. 7). The  $\delta^{18}\text{O}$  value of metamorphic and igneous waters ranges from about 6‰ to 20‰ and 8‰ to 16‰ V-SMOW respectively, while the

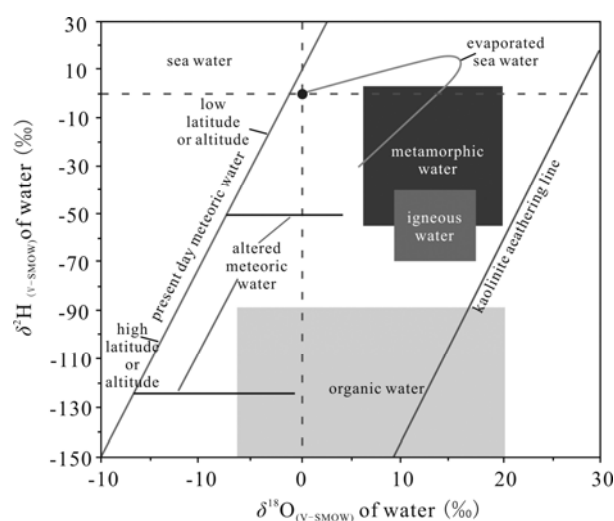


Fig. 7. Light stable isotope ( $\delta^{18}\text{O}$  and  $\delta\text{D}$ ) characteristics in the clay minerals forming from different types of diagenetic fluid in sandstone reservoirs (from Morad et al., 2003).

$\delta D$  values vary from about  $-55\text{‰}$  to  $6\text{‰}$  and  $-70\text{‰}$  to  $-40\text{‰}$  V-SMOW, respectively (Fig. 7).

## 5.2 Formation temperature of clay minerals

As with calcite and quartz cements, clay minerals formation temperatures also can be calculated by equilibrium isotope fractionation equations between clay minerals and the reacting water. Previous studies have shown that both oxygen and hydrogen isotopes could be used to calculate the precipitation temperature of different types of clay minerals (Wenner and Taylor, 1971; Land and Dutton, 1978; Yeh, 1980; Lambert and Epstein, 1980; Lee, 1984; Cole, 1985; Savin and Lee, 1988, Capuano, 1992; Sheppard and Gilg, 1996). By comparison, oxygen isotopes are more sensitive to temperature than hydrogen isotopes, and temperature-dependent isotope fractionations are much less well known for hydrogen than for oxygen isotopes (Morad et al., 2003). Therefore, oxygen isotopes are chosen as an important and prioritized means for formation temperature calculations of different types of clay minerals. Based on the theoretical and experimental methods, several calculation models were proposed and calibrated for common clay minerals in sandstone

reservoirs, such as kaolinite, smectite, illite and chlorite (Fig. 8). For kaolinite, differences between the fractionation equations are more distinct at higher temperature, while they are similar at lower temperatures conditions (Fig. 8). Generally, there are insignificant differences between each fractionation equation for smectite and illite (Figs. 8b, 8c). The models for chlorite are, however, more complicated than others because of the variable mineral composition and estimated temperature (Fig. 8d). Most diagenetic chlorites are Fe-rich with the hydroxyl cations dominated by Fe and Mg (Morad et al., 2003), so the equations for Al-Mg-Fe and Fe-Mg in hydroxyl sheet are representative of diagenetic chlorite-water isotope fractionation (Fig. 8). Generally, the application of these models in sandstone reservoir should be better combined with diagenesis paragenetic sequence, absolute dating of K-bearing minerals, microthermometric studies of fluid inclusion in association with calcite and quartz, since the oxygen isotopic composition of the parent fluids where the minerals are formed is poorly defined and the occurrence of isotopic equilibrium between clay minerals and their ambient water is difficult to prove (Morad et al., 2003).

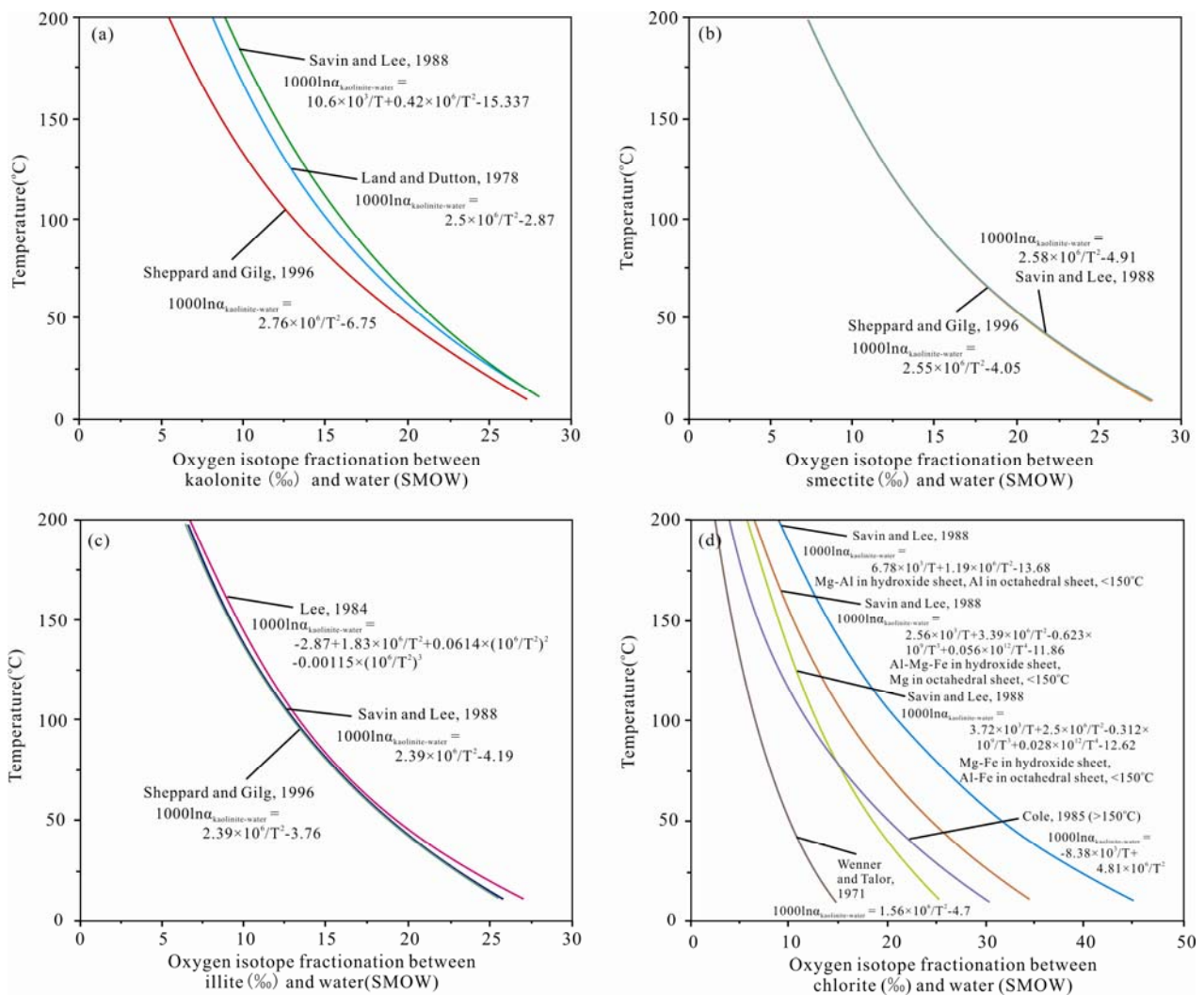


Fig. 8. Summary of experimentally derived clay-mineral-water oxygen isotope fractionation factors. (a) kaolinite, (b) smectite, (c) illite and (d) chlorite (Modified from Morad et al., 2003).

## 6 Oxygen Isotope Fractionation and Its Controlling Factors

Although light stable isotopes can be used in the study of sandstone reservoir diagenesis referring to origin and temperature of authigenic minerals, the  $\delta^{18}\text{O}$  values of pore water keep changing under the influence of various factors during burial diagenesis process. In general, controlling processes of oxygen isotope fractionation include hydration of volcanic materials, changes of geothermal gradient, oil emplacement, deep fluid or meteoric water injection, dissolution and precipitation of minerals and transformation of clay minerals (Gieskes and Lawrence, 1981; Ayalon and Longstaffe, 1988; Haszeldine et al., 1992; Williams et al., 1997; Noh and Lee, 1999; Marchand et al., 2002; Sample et al., 2017). Water-rock reaction and temperature increase can result in enrichment of  $\delta^{18}\text{O}$  in pore water (Ayalon and Longstaffe, 1988; Haszeldine et al., 1992). When strata are subjected to meteoric water infiltration, the  $\delta^{18}\text{O}$  will be gradually depleted in pore water (Noh and Lee, 1999; Marchand et al., 2002). On the contrary, the pore water will be enriched in  $\delta^{18}\text{O}$  by injection of deep fluid with high  $\delta^{18}\text{O}$  values (Sample et al., 2017). Also, diagenetic alteration of smectite to illite release  $\delta^{18}\text{O}$  enriched clay-bound water to mix with existing pore water, where temperatures exceed  $60^\circ\text{C}$ , the threshold for the smectite-illite transition (Sample et al., 2017; Fig. 9). Volcanogenic material alterations in sandstone reservoirs are very significant and for oxygen isotope fractionation (Chen and Zhang, 1992; Fu et al., 2017). For example, transformation of volcanic rock fragments to clay minerals will decrease the  $\delta^{18}\text{O}$  of pore water at low temperature (Gieskes and Lawrence, 1981; Sample et al., 2017; Fig. 9), whereas the  $\delta^{18}\text{O}$  of pore water will be enriched intensively if volcanogenic materials are altered to heulandite cements (Noh and Lee, 1999). Accordingly, samples with negligible influence of the above factors should be chosen in analysis of sandstone diagenesis.

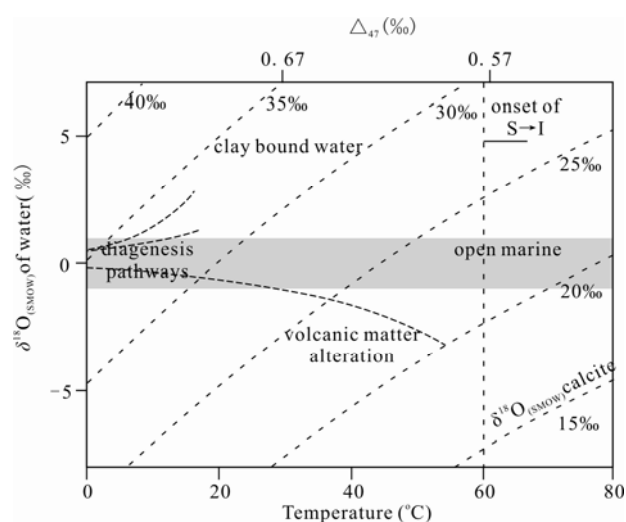


Fig. 9. Oxygen isotope fractionation induced by volcanic matter alteration and clay minerals transformation in sandstone reservoirs (from Sample et al., 2017).

## 7 Conclusions

Light stable isotope analysis, i.e. carbon, oxygen, hydrogen, provides effective ways to study the origin and formation temperature of authigenic carbonate, quartz and clay minerals. The  $\delta^{13}\text{C}$  values reveal the source of carbon and origin of carbonate cements. The  $\delta^{18}\text{O}$  values can be used to calculate the formation temperature of carbonate, quartz and clay-mineral cements. Combination of hydrogen and oxygen isotopes analysis, the origins of authigenic clay minerals are determined effectively. Clumped isotope computations reconstruct the temperature of carbonate precipitation that requires no assumptions about the  $\delta^{18}\text{O}$  of initial waters. However, oxygen isotope fractionation caused by various factors during burial diagenesis should be paid attention.

Further research is needed for use of light stable isotope analysis in the investigation of authigenic clay minerals. In situ analysis of light stable isotopes should be extensively developed in the sandstone diagenesis studies. It is very essential to generalize clumped isotope analysis in the studies on carbonate cements formation. More fundamentally, an in-depth knowledge of light stable isotopes may provide valuable clues for greater understanding of diagenetic processes, which can make the studies on origin and formation of authigenic minerals more accurate and give the reliable guidance on oil and gas exploration in sandstone reservoirs.

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