



A review of methods used for equilibrium isotope fractionation investigations between dissolved inorganic carbon and CO₂

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ABSTRACT

Fractionation of stable carbon isotopes between individual dissolved inorganic carbon (DIC) species (H₂CO₃^{*}, HCO₃[−], CO₃^{2−}) and gaseous CO₂ (CO_{2(g)}) at various temperatures has been studied by numerous authors. The maximum temperature, up to which experiments were conducted, was 286 °C, with most investigations only covering substantially lower temperature ranges. However, results of published data show discrepancies in their fractionation factors, especially at higher temperatures, where experimental data are scarce and results show significant scatter. The methodology and the experimental environment are considered the main reasons for the variable equilibrium fractionations. The largest discrepancies between published results were observed between CO₃^{2−} and CO_{2(g)} and least between HCO₃[−] and CO_{2(g)}. This review establishes an overview of the methods used to investigate the temperature-dependent isotope fractionation between the individual DIC species and CO_{2(g)} and discusses the accompanying results.

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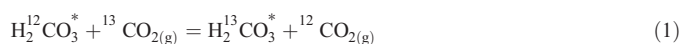
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1. Introduction

Carbon isotope analyses are useful when studying aquatic and hydrogeological systems in contact with CO₂. Examples of such applications include investigations in carbon cycles and fluxes (Barth and Veizer, 1999; Karim et al., 2011; Schulte et al., 2011), chemical weathering (Skidmore et al., 2004), degassing from springs (Becker et al., 2008; Assayag et al., 2009), hydrothermal systems (Zheng, 1990) and, as a relatively new field, geochemical trapping in CO₂ injection projects (Raistrick et al., 2006; Myrntinen et al., 2010; Becker et al., 2011; Myrntinen et al., 2012a, 2012b).

The fundamental works by Mills and Urey (1940) described for the first time the isotopic exchange reactions between dissolved inorganic carbon (DIC) and CO₂. DIC consists of the species H₂CO₃^{*}, HCO₃[−]

and CO₃^{2−}. For this review, dissolved CO₂ is expressed as H₂CO₃^{*}, the bulk term for the sum of H₂CO₃ and CO_{2(aq)}. The isotope fractionation between the individual DIC species and CO_{2(g)} can be described by the following equations, respectively:



Overall, the equilibrium fractionation factor between DIC and gaseous CO₂ (CO_{2(g)}), depends on the proportions of the three DIC species that in turn depend on the pH (Clark and Fritz, 1997). H₂CO₃^{*} dominates the carbonate system up to pH 6.4, HCO₃[−] between

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pH 6.4 and 10.3 and CO_3^{2-} above pH 10.3 (e.g. Drever, 1997). Each species has individual temperature-dependent fractionation factors in equilibrium with $\text{CO}_{2(g)}$ (Emrich et al., 1970; Zhang et al., 1995). These can be described by polynomial equations in the following format:

$$10^3 \ln \alpha = a \left(10^6 / T_K^2 \right) + b \left(10^3 / T_K \right) + c \quad (4)$$

where α is the fractionation factor:

$$\alpha_{i-g} = R_i / R_g \quad (5)$$

with R as the isotope ratio of the specific DIC species (i) and of $\text{CO}_{2(g)}$ (g). The fractionation factors α between the individual DIC species and $\text{CO}_{2(g)}$ then are, respectively:

$$\alpha = \left({}^{13}\text{C}/{}^{12}\text{C} \right)_{\text{H}_2\text{CO}_3^*} / \left({}^{13}\text{C}/{}^{12}\text{C} \right)_{\text{CO}_{2(g)}} \quad (6)$$

$$\alpha = \left({}^{13}\text{C}/{}^{12}\text{C} \right)_{\text{HCO}_3^-} / \left({}^{13}\text{C}/{}^{12}\text{C} \right)_{\text{CO}_{2(g)}} \quad (7)$$

$$\alpha = \left({}^{13}\text{C}/{}^{12}\text{C} \right)_{\text{CO}_3^{2-}} / \left({}^{13}\text{C}/{}^{12}\text{C} \right)_{\text{CO}_{2(g)}} \quad (8)$$

Eq. (4) is often considered to be equivalent to:

$$\varepsilon = aT^2(^{\circ}\text{C}) + bT(^{\circ}\text{C}) + c \quad (9)$$

assuming that,

$$\varepsilon = 10^3(\alpha - 1) \approx 10^3 \ln \alpha. \quad (10)$$

Temperature-dependency of isotope fractionation is usually described either by Eq. (4) or Eq. (10). However, in order to compare equations used by various authors in a uniform manner, we describe isotope fractionation by using the fractionation factor “ α ”, as described in Eq. (4), rather than the enrichment factor “ ε ”, which describes the magnitude of isotopic difference. If the isotopic difference between two substances is small (<10‰), ε serves as a good approximation of α ; however, at greater magnitudes these factors tend to deviate from one another (Clark and Fritz, 1997; Sharp, 2007). Also, some authors such as Sharp (2007) have recommended that α function is rather used in stable isotope work than ε , which is used in radiogenic isotope geochemistry for a different purpose.

The total fractionation between total DIC and $\text{CO}_{2(g)}$ at a specific temperature is termed:

$$10^3 \ln \alpha^{13}\text{C}_{\text{DIC}-\text{CO}_{2(g)}} = 10^3 \ln \left[\left(\delta^{13}\text{C}_{\text{DIC}} + 1000 \right) / \left(\delta^{13}\text{C}_{\text{CO}_{2(g)}} + 1000 \right) \right]. \quad (11)$$

Eq. (11) can be modified to the following equation (Zhang et al., 1995) if individual DIC species are considered:

$$10^3 \ln \alpha^{13}\text{C}_{\text{DIC}-\text{CO}_{2(g)}} = \sum f_i 10^3 \ln \alpha^{13}\text{C}_{i-g} \quad (12)$$

where, f is the fraction of each DIC species (i).

Temperature-dependency typically cannot be described using simpler polynomials (than Eq. (4)) when large temperature ranges are considered in which isotope methods are applied. This is because the order of the temperature–fractionation relation is likely to change during the transition from lower to higher temperatures (Clayton, 1981; Chacko et al., 2001). At the crossover point, where $10^3 \ln \alpha = 0$, fractionation does not occur. If this point is crossed, α changes from positive to negative (or vice versa), i.e. the heavier isotope (in this case ^{13}C) becomes more dominant in the opposing phase.

Furthermore, fractionation increases in both directions moving away from this point. Therefore, a further aspect of this study is to discuss the defined temperature of the crossover points between the individual DIC species and $\text{CO}_{2(g)}$ presented by most studies.

Knowing which isotope fractionations occur under which conditions is especially important when fractionation corrections are required. For instance, this is necessary for reactions where direct isotope measurements of two equilibrium phases are taken (Emrich et al., 1970). Such corrections are also important when conducting isotope mass balance calculations, for example to quantify CO_2 dissolution (Myrntinen et al., 2010). This requires the end member value of the reacting CO_2 , which however, will shift due to the isotope fractionation during the dissolution reaction.

The development of isotope compositions of DIC also depends on open or closed system conditions with respect to CO_2 supply if the dissolution of carbonate minerals is possible. In order to determine the $\delta^{13}\text{C}$ value, in both an open or closed system, the fractionation factors between CO_2 and the individual DIC species need to be considered together with the concentrations of the respective DIC species that are denoted in square brackets in Eqs. (13) and (14). Such systems have been described for natural waters at atmospheric pressure by Clark and Fritz (1997), as well as for elevated pressures by Becker et al. (2011). An open system is in contact with an unlimited amount of $\text{CO}_{2(g)}$ with respect to the turnover of the involved reactions. In this scenario, $\delta^{13}\text{C}_{\text{DIC}}$ can be calculated as:

$$\delta^{13}\text{C}_{\text{DIC}} = \frac{\left([\text{H}_2\text{CO}_3^*] \left(\delta^{13}\text{C}_{\text{CO}_2} + 10^3 \ln \alpha^{13}\text{C}_{\text{H}_2\text{CO}_3^*-\text{CO}_{2(g)}} \right) + [\text{HCO}_3^-] \left(\delta^{13}\text{C}_{\text{CO}_2} + 10^3 \ln \alpha^{13}\text{C}_{\text{HCO}_3^--\text{CO}_{2(g)}} \right) \right) + [\text{CO}_3^{2-}] \left(\delta^{13}\text{C}_{\text{CO}_2} + 10^3 \ln \alpha^{13}\text{C}_{\text{CO}_3^{2-}-\text{CO}_{2(g)}} \right)}{[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}]} \quad (13)$$

Closed systems are either devoid of CO_2 contact or are only connected to a limited reservoir, e.g. soil gas in a confined pore space. Therefore closed systems show changing partial pressures of CO_2 ($p\text{CO}_2$) during equilibration. Furthermore, in closed system conditions, the $\delta^{13}\text{C}$ of dissolving carbonate minerals can significantly influence the baseline $\delta^{13}\text{C}$ of the DIC because, other than under open system conditions, they are the main source of DIC. In case of a closed system, $\delta^{13}\text{C}_{\text{DIC}}$ can be calculated as:

$$\delta^{13}\text{C}_{\text{DIC}} = \frac{\left([\text{H}_2\text{CO}_3^*] \left(\delta^{13}\text{C}_{\text{CO}_2} + 10^3 \ln \alpha^{13}\text{C}_{\text{H}_2\text{CO}_3^*-\text{CO}_{2(g)}} \right) + [\text{HCO}_3^-] \left(\delta^{13}\text{C}_{\text{CO}_2} + 10^3 \ln \alpha^{13}\text{C}_{\text{HCO}_3^--\text{CO}_{2(g)}} \right) \right) + [\text{CO}_3^{2-}] \left(\delta^{13}\text{C}_{\text{CO}_2} + 10^3 \ln \alpha^{13}\text{C}_{\text{CO}_3^{2-}-\text{CO}_{2(g)}} \right) + [\text{CaCO}_3]_{\text{diss}} \delta^{13}\text{C}_{\text{calcite}}}{[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] + [\text{CaCO}_3]_{\text{diss}}} \quad (14)$$

Numerous authors have analysed and described the temperature-dependency of isotope fractionation between CO_2 gas and its various DIC-species. Compilations of the various isotope fractionations with temperature are available for example in Friedman and O'Neil (1977), Clark and Fritz (1997), and Zeebe and Wolf-Gladrow (2001). However, so far, compilations describing the methods used to investigate these isotope fractionation dependencies with temperature do not exist. This is striking as the applied methods partially varied greatly and consequently produced deviating results. This manuscript therefore intends to provide an overview of the different methods used in order to ease comparison between the different techniques applied. This may help to apply the correct method and its associated isotope factors for specific applications. The methods summarised in the following sections focus on experiments that describe fractionation over a wider temperature range, while detailed descriptions of methods that focused only on fractionation at one or two temperatures are excluded here. Nonetheless the data points resulting from those experiments are included here for comparison.

1.1. Isotope equilibration between H_2CO_3^* and $\text{CO}_{2(g)}$

Various authors have described temperature-related fractionation trends between these two phases either experimentally or theoretically:

Thode et al. (1965) determined fractionation between H_2CO_3^* and $\text{CO}_{2(g)}$ theoretically by isotope equilibrium calculations based on experimental data of the exchanging species between 0 and 100 °C. These theoretical considerations were later corrected by Szaran (1998).

In contrast, Vogel et al. (1970) took an experimental approach. In order to reach the necessary isotopic equilibrium for the experiments, 25 mL of de-mineralised water was placed into a 300 mL flask. After this, the headspace was repeatedly evacuated after freezing the water. $\text{CO}_{2(g)}$ was then filled into the headspace to a pressure of 50 cm mercury (i.e. 0.7 bar). In order to ensure reaching equilibrium at different temperatures, the closed flasks were then placed into water baths for time periods of at least 20 h for temperatures above 25 °C and time periods of 40 to 70 h for temperatures below 20 °C. After equilibration, three different methods (a, b and c) were tested to establish the most reliable method of separating the gas from the fluid phase for isotope fractionation investigations. In method (a) the fluid was evacuated into a 30 mL flask and closed off from the gas phase. The gas phase was collected subsequently in an attached container and cooled with liquid nitrogen. The collected $\text{CO}_{2(g)}$ was then dried by passing through a dry-ice trap before measurement. In method (b) the aqueous solution was rapidly frozen with dry ice in a 100-mL flask. The gas was then removed and dried and transferred into another container for analysis. In method (c) the aqueous solution was shaken through an open stop-cock into a 25 mL flask. The gas was separated from the liquid phase as in method (b). The results of these three methods were in good agreement with each other.

Zhang et al. (1995), on the other hand, froze pure CO_2 in an evacuated bottle and equilibrated it with degassed and acidified water at a pH of about 2. The low pH ensured H_2CO_3^* to be the dominant DIC species in the fluid. The flasks were equilibrated at temperatures ranging between 5 and 25 °C in a water bath for 7 to 10 days. The minimum equilibration time was reached within 4 days. After equilibrium was established, a sample of CO_2 was removed from the headspace for determination of its $^{13}\text{C}/^{12}\text{C}$ ratio. The isotope fractionations were determined via Eq. (12). The mass distribution of carbon between the gas phase and the solution was determined by using CO_2 equilibrium dissociation equations. For this, the partial pressure of CO_2 and the total C added to the flask were measured, as well as the total alkalinity by Gran titration.

The results of these experiments are listed in Table 1 and plotted in Fig. 1. The fractionation curves by all authors show a positive slope with increasing temperature. The calculated values presented by Thode et al. (1965) yield smaller $10^3\ln\alpha$ values than the experimental ones by Vogel et al. (1970) and Zhang et al. (1995). The $\delta^{13}\text{C}_{\text{DIC}}$ values obtained by Zhang et al. (1995) differ by only about 0.1‰ compared to the ones obtained by Vogel et al. (1970).

Most other studies (Wendt et al., 1963; Deuser and Degens, 1967; Turner, 1982; Szaran, 1998) were carried out at one temperature. Deuser and Degens (1967), Wendt (1968) and Turner (1982) showed higher fractionation values than those published by Thode et al. (1965), Vogel et al. (1970) and Zhang et al. (1995). This is possibly due to HCO_3^- remaining unintentionally in the fluid shifting the $10^3\ln\alpha$ to a higher value. Deuser and Degens (1967), for instance, used a pH of 5.2 for

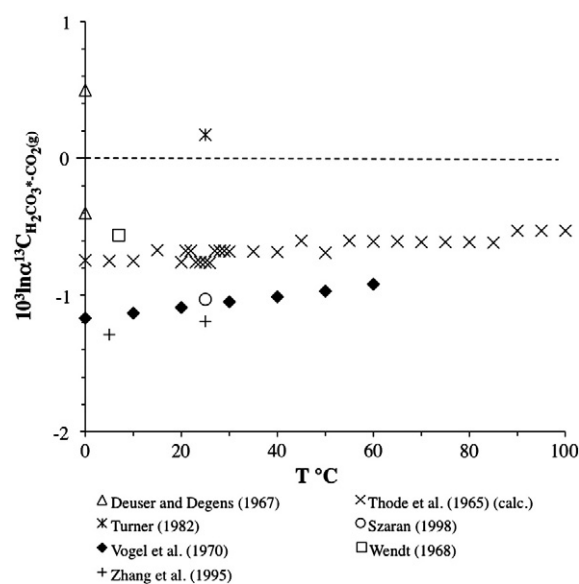


Fig. 1. Carbon isotopic difference, $10^3\ln\alpha^{13}\text{C}_{\text{H}_2\text{CO}_3^*-\text{CO}_{2(g)}}$ against temperature (°C). The dashed line indicates where $10^3\ln\alpha=0$.

forming H_2CO_3^* . Although at this pH value, most of the DIC should be present as H_2CO_3^* , using carbon mass distribution equations, at least 4% of the HCO_3^- remains unreacted at 0 °C. In case the reaction after acidification was incomplete, even higher percentages of HCO_3^- may have remained in the solution. This was possibly the reason why Deuser and Degens (1967) published $10^3\ln\alpha$ values up to about 1.7‰ higher than those of Vogel et al. (1970) (Fig. 1). Turner (1982) explained discrepancies between his data and those of Wendt (1968) and Vogel et al. (1970) with analytical difficulties associated with sample-extraction. As opposed to most other authors he used an open system that may have produced different results. On the other hand, values from experiments at 25 °C reported by Vogel et al. (1970) were confirmed by Szaran (1998), who presented experiments in open and closed systems and did not find significant differences.

The data assembled here suggest that sampling extraction methods exert the strongest influences on equilibration factors between H_2CO_3^* and $\text{CO}_{2(g)}$. Ensuring a consistently low pH may be a major driving factor for the accurate determination of fractionation between these two phases. Even though methods may vary significantly, results as described by Vogel et al. (1970) and Zhang et al. (1995), together with the ones of Szaran (1998) show best similarities between independent experiments and thus should present the most reliable methods for determining fractionation factors between H_2CO_3^* and $\text{CO}_{2(g)}$ within their mentioned temperature ranges. However, for unclear reasons, experimental data for temperatures beyond 60 °C is not available, and hence the actual isotope fractionation behaviour between H_2CO_3^* and $\text{CO}_{2(g)}$ at higher temperatures, as well as the temperature at which crossover occurs, is uncertain.

1.2. Isotope equilibration between HCO_3^- and $\text{CO}_{2(g)}$

The fractionation factor between HCO_3^- and $\text{CO}_{2(g)}$ has so far been determined independently by the most working groups and covers

Table 1
Carbon isotope fractionation temperature dependencies in the system $\text{H}_2\text{CO}_3^*-\text{CO}_{2(g)}$.

Authors	Type of investigation	Temp. range (°C)	$10^3\ln\alpha^{13}\text{C}_{\text{H}_2\text{CO}_3^*-\text{CO}_{2(g)}}$
Thode et al. (1965)	Calculated	0–100	$10^3\ln\alpha = -0.2308(10^3/T_K) + 0.071$
Vogel et al. (1970)	Experimental	0–60	$10^3\ln\alpha = -0.3728(10^3/T_K) + 0.1868$
Zhang et al. (1995)	Experimental	5–25	$10^3\ln\alpha = -0.4147(10^3/T_K) + 0.201$

temperature ranges between 0 and 200 °C (Abelson and Hoering, 1961; Wendt et al., 1963; Deuser and Degens, 1967; Malinin et al., 1967; Wendt, 1968; Emrich et al., 1970; Vogel et al., 1970; Mook et al., 1974; Turner, 1982; Lesniak and Sakai, 1989; Zhang et al., 1995; Szaran, 1997). The most probable reason that more authors are interested in the isotope fractionation between these two species is caused by the fact that HCO_3^- is the dominant DIC species in most natural waters.

In order to determine $(^{13}\text{C}/^{12}\text{C})_{\text{HCO}_3^-}$ for the fractionation factor between HCO_3^- and $\text{CO}_{2(g)}$, a number of studies used either of the following methods:

Method 1: Direct measurement of the isotope values of the equilibrated two phases.

Method 2: Isotope measurements of only the equilibrated $\text{CO}_{2(g)}$. The $\delta^{13}\text{C}_{\text{HCO}_3^-}$ value was calculated and corrected for the presence of H_2CO_3^* and CO_3^{2-} .

The results of the experiments are listed in Table 2 and plotted in Fig. 2.

Deuser and Degens (1967) conducted experiments at temperatures between 0 and 30 °C. In their experiments 50 mL of a sample containing NaHCO_3 was placed into a 300 mL flask that was frozen and evacuated to clear the headspace. After thawing the sample, $\text{CO}_{2(g)}$ was transferred into the flask, which was placed into a water bath. Equilibration was allowed to occur at least for 18 h with periodical mixing at a pH of 8.4. Method 1 was used for isotope analyses for which the fluid phase was previously acidified to turn the HCO_3^- into $\text{CO}_{2(g)}$. The CO_2 was then cryogenically trapped for analysis.

Malinin et al. (1967) conducted experiments between 23 and 286 °C. To withstand the high temperatures, autoclaves were used. These were filled with 0.5 mol L⁻¹ of NaOH, Na_2CO_3 or KOH. Subsequently the headspace was evacuated and replaced with CO_2 in order to produce HCO_3^- . The autoclaves were placed into a temperature-regulated furnace, which was swung for most of the duration of the experiment in order to mix the contents. In order to reach chemical and isotopic equilibrium, the experiment at 25 °C was run for 30 days, whereas for higher temperatures the experimental time ranged between 1 and 6 days. Method 1 was used for isotope analyses. For this, CaCl_2 solution was introduced into the autoclaves from a nitrogen-pressurised vessel to form a CaCO_3 precipitate, in order to separate the carbon from the fluid phase at the end of the experiment. The precipitate was converted into $\text{CO}_{2(g)}$ for isotope measurements and was considered to resemble the $^{13}\text{C}/^{12}\text{C}$ of HCO_3^- . The CO_2 in the headspace was measured separately by absorbing it first with a 40% KOH solution and subsequently adding CaCl_2 to it to also form a CaCO_3 precipitate, converted then to CO_2 , for isotope measurements.

Emrich et al. (1970) conducted experiments between 20 and 60 °C with a 5 L vessel containing a 1 L $\text{Ca}(\text{HCO}_3)_2$ solution in equilibrium with $\text{CO}_{2(g)}$. A thermostatic bath was used to ensure constant temperatures. The HCO_3^- solution was separated from the $\text{CO}_{2(g)}$ by transferring it to a 1 L vessel and isolating it from the gas phase. The solution was then acidified and the evolved $\text{CO}_{2(g)}$ was frozen into a cold trap with liquid nitrogen and subsequently analysed for its $^{13}\text{C}/^{12}\text{C}$ ratio by using Method 1.

Table 2

Carbon isotope fractionation temperature dependencies in the system HCO_3^- – $\text{CO}_{2(g)}$.

Authors	Type of investigation	T range (°C)	$10^3 \ln \alpha^{13}\text{C}_{\text{HCO}_3^- - \text{CO}_{2(g)}}$
Deuser and Degens (1967)	Experimental	0–30	$10^3 \ln \alpha = 0.659(10^3/T_K) - 15.11$
Emrich et al. (1970)	Experimental	20–60	$10^3 \ln \alpha = 9.341(10^3/T_K) - 23.53$
Malinin et al. (1967)	Experimental	23–286	$10^3 \ln \alpha = 9.8724(10^3/T_K) - 23.62$
Mook et al. (1974)	Experimental	0–126	$10^3 \ln \alpha = 9.552(10^3/T_K) - 24.1$
Szaran (1997)	Experimental	7–70	$10^3 \ln \alpha = 9.1301(10^3/T_K) - 22.722$
Zhang et al. (1995)	Experimental	5–25	$10^3 \ln \alpha = 9.36(10^3/T_K) - 23.5$

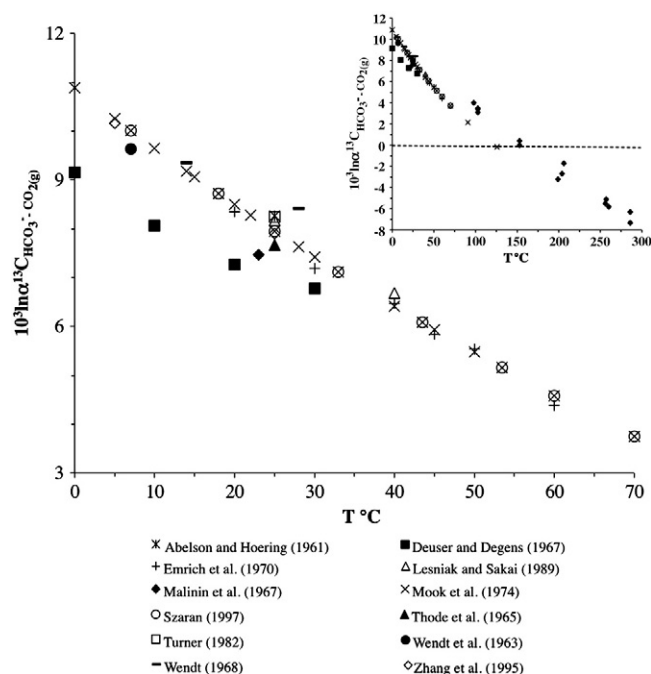


Fig. 2. Isotope fractionation $10^3 \ln \alpha^{13}\text{C}_{\text{HCO}_3^- - \text{CO}_{2(g)}}$ against temperature (°C). Note: the results presented by Mook et al. (1974) were modified according to Friedman and O'Neil (1977). The graph in the top right corner includes the data above 70 °C by Malinin et al. (1967) and Mook et al. (1974). The dashed line indicates where $10^3 \ln \alpha = 0$.

The results provided by Mook et al. (1974) are often quoted to describe fractionation between HCO_3^- and $\text{CO}_{2(g)}$. These authors used two different methods for analysing fractionation between 5 and 25 °C. In the first method isotope equilibration between bicarbonate solution and $\text{CO}_{2(g)}$ was achieved by freezing 50 mL of distilled water at -80 °C in a 100 mL flask and adding 2.5 g of NaHCO_3 . The flask was then evacuated and filled with 12 mL of CO_2 , which was frozen into the flask at -190 °C. For the exchange reaction, the flask was placed into a water bath at the temperature of interest for several days. In the second method, a 100 mL flask containing 2.5 g of solid NaHCO_3 was evacuated and then filled with distilled water. The solution was then frozen at -80 °C, after which 12 mL of CO_2 was frozen into the reaction vessel. In both methods about half of the $\text{CO}_{2(g)}$ was expanded, after equilibrium was achieved. It was then dried and an aliquot of it was isotopically analysed using Method 2.

In order to establish the crossover point at elevated temperatures, experiments above 25 °C were modified. Brass vessels were used to tolerate higher temperatures and pressures. 2.73 g of NaHCO_3 was added to a 99 mL vessel containing 55 mL of degassed and distilled water that was frozen at -80 °C. This vessel was connected to a second one with a volume of 59.7 mL. Both vessels were then evacuated and 3 mmoles of $\text{CO}_{2(g)}$ were injected into the headspace at room temperature and left to equilibrate for several days. The $\text{CO}_{2(g)}$ in the second vessel was then extracted, dried and isotopically measured using Method 2. To calculate $\delta^{13}\text{C}_{\text{HCO}_3^-}$, fractionations between

H_2CO_3^* and $\text{CO}_{2(\text{g})}$ from Vogel et al. (1970) and between CO_3^{2-} and $\text{CO}_{2(\text{g})}$ from Thode et al. (1965) were used in the following equation:

$$\begin{aligned} \delta^{13}\text{C}_{\text{HCO}_3^-} = & (\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}} [\text{CO}_{2(\text{g})}] + \delta^{13}\text{C}_{\text{NaHCO}_3} [\text{NaHCO}_3] \\ & - [\text{CO}_{2(\text{g})} + \text{H}_2\text{CO}_3^* + \text{CO}_3^{2-}(\text{aq})] \delta^{13}\text{C}_{\text{CO}_2} \\ & - [\text{H}_2\text{CO}_3^*] 10^3 \ln \alpha^{13}\text{C}_{\text{H}_2\text{CO}_3^* - \text{CO}_{2(\text{g})}} \\ & - [\text{CO}_3^{2-}] 10^3 \ln \alpha^{13}\text{C}_{\text{CO}_3^{2-} - \text{CO}_{2(\text{g})}}) / \text{HCO}_3^- \end{aligned} \quad (15)$$

The fractionation between HCO_3^- and $\text{CO}_{2(\text{g})}$ was then calculated by using a modified version of Eq. (4):

$$10^3 \ln \alpha^{13}\text{C}_{\text{HCO}_3^- - \text{CO}_{2(\text{g})}} = [\delta^{13}\text{C}_{\text{CO}_{2(\text{g})}} - \delta^{13}\text{C}_{\text{HCO}_3^-}] / [1 + \delta^{13}\text{C}_{\text{HCO}_3^-} \cdot 10^{-3}]. \quad (16)$$

Zhang et al. (1995) conducted experiments between 5 and 25 °C. For the equilibration reaction, CO_2 was transferred into a previously evacuated flask containing a 0.5 M NaHCO_3 solution, placed into a water bath. Equilibration times ranged between four and ten days. After equilibrium was established, Method 1 was used: a sample of $\text{CO}_{2(\text{g})}$ was removed from the headspace for isotope measurements and DIC was separately analysed for its $^{13}\text{C}/^{12}\text{C}$ ratios. The isotope fractionations were determined via Eq. (12). The mass distribution of carbon between the gas phase and the solution was determined by using CO_2 equilibrium dissociation equations. For this, the partial pressure of CO_2 and the total C added to the flask was measured, as well as the total alkalinity by Gran titration.

Szaran (1997) conducted experiments between 7 and 70 °C. The experimental setup consisted of an upper container and a lower glass container that were joined via a bottleneck with a valve. The upper flask contained $\text{CO}_{2(\text{g})}$ and the bottom flask, 200 mL of NaHCO_3 solution (0.6 mol L⁻¹). The bottom flask was evacuated prior to the equilibration reaction with $\text{CO}_{2(\text{g})}$, which started when the valve between the upper and lower glass bulbs was opened. The apparatus was kept in a temperature-controlled environment. After equilibration, Method 2 was used to remove the gas from the headspace that was trapped cryogenically afterwards. The isotope values of both phases were inserted into Eq. (17) in order to determine the $\delta^{13}\text{C}_{\text{HCO}_3^-}$ value. The contribution of H_2CO_3^* and CO_3^{2-} was neglected based on the assumption that their effect is negligible at pH values of about 8.

$$\delta^{13}\text{C}_{\text{HCO}_3^-} = \delta^{13}\text{C}_{\text{in}} + (\delta^{13}\text{C}_{\text{in}} - \delta^{13}\text{C}_{\text{CO}_{2(\text{g})}}) [\text{CO}_{2(\text{g})}] / [\text{HCO}_3^-] \quad (17)$$

where, $\delta^{13}\text{C}_{\text{in}}$ = initial $\delta^{13}\text{C}$ in system, i.e. of total DIC, which was also equal to $\text{CO}_{2(\text{g})}$.

The temperature dependency trends are summarised in Table 2 and shown in Fig. 2. The fractionation curves by all authors show a negative slope with increasing temperature.

Deuser and Degens (1967), Malinin et al. (1967) as well as Emrich et al. (1970) measured the $\delta^{13}\text{C}$ of both phases, HCO_3^- and $\text{CO}_{2(\text{g})}$, whereas, Mook et al. (1974), Zhang et al. (1995) and Szaran (1997) measured just equilibrated $\text{CO}_{2(\text{g})}$ and calculated the $\delta^{13}\text{C}_{\text{HCO}_3^-}$ value for determining $10^3 \ln \alpha$ between the two phases. However, as there is no disagreement, for instance, between the results of Emrich et al. (1970) and Mook et al. (1974), either Method 1 or Method 2 may be considered applicable. Most authors, including those who conducted experiments only at one or two temperatures, show good agreement with each other. Turner (1982) and Lesniak and Sakai (1989) conducted open system experiments, which also fit well with the other closed system experiments. Isotope fractionations determined by Deuser and Degens (1967) are lower than those reported by other authors, especially for cooler temperatures. As discussed in the $\text{H}_2\text{CO}_3^* - \text{CO}_{2(\text{g})}$ fractionation section, this could be due to a mixture of H_2CO_3^* and

HCO_3^- , with the former decreasing the fractionation factor. However, when extrapolating the values to higher temperatures, they approach the findings of the other groups at about 40 °C (Fig. 2). The results by Malinin et al. (1967) only fit with the isotope fractionations by the other authors at 23 °C. At higher temperatures, their results lie higher (Fig. 2). Considering the large scatter beyond about 100 °C, one can conclude that the method used produces increasingly inaccurate results with temperature. The crossover point (150 °C) reported by Malinin et al. (1967) differs by about 25 °C compared to the one reported (124 °C) by Mook et al. (1974). Mook et al. (1974), however, noted that their experiments are most accurate up to 25 °C. Nevertheless they feel confident in applying their fractionation equation up to temperatures of 150 °C. Since Szaran (1997) conducted experiments with similar results as Mook et al. (1974) up to 70 °C, we propose high accuracy to be reliable only up to this temperature with increasing uncertainty above it.

The key challenge in undertaking such experiments consists of the complete separation of the dissolved HCO_3^- or the $\text{CO}_{2(\text{g})}$ after equilibration. This is necessary to prevent shifts in the equilibrium by, for instance, kinetic reactions (Thode et al., 1965; Mook et al., 1974). Even though specifically HCO_3^- was targeted, it is only possible to extract the sum of dissolved inorganic carbon species (Szaran, 1997). This is uncritical as long as the pH is fixed to a value where HCO_3^- is the dominant species. Principally, Mook et al. (1974) and Szaran (1997) used the same approach to calculate $\delta^{13}\text{C}_{\text{HCO}_3^-}$ values. Mook et al. (1974) however, corrected for fractionations between $\text{H}_2\text{CO}_3^* - \text{CO}_{2(\text{g})}$ and between $\text{CO}_3^{2-} - \text{CO}_{2(\text{g})}$ by applying fractionation factors by Vogel et al. (1970) and the theoretical values by Thode et al. (1965), respectively. Zhang et al. (1995) noted that if their $\text{CO}_3^{2-} - \text{CO}_{2(\text{g})}$ fractionation factors were applied, instead of those of Thode et al. (1965), the calculated values by Mook et al. (1974) for $\text{HCO}_3^- - \text{CO}_{2(\text{g})}$ would decrease by 0.03‰ and fit within the uncertainty range of their results. Szaran (1997), on the other hand, suggested to use the fractionation factor reported by Halas et al. (1997). This illustrates discrepancies in selection of a suitable CO_3^{2-} and $\text{CO}_{2(\text{g})}$ fractionation factor for correcting for $\delta^{13}\text{C}_{\text{HCO}_3^-}$ values. Fractionation between CO_3^{2-} and $\text{CO}_{2(\text{g})}$ is discussed in more detail in the following section.

1.3. Isotope equilibration between CO_3^{2-} and $\text{CO}_{2(\text{g})}$

Similar to the equilibrium factors between H_2CO_3^* and CO_2 , Thode et al. (1965) also calculated equilibrium factors for data between 0 and 100 °C based on spectroscopic data of the exchanging species. Experimental data was also reported but showed a lack of reproducibility and agreement with calculated data; hence the methods are not further discussed here. Malinin et al. (1967) also used spectroscopic data and extended the equilibrium constant calculations up to 927 °C.

Deines et al. (1974) provided an estimate for the fractionation factor between CO_3^{2-} and $\text{CO}_{2(\text{g})}$, as well as for the $10^3 \ln \alpha$ dependency with temperature (Table 3). The former was established with the following equation:

$$\alpha_a = \alpha_b \times \alpha_c \quad (18)$$

where,

$$\alpha_a = (^{13}\text{C}/^{12}\text{C})_{\text{CO}_3^{2-}} / (^{13}\text{C}/^{12}\text{C})_{\text{CO}_2} \quad (19)$$

$$\alpha_b = (^{13}\text{C}/^{12}\text{C})_{\text{CO}_3^{2-}} / (^{13}\text{C}/^{12}\text{C})_{\text{CaCO}_3} \quad (20)$$

$$\alpha_c = (^{13}\text{C}/^{12}\text{C})_{\text{CaCO}_3} / (^{13}\text{C}/^{12}\text{C})_{\text{CO}_2} \quad (21)$$

Zhang et al. (1995) applied a method similar to the one for equilibration between HCO_3^- and $\text{CO}_{2(\text{g})}$ by using a 0.5 M solution of NaHCO_3 mixed with Na_2CO_3 . In addition, the partial pressure of the

Table 3Carbon Isotope fractionation temperature dependencies in the system CO_3^{2-} – $\text{CO}_{2(g)}$.

Authors	Type of investigation	T range (°C)	$10^3 \ln \alpha^{13}\text{C}_{\text{CO}_3^{2-}-\text{CO}_{2(g)}}$
Deines et al. (1974)	Experimental	n.a.	$10^3 \ln \alpha = 0.87(10^6/T_K^2) - 3.4$
Halas et al. (1997)	Extrapolated	0–200 (100–200)	$10^3 \ln \alpha = -0.0018(10^6/T_K^2) + 0.0932(10^3/T_K) + 2.9463$
	Experimental	0–80	$10^3 \ln \alpha = -0.0802(10^3/T_K) + 2.9484$
Zhang et al. (1995)	Experimental	5–25	$10^3 \ln \alpha = 4.12(10^3/T_K) - 7.83$

$\text{CO}_{2(g)}$ was determined by measuring the volumetric ratio between a vessel side arm and the main part of the flask. The isotope fractionations were determined via Eq. (12). The mass distribution of carbon between the gas phase and the solution was determined by using CO_2 equilibrium dissociation equations. For this, the partial pressure of CO_2 and the total C added to the flask were measured, as well as the total alkalinity by Gran titration.

Halas et al. (1997) investigated fractionation between these two phases experimentally at temperatures between 4 and 80 °C and extrapolated the data to 200 °C. The apparatus they used consisted of two attached vessels, initially closed off from each other with a stop-cock. 10 g of thermally treated Na_2CO_3 , as well as frozen CO_2 , were placed into the lower vessel, which was then evacuated. The upper vessel was also evacuated and contained 250 mL of distilled and degassed water. For the equilibrium reaction, the stop-cock between the vessels was opened to allow the water to flow into the lower vessel. This vessel was then kept in a temperature-controlled environment for periods between one day and one week. The equilibrated CO_2 gas was sampled by closing the stop-cock and cryogenically sampling the CO_2 gas from the upper vessel. Since the DIC of the solution did not differ isotopically from the given Na_2CO_3 , only the equilibrated CO_2 gas was analysed for its isotope ratio. Also, because of difficulties to completely separate CO_3^{2-} from HCO_3^- , $\alpha^{13}\text{C}_{\text{CO}_3^{2-}-\text{CO}_2}$ was calculated with the following equation:

$$\alpha^{13}\text{C}_{\text{CO}_3^{2-}-\text{CO}_2} = [\alpha^{13}\text{C}_{\text{DIC}-\text{CO}_2} - x_{\text{HCO}_3^-}(\alpha^{13}\text{C}_{\text{HCO}_3^--\text{CO}_2})] / x_{\text{CO}_3^{2-}} \quad (22)$$

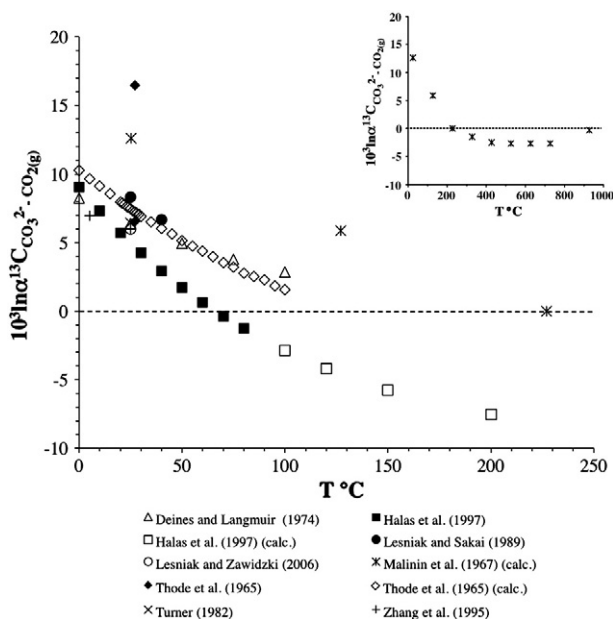


Fig. 3. Isotope fractionation $10^3 \ln \alpha^{13}\text{C}_{\text{CO}_3^{2-}-\text{CO}_{2(g)}}$ against temperature. The dashed line indicates where $10^3 \ln \alpha = 0$. The graph in the top right corner shows the calculated data by Malinin et al. (1967) above 250 °C.

where,

$$x_{\text{HCO}_3^-} = [\text{HCO}_3^-] / [\text{DIC}] \quad (23)$$

$$x_{\text{CO}_3^{2-}} = [\text{CO}_3^{2-}] / [\text{DIC}]. \quad (24)$$

The value for $\alpha^{13}\text{C}_{\text{HCO}_3^--\text{CO}_2}$ was taken from reported values by other authors (e.g. Mook et al. 1974). The amount of H_2CO_3 in the total DIC was assumed negligible due to the high pH (10.3) and, hence, was not considered.

The results of the experiments are listed in Table 3 and plotted in Fig. 3. The fractionation curves by all authors show a negative slope with increasing temperature.

Significant discrepancies exist between the measurements made by the various authors investigating fractionation at a temperature range, and those who investigated only one or two temperatures. Thode et al. (1965) were the first to measure the fractionation between CO_3^{2-} and $\text{CO}_{2(g)}$ and found $10^3 \ln \alpha$ values that varied between 6.6 and 16.6‰. Thode et al.'s (1965) calculated results match those of Lesniak and Sakai (1989), whereas the ones of Deines et al. (1974) and Turner (1982) are comparable with each other. Halas et al. (1997) mention, however, that fractionation factors reported by previous authors are too high, when compared to his own measurements. Lesniak and Sakai (1989), for instance, performed open system experiments, which provided results that were probably too high due to either a too short reactor height to allow equilibration (Lesniak and Zawidzki, 2006) or due to kinetic effects affecting the system (Halas et al., 1997). Lesniak and Zawidzki (2006) experimentally determined fractionation in an open system at 25 °C and stated that open system experiments yield more reliable results. They argue that a theoretically infinite number of samples can be extracted with considerably less uncertainties in the $^{13}\text{C}/^{12}\text{C}$ ratio and further, a two-direction approach allows to attain isotopic equilibrium between CO_3^{2-} gas and $\text{CO}_{2(g)}$ from opposite directions. The results by Zhang et al. (1995) and Lesniak and Zawidzki (2006) fit the ones by Halas et al. (1997). Halas et al. (1997) were among the few authors to describe measured isotope fractionation up to 80 °C and extrapolated data up to 200 °C. They thus covered the widest experimentally determined temperature range. A non-linear temperature dependency was suggested, however, if one would consider only the experimental data up to 80 °C, a linear relationship would be established (Table 3). However, the results showed significant scattering at temperatures higher than 40 °C. This was explained by leakage or diffusion of CO_2 out of the experimental apparatus. Hence, the actual isotope fractionation trend becomes increasingly unclear above this temperature. The crossover point at about 63 °C reported by Halas et al. (1997) therefore requires verification. Malinin et al. (1967) calculated isotope equilibrium constant values up to 927 °C. Their results lie higher than reported by the other authors. According to these results, the fractionation curve between CO_3^{2-} and CO_2 reaches its minimum at about 600 °C and a crossover point would occur at least twice, theoretically, at 227 and close to 930 °C (Fig. 3). However, they note that no definite statement on the actual exchange reaction behaviour can be made at higher temperatures without experimental verification.

So far, it has not been possible to establish repeatable experiments in high accuracy to measure fractionation factors between CO_3^{2-} and $\text{CO}_{2(g)}$. This may be related to the reason that most experiments were carried out at different ionic strengths and measurements then become increasingly difficult (Lesniak and Sakai, 1989; Lesniak and Zawidzki, 2006). Other challenges consist of attaining chemical and isotope equilibrium between CO_3^{2-} ions and $\text{CO}_{2(g)}$. Further experiments are recommended to investigate fractionation between CO_3^{2-} and $\text{CO}_{2(g)}$ at higher temperatures, especially above 40 °C, to verify already published data and to minimise uncertainty.

2. Conclusions

In this review, an overview of the methods used to investigate the temperature dependency of isotope fractionation between individual dissolved inorganic carbon species (H_2CO_3^* , HCO_3^- and CO_3^{2-}) and $\text{CO}_{2(g)}$, as well as a discussion of the accompanying results, was presented. The methodology and the experimental environment chosen posed the main reason for discrepancies among the different studies. The results presented for isotope exchange between H_2CO_3^* and $\text{CO}_{2(g)}$ showed that fractionation values reported by Vogel et al. (1970) show good agreement with Zhang et al. (1995) and Szaran (1998), thus suggesting that the methods described by these authors seem to be the most reliable for isotope fractionation factor investigations between these two phases. However, experimental data above 60 °C is lacking. HCO_3^- is the key anion for pH levels found most commonly in nature. Most carbon isotope fractionation values between HCO_3^- and $\text{CO}_{2(g)}$ reported by the various authors agree well with each other. The results by Mook et al. (1974) have been verified by other authors and cover the largest temperature ranges. Hence, even though investigation methods may have differed from each other, most of the described methods can be considered reliable for carbon isotope fractionation investigations between HCO_3^- and $\text{CO}_{2(g)}$. CO_3^{2-} and $\text{CO}_{2(g)}$ pose as the most challenging pair in terms of equilibrium isotope fractionations. The methods used for this pair all differed in technique from each other and ranged from open to closed systems. Therefore, the results by the described authors also varied significantly. Particularly at higher temperatures, a larger scatter of fractionation factors exists, especially in the CO_3^{2-} – $\text{CO}_{2(g)}$ system. CO_3^{2-} may be present under more variable conditions that are difficult to maintain experimentally and thus may be subject to more rapid changes. Further experiments in this system are, therefore, highly recommended, in open and closed systems, to verify previously published results and to minimise uncertainty.

All experiments showed at low temperatures a decreasing magnitude of fractionation with increasing temperatures. The DIC– CO_2 fractionation behaviour at higher temperatures, which is essential information for instance in hydrothermal isotope studies, where temperatures may reach over 350 °C (Macdonald et al., 1980), however, remains unclear. Therefore fractionation experiments at elevated temperatures are recommended to verify previously published extrapolated data, as well as to clarify the actual isotope fractionation behaviour at high temperatures in the carbonate system. Other uncertainties are variable salinity and pressure regimes that should also be investigated in future studies under open and closed system conditions.

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