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Calcium isotope fractionation during the partial dissolution of artificial calcite

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ABSTRACT

We studied the calcium (Ca) isotope fractionation during the partial dissolution of artificial calcite in pure water and in artificial seawater at 20 °C. Calcite (1.00 g) was stirred in 500 ml solution while bubbling it with air rich in CO_2 gas (400 and 500 ppm). Depending on the composition of the dissolving medium, the measured pH close to equilibrium decreased with increasing concentration of CO_2 in air. The dissolution rate (R*; μmol/m^2·h) increased with the concentration of CO_2 in air. The Ca isotope composition ($\delta^{44/40}$Ca) of the dissolved Ca in pure water during different intervals of partial dissolution process was almost constant and very close to that of calcite (1.06‰ ± 0.11‰). This phenomenon indicated that partial dissolution occurred without Ca isotope fractionation. By contrast, the isotope composition of Ca in artificial seawater (0.92‰ ± 0.17‰) was almost constant during the partial dissolution of calcite (<10% of calcite dissolved) because the Ca isotope composition in both calcite and in the artificial seawater were close to each other and the change in [Ca^{2+}] ions due to dissolution was not >9%.

1. Introduction

The study of the Ca isotope fractionation factors of authigenic calcium carbonate ($CaCO_3$) is recently used as a tracer to understand various geochemical processes (e.g., precipitation rate, temperature, pH, and salinity) (Gussone et al., 2003; Tang et al., 2008a, 2008b). Calcite is never found in nature as pure mineral. It is always precipitate including other trace elements as strontium. Environmental conditions and vital effects influence the ratios of trace elements to Ca in biogenic and inorganic precipitated $CaCO_3$ and the isotopic composition of different elements to Ca (Alkhatib and Eisenhauer, 2017a; Alkhatib and Eisenhauer, 2017b). $CaCO_3$ is one of the most common minerals in the soil and marine environments. Understanding the isotope fractionation of $CaCO_3$ during dissolution is important for many environmental applications, because $CaCO_3$ is the main component of the carbon budget and marine sediments (Lemarchand et al., 2019). Isotope composition of dissolved ions of minerals is directly related to their mother source, if partial dissolution is not accompanied by isotope fractionation. Analysis of the aqueous solution indicates its original sources, whether from natural or anthropogenic sources (Andrews et al., 1997). This subject has a very important contribution to understand environmental issues. Such analysis is an important tool for determining the environmental conditions of precipitation and dissolution of $CaCO_3$. Precipitation is usually accompanied by Ca isotope fractionation (i.e., the isotope composition of the mineral is different from the aqueous solution). The application of isotope techniques as a powerful method for evaluating the sources, pathways, transformation, and fate of minerals in the systems could assist environmental management (Gussone et al., 2003; Tang et al., 2008a, 2008b).

The reported values of Ca isotopic fractionation between calcite and aqueous solution as a function of precipitation rate have certain discrepancies. Lemarchand et al. (2019) showed that as the precipitation rate increases, $\Delta^{44/40}$Ca increases. However, the opposite behavior was obtained by Tang et al. (2008a, 2008b), that is, as precipitation rate increases, $\Delta^{44/40}$Ca decreases. Then, Alkhatib and Eisenhauer (2017a, 2017b) proved both contrasting results and showed that the mechanism of fractionation is dependent on the chemistry of the aqueous solution and temperature of precipitation.

$CaCO_3$ mineral (calcite in this case) is not pure (Morse and Mackenzie, 1990; Garrels and Christ, 1965) but contains various trace elements, mostly alkaline-earth elements, such as magnesium, strontium and barium, and other elements, such as lithium, boron, cadmium, uranium, and thorium. The enrichment of these trace elements in biogenic and inorganic $CaCO_3$ relative to Ca reflects their specific

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environmental conditions (e.g., temperature, growth rate, pH, salinity, and composition of seawater) at the time of formation (e.g., Alkhatib and Eisenhauer, 2017a; Alkhatib and Eisenhauer, 2017b; Morse and Bender, 1990; Lopez et al., 2009; Tang et al., 2012). In the case of biogenic origin, $CaCO_3$ is also affected by the species or biologic effects (vital effects) (Lea et al., 1999). The ratios of trace elements to Ca in $CaCO_3$ provide a valuable archive (proxy) of oceanographic data, so such value is important for reconstructing the paleoenvironmental conditions of oceans (Oelkers et al., 2019; Gaetani et al., 2011).

The precipitation and dissolution of $CaCO_3$ minerals (mainly calcite and aragonite) in the oceans are the main factors in the carbon cycle. They are strongly related to controlling atmospheric CO_2 during time scales. The annual rate increase in atmospheric CO_2 due to industry and other human activities is mostly absorbed by the oceans. CO_2 is not simply dissolved in water but reacts to form bicarbonate and carbonate and evolves $H^+_{(aq)}$ and increases seawater acidity, according to the following sequential reactions (Zeebe and Wolf-Gladrow, 2003):

$$CO_2(g) + H_2O \rightleftharpoons CO_2(aq) \quad (1)$$

$$CO_2(aq) + H_2O \rightleftharpoons H_2CO_3 \quad (2)$$

$$H_2CO_3 \rightleftharpoons HCO_3^-(aq) + H^+(aq) \quad (3)$$

$$HCO_3^-(aq) \rightleftharpoons CO_3^-(aq) + H^+(aq) \quad (4)$$

K1 and K2 are the equilibrium constants for the first and the second dissociations of carbonic acid (H_2CO_3), respectively. These constants are dependent on temperature, pressure and salinity (Sulpisa et al., 2018; Millero, 1995).

$$K1 = [HCO_3^-(aq)][H^+(aq)]/[CO_2(aq)] \quad (5)$$

$$K2 = [CO_3^{2-}(aq)][H^+(aq)]/[HCO_3^-(aq)] \quad (6)$$

The sum of the dissolved $CO_2(aq) + HCO_3^-(aq) + CO_3^{2-}(aq)$ is called the total dissolved inorganic carbon (DIC). At a typical seawater condition (when CO_2 was 365 ppm and the pH level of seawater is 8.1), the abundance ratio of DIC components is $[CO_2(aq)]$: $[HCO_3^-(aq)]$: $[CO_3^{2-}(aq)] \approx 0.5\%$: 86.5%: 13% (Zeebe and Wolf-Gladrow, 2003). This value indicates that the dominant species is $HCO_3^-(aq)$. With decreasing ocean depth, the temperature decreases, and as a result, the negative log of the equilibrium constants pK1 and pK2 increase, which in turn would decrease the concentration of carbonate ions. Increasing anthropogenic CO_2 will increase the seawater acidity, which will finally be neutralized by the dissolution of $CaCO_3$ sediments and the shells of marine organisms according to the overall dissolution reaction (7) (Sulpisa et al., 2018).

$$CaCO_3(s) + CO_2(g) + H_2O \rightarrow Ca^{2+}(aq) + 2HCO_3^-(aq) \quad (7)$$

The factor that determines whether precipitation or dissolution will occur is the saturation state (Ω) with respect to the $CaCO_3$ minerals:

$$\Omega_{calcite} = [Ca^{2+}(aq)][CO_3^{2-}(aq)]/Ksp_{calcite} \quad (8)$$

where Ω is a function of temperature, pressure, and salinity (Millero, 1995). $Ksp_{calcite}$ is the solubility product constant of calcite. The value of $\Omega > 1$ corresponds to supersaturation, and the value of $\Omega < 1$ corresponds to undersaturation. $[Ca^{2+}]$ at sea surface is constant and equal to 10.28 mmol/kg. The saturation state of $CaCO_3$, mainly depends on the carbonate ion concentration. Calcite mineral continuously decreases with seawater depth. The solubility of different $CaCO_3$ minerals (amorphous calcium carbonate (ACC), vaterite, aragonite and calcite) increases with the seawater depth because of the decreasing temperature and increasing pressure. Thus, the supersaturation with respect to $CaCO_3$ minerals decreases with ocean depth until it reaches the line where $\Omega = 1$. This line is called the saturation depth, saturation horizon, or saturation level (Z_{sat}) (Boudreau et al., 2010). The Z_{sat} of calcite is deeper than that of aragonite, because aragonite is more soluble than calcite. Below the Z_{sat}, $CaCO_3$ starts to dissolve. The depth at which a rapid increase in dissolution rate occurs is called the lysocline. By contrast, the depth at which no more conservation (complete dissolution) of $CaCO_3$ happens is called the $CaCO_3$ compensation depth (CCD) (Zeebe and Wolf-Gladrow, 2003). Anthropogenic CO_2 will not only increase the acidity of seawater but also increase Z_{sat} and CCD of different $CaCO_3$ minerals and shorten the distance between these depths (Sulpisa et al., 2018). The lysocline will also move upwards in the ocean depth. For example, the pH level of historical surface seawater before the industrial revolution (1870) was 8.18. In 2005, when pCO_2 was ~380 ppm, the pH level decreased to 8.08 (Orr et al., 2005). The pH levels for the artificial seawater approaching equilibrium when pCO_2 levels were 400 ppm and 500 ppm are 7.79 and 7.71, respectively. The differences may seem small, but pH is a logarithmic function. The decline in the pH levels between the surface seawater before the year 1870 and the present results at pCO_2 500 ppm shows a 195% increase in acidity. Even considerably smaller changes already pose a problem for many marine creatures, which rely on their ability to construct protective shells and skeletons.

The dissolution of $CaCO_3$ has been extensively and rigorously studied (e.g., Berner and Morse, 1974; Morse, 1978; Plummer et al., 1978; Morse et al., 1979; Kier, 1980; Walter and Morse, 1984; Walter and Morse, 1985; Morse and Arvidson, 2002; Subhas et al., 2015) to understand the factors affecting the dissolution rate and to model the impact of fossil fuel CO_2 on the climate and diagenesis of sediments and sedimentary rocks.

Two main methods are used to study the $CaCO_3$ dissolution. The first technique is the pH–stat rate measurements, in which the pH and chemical composition remain constant during dissolution. The second technique is the free drift method (similar to this work), in which the dissolution is allowed to proceed to equilibrium at fixed pCO_2 and temperature, while the solution chemistry changes progressively with the extent of reaction (Plummer et al., 1978). The most commonly used equation in the geosciences to describe the rate of $CaCO_3$ dissolution is as follows (Morse and Arvidson, 2002):

$$R = \frac{dm\ calcite}{dt} = \left(\frac{A}{V}K\right)(1-\Omega)^n \quad (9)$$

where R is the normalized dissolution rate (μ mole/m^2·h); m is the number of moles of calcite; A is the total surface area of the solid; V is the volume of the solution (liter); Ω is the saturation state; K is the rate constant; and t is time.

The mechanism of dissolution is dependent on the pH level. As the pH level increases, the mechanism of dissolution changes from diffusion control to a chemically or surface-controlled mechanism (pH > 7) [25]. Plummer et al. (1978) showed that the dissolution rate is directly proportional to the CO_2 bulk solution ($[CO_2]$), where $[CO_2] = [CO_2](aq) + [H_2CO_3](aq)$.

Oelkers et al. (2019) studied the Ca isotopic fractionation during dissolution and reprecipitation of the dissolved Ca ions of calcite and found isotope fractionation during their study.

According to our knowledge, no robust data are available to confirm that dissolution occurs without isotope fractionation of different minerals. Oelkers et al. (2019) showed that partial dissolution of calcite was accompanied by isotope fractionation during the partial dissolution of calcite. This lack of information has motivated us to perform this isotope analysis of the partial dissolution of calcite. This important subject needs more studies to solve the discrepancies in the different reported results.

Very few published research has studied the effect of partial dissolution on the isotopic composition of $CaCO_3$. In this research, we explored the dissolution of synthetic calcite powder in pure water and in carbonate-free artificial seawater at 20 °C. Air rich in CO_2 (400 and 500 ppm) was bubbled into calcite, stirred, and suspended in solutions. We performed this study to determine the effect of increasing CO_2

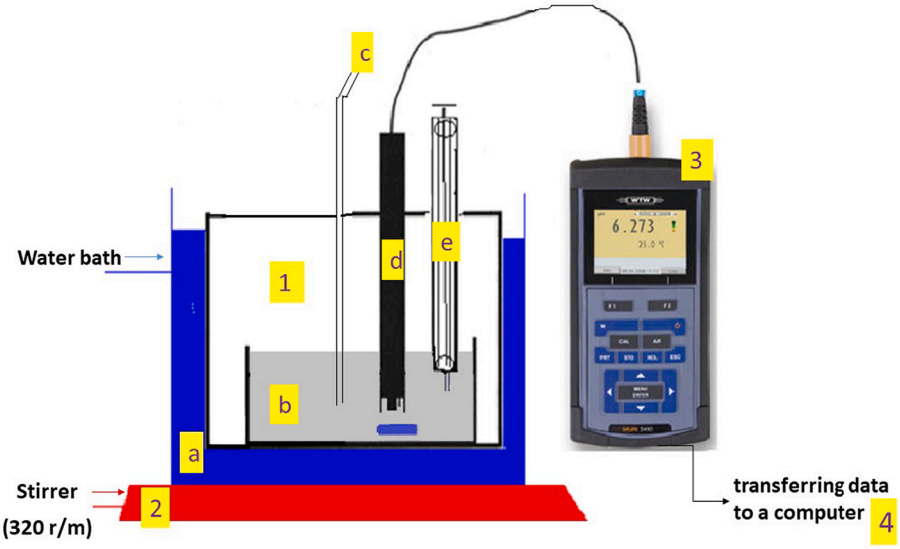

Fig. 1. Schematic design of the experimental setup: (1) the reaction chamber which is a sealed plastic container consisting of a copper tubing (a) where water is circulating to keep a constant temperature, (b) a beaker that contains the reacting solution, (c) a tubing through which air enriched with carbon dioxide gas is bubbled, (d) pH and temperature sensors, (e) syringe to withdraw samples from the reacting solution, (2) magnetic stirrer, (3) pH meter and (4) computer recording the measured data in an excel sheet.

concentration in the atmosphere on the dissolution of calcite. We also distinguished whether calcium isotopic fractionation occurs due to the partial dissolution of synthetic calcite powder and how the partial dissolution of Ca^{2+} ions would affect the bulk Ca isotope composition of seawater.

2. Material and methods

2.1. Materials and experimental setup

The experimental setup was composed of a sealed chamber with a copper tubing coil to control the internal temperature (20 ± 0.5 °C), as shown in Fig. 1. Commercial calcite (1 g, Roth, $CaCO_3$ > 99%, Art.-Nr. P012.2), with a surface area of 0.5 m^2/g (as previously determined by Alkhatib and Eisenhauer), was suspended and stirred (320 rpm) in 500 ml of either pure water [reactions (1) and (3)] or an artificial carbonate-ion-free seawater [reactions (2) and (4)], which was prepared according to the work of Kester et al. (1967). Artificial carbonate-free seawater had a pH level of 5.97 and salinity of 33 g/kg. All chemicals were ACS-grade (Merck), and all aqueous solutions were prepared using deionized water (18.2 MΩ). Air enriched with CO_2 (g) [400 ppm in reactions (1) and (2), and 500 ppm in reactions (3) and (4)] was bubbled into the suspended calcite solutions (60 ml/min). CO_2 gas was reacted with water according to reactions (1)–(4) and its acidity was increased, resulting in the partial dissolution of calcite according to reaction (7). A constant CO_2 concentration was achieved by using commercial bottles with the required concentration. The commercial gas with the required concentration was continuously pumped into the reactant to produce a constant concentration in air.

The progress of calcite dissolution was monitored by a WTW 3100 pH meter (pH accuracy was ±0.001), which was standardized against buffer solutions with pH levels of 4, 7, and 10 before each experiment. The pH meter was connected to a computer to continuously monitor online the pH values and the temperature of the solution (Fig. 1) and to record the measured data in an Excel sheet. During each experiment, the extent of dissolution of calcite as a function of time was monitored by sampling ~2 ml of the suspended solution at distinct time intervals and filtered with Whatman syringe filters with pore size of 5 μm. Each sample was then diluted by 1:1 with 2% super-pure nitric acid, and the concentration of the Ca ions and Ca isotope composition were measured.

2.2. Analysis

2.2.1. Elemental analysis

We analyzed the concentrations of Ca ions in the bulk suspended solutions at different intervals of time during each dissolution reaction by using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 7500cx- in Al-Quds University, Jerusalem, Palestine), with indium (In) as an internal standard. All samples were diluted in 2% HNO_3 to reach 25.0 ± 2.5 ppm Ca to avoid matrix effects. For quality control and accuracy, In, as an internal standard, was used in combination with a multistandard calibration method. Each sample was analyzed thrice. Coral standard JCP-1 was used as a reference material and measured once after measurements in each run. The JCP-1 Sr/Ca and Mg/Ca ratios were calculated to be 8.82 ± 0.03 and 4.22 ± 0.04 mmol/mol, respectively, which matched within the statistical uncertainty of the reported values of 8.84 ± 0.09 Sr/Ca and 4.2 ± 0.1 Mg/Ca mmol/mol (Hathorne et al., 2013).

2.2.2. PHREEQC model

PHREEQC is a geochemical model that is capable of simulating a wide range of equilibrium reactions between water and minerals, ion exchangers, surface complexes, solid solutions, and gases(Charlton and Parkhurst, 2011). For example, the variables used for modeling experiment 2 were as follow:

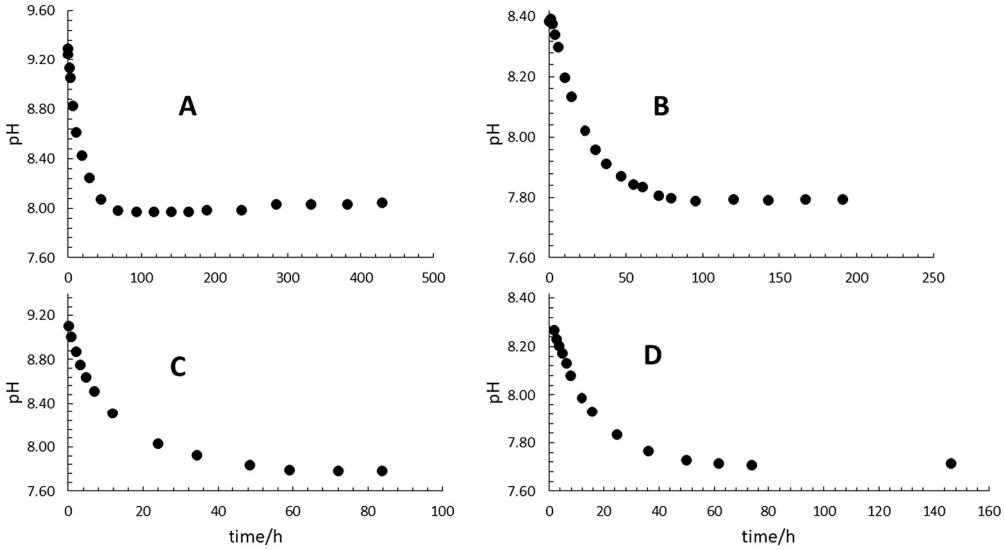

Fig. 2. Changing pH during calcite dissolution, **A** for reaction **1**, when 1.0 g calcite was suspended and stirred into 500 ml pure water, while bubbled with air rich in (400 ppm) CO_2 g; **B** for reaction **2**, when 1.0 g calcite was suspended and stirred into 500 ml of free carbonate artificial seawater, while bubbled with air rich in (400 ppm) CO_2 g; **C** for reaction **3**, when 1.0 g calcite was suspended and stirred into 500 ml pure water, while bubbled with air rich in (500 ppm) CO_2 g; **D** for reaction **4**, when 1.0 g calcite was suspended and stirred into 500 ml free carbonate artificial seawater, while bubbled with air rich in (500 ppm) CO_2 g.

```
GAS_PHASE 1
    -fixed pressure
    -pressure 1
    -volume 1
    -temperature 20
    CO2(g)     0.0004

EQUILIBRIUM_PHASES 1
    Calcite    0 0.01 (moles)

SOLUTION 1
    temp       20
    pH         5.97
    pe         4
    redox      pe
    units      mmol/kgw
    density    1
    B          0.421
    Br         0.826
    Ca         10.9
    Cl         545.9 charge
    F          0.053
    K          9.897
    Mg         53.27
    Na         468.3
    S(6)       28.22
    Sr         0.091
    -water     1 # kg
     End
```

2.2.3. Analysis of calcium isotope

Measurements were carried out at the GEOMAR mass spectrometer facilities in Kiel, Germany, with a ThermoFisher Triton T1 Thermal-Ionization-Mass-Spectrometer (TIMS). As described by Alkhatib and Eisenhauer (2017a), Ca ($\delta^{44/40}$Ca) isotope composition was measured for the solid calcite and some randomly selected samples of aqueous solutions of the dissolution reactions at various intervals, as described earlier by Heuser et al. (2005) and Böhm et al. (2006), respectively. For each sample to be analyzed, 3000 ng of Ca were spiked with 120 µl of ^{43}Ca/^{48}Ca double spike to correct for isotope fractionation in the mass spectrometer during the analysis of the Ca isotope. The mixture was evaporated to dryness and then redissolved in 100 µl of 0.9 N HCl. The solution was loaded onto an ion exchange column (BIO RAD of 800 µl bed volume; cation exchange resin MCI Gel, CK08P, 75–150 µ, Mitsubishi chemical composition) to extract the Ca-fraction.

After the column was washed with pure water (18.2 MΩ) and then with 1.5 N HCl, the sample was loaded to the column and washed again with 3.5 ml of 1.5 N HCl. The Ca fraction was then eluted after the column was rinsed with 9 ml of 1.5 N HCl. Then, the solution was evaporated to dryness and redissolved in 20 µl of 2.5 N HCl. This quantity was enough to load ten filaments to be measured into ten separate runs. In each run session, NIST SRM915a was measured four times, and CaF_2 was measured twice and used as a control standard. Each sample was measured at least five times. The isotopic ratio of each sample and CaF_2 was normalized to the mean of the four ^{44}Ca/^{40}Ca NIST SRM915a analysis and reported in the common delta notation, $\delta^{44/40}$Ca (‰) = $[(^{44}Ca/^{40}Ca)_{sample}/(^{44}Ca/^{40}Ca)_{standard} - 1] \times 1000$. The blank values of our chromatographic column separations were < 17 ng of Ca as a whole procedure blank in all batches we prepared. The average $\delta^{44/40}$Ca of the separated NIST SRM915a by column chemistry was measured thrice. The measured value was 0.02‰ ± 0.02‰, indicating nonsignificant deviation due to the column separation of the standard. The average $\delta^{44/40}$Ca of CaF_2 measured in six different runs was 1.4‰ ± 0.2‰ (n = 12), which is in agreement with earlier measurements (Heuser et al., 2005).

Table 1
Summary of results of reactions: equilibrium pH of the dissolution medium, dissolution rate (µM /h) and the normalized dissolution rate (µmol/m^{2}·h).

Experiment number	[CO_2] (ppm) in air	Dissolution medium	Near equilibrium pH	Dissolution rate (R) (µM/h)	Normalized rate (R*) (µmol/m^{2}·h)
1	400	Pure water	8.040	6.7	6.7
2	400	Free carbonate artificial seawater	7.791	9.5	9.5
3	500	Pure water	7.775	12.1	12.1
4	500	Free carbonate artificial seawater	7.710	13.5	13.5

Notes: Dissolution rate R (µM /h) equals the slopes of the linear parts of the curves of Fig. 3, normalized dissolution rate R* (µmol/m^{2}·h) (equals R* volume of solution) (L)/area of solid calcite, while volume of solution = 0.5 L and area of 1 g of calcite = 0.5 m^{2}, so numerically R = R*.

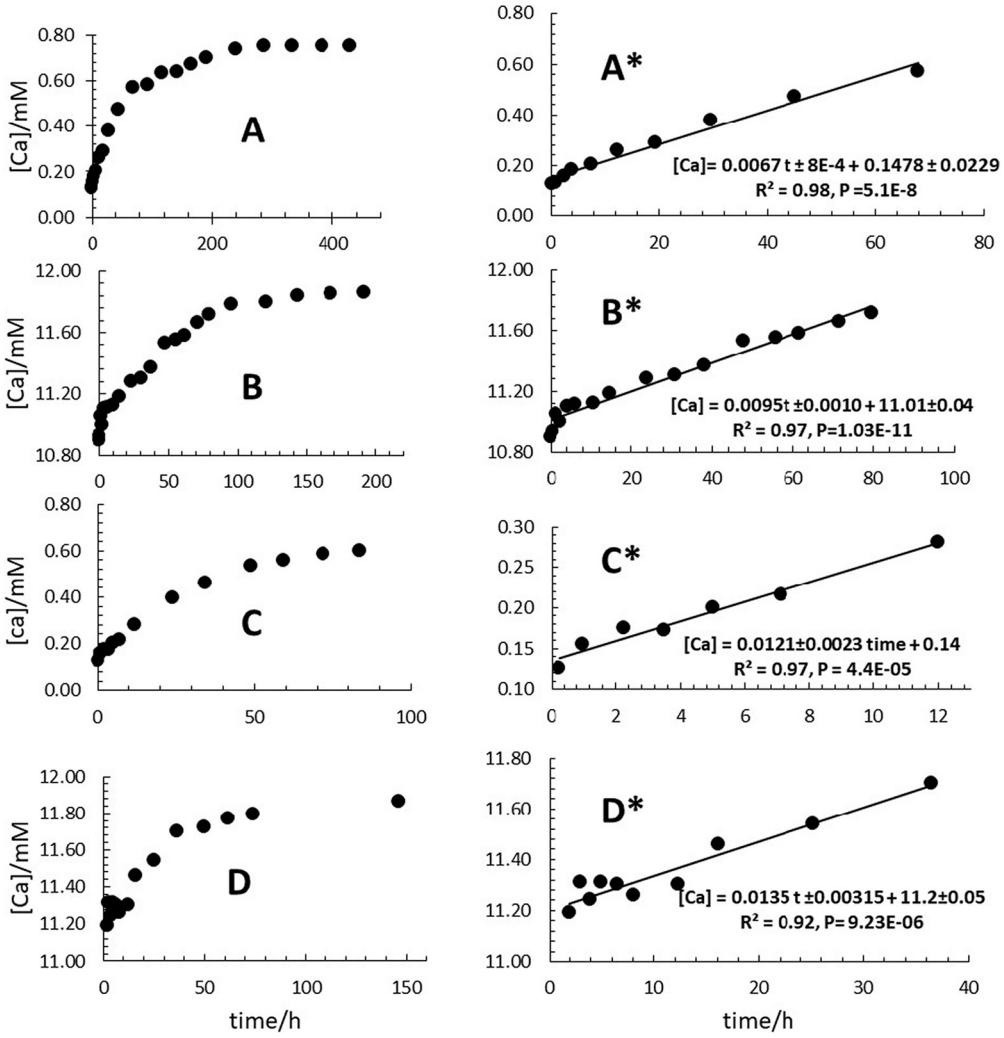

Fig. 3. Changing [Ca^{2+}] during calcite dissolution as function of time/h, **A** for reaction **1**, **A*** shows the linear part of fig. A, its slope equal to the rate of dissolution (mM/h); **B** for reaction **2**, **B*** shows the linear part of fig. B, **C** for reaction **3**, **C*** shows the linear part of fig. C and **D** for reaction **4**, **D*** shows the linear part of fig. D.

3. Results

3.1. Variation in pH level during dissolution

Once calcite was added to the dissolution medium (pure water or/ and artificial seawater), the pH level rose due to the solubility of calcite according to the following reaction:

$$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq) \quad (10)$$

However, continuous bubbling of CO_2-rich air in aqueous solution will produce H^+ (aq) [reactions (1)–(4)], which will gradually decrease the pH level and dissolve calcite and increase [Ca^{2+}] as in reaction (7) for all sample reactions, as shown in Fig. 2. The pH level of the reacting solutions near equilibrium is almost constant, because the solution is buffered by the carbonate/bicarbonate system. The solution would resist any further decrease in pH level due to the dissolution of the CO_2 gas, as shown in Table 1. At near equilibrium (334, 168, 84 and 164 h, respectively for the reactions 1,2,3 and 4 as shown in in Fig. 3), equilibrium was not achieved since dissolution is still dominant over precipitation ([Ca^{2+}] still increased in the solution), as shown in Fig. 3. At near equilibrium, for all solutions, as the concentration of CO_2 gas in air increases, the pH level of the aqueous solution decreases (Table 1). At the same concentration of CO_2 in the air, the pH level of seawater is lower than that of pure water, because pH level is dependent on composition and salinity (Millero, 1995).

3.2. Dissolution rate

Throughout the dissolution process, [Ca^{2+}] increases in the aqueous solution with time. In the beginning, the increase in [Ca^{2+}] is linear. However, with time, the relationship deviates from linearity as the process approaches equilibrium, as shown in Fig. 3. From the linear parts in Fig. 3, which is indicated with a star (*), the initial rate (R) of the dissolution rate of reaction is equal to the slope of the straight line in the unit of micromolar per hour. While the dissolution reaction varies, the rate of reaction has to be normalized to the surface area of calcite powder: Normalized rate (R*) $= \frac{R.V}{S}$, where V is the volume of solution in L = 0.5, and S is the surface area of the solid powder (0.5 m^2). In this case, R is numerically equal to R* (its unit is μmol/m^2·h). Table 1 shows that R* increases with the CO_2 gas in air, and this result is in agreement with that reported by Plummer et al. (1978). In addition, at the same CO_2 gas concentration in air, R* in the artificial seawater is higher than that in pure water due to the electrostatic attraction forces between ions in the solution and ions in the solid phase.

3.3. Analysis of the calcium isotope during the dissolution of calcite

The isotope composition ($\delta^{44/40}$Ca‰) of the solid calcite is 1.06‰ ±

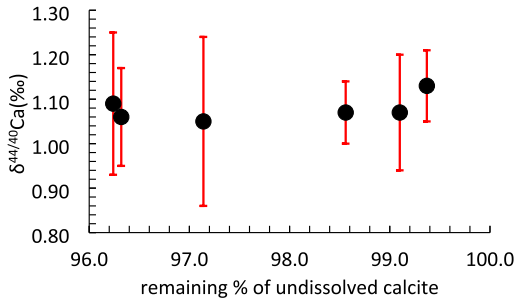

Fig. 4. Calcium isotope composition ($\delta^{44/40}$Ca‰) during calcite partial dissolution as function of remaining % of undissolved calcite of reaction 1 in which 1.0 g calcite was suspended and stirred into 500 ml pure water, while bubbled with air rich in (400 ppm) CO_2 g.

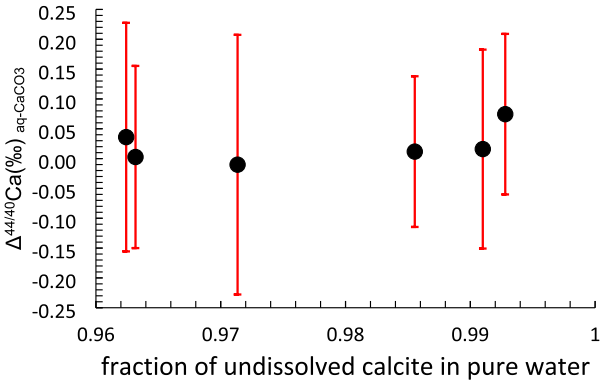

Fig. 5. Calcium isotope fractionation ($\Delta^{44/40}$Ca‰ $_{calcite\text{-}aq}$) during calcite partial dissolution as function of remaining % of undissolved calcite of reaction 1 in which 1.0 g calcite was suspended and stirred into 500 ml pure water, while bubbled with air rich in (400 ppm) CO_2 g.

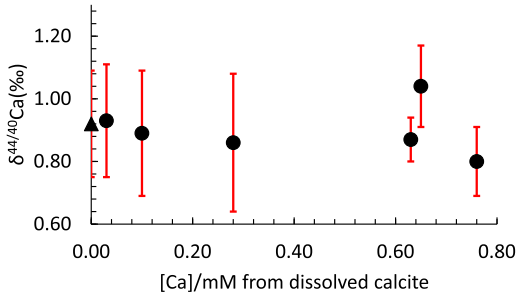

Fig. 6. Calcium isotope composition ($\delta^{44/40}$Ca‰) of the aqueous solution during calcite partial dissolution as function of dissolved [Ca^{2+}] from calcite of reaction 2 in which 1.0 g calcite was suspended and stirred into 500 ml of carbonate free artificial seawater, while bubbled with air rich in (400 ppm) CO_2 g.

0.11‰, while those of the dissolved Ca^{2+} at different intervals of time during the partial dissolution of calcite in reaction (1) (pure water; 400 ppm CO_2) are very close to this value as shown in Fig. 4. Thus, the isotope fractionation expressed as $\Delta^{44/40}$Ca, ($\Delta^{44/40}Ca = \delta^{44/40}Ca_{calcite} - \delta^{44/40}Ca_{(aq)}$) is negligible and close to zero, as shown in Fig. 5. From the data of reaction (2) (in artificial seawater; 400 ppm CO_2) as shown in Fig. 6, the isotopic compositions of aqueous Ca^{2+} ions ($\delta^{44/40}$Ca‰) during the dissolution process is almost constant and very close to the $\delta^{44/40}$Ca‰ value of the artificial seawater solution before any calcite dissolution (0.92‰ ±0.17‰) occurred (presented as a triangle point in Fig. 6). This phenomenon is due to the fact that $\delta^{44/40}$Ca‰ of both the solid (1.06‰ ± 0.11‰,) and the original solution (0.92‰ ± 0.17‰) are close to each other and the composition of the aqueous changed only by ~10% at the end of the experiment as a result of the partial dissolution of calcite.

3.4. PHREEQC modeling

PHREEQC modeling was applied for all experiments. The results show that the saturation index (SI) for all experiments were zero for calcite, which means that the dissolution of calcite is the predominant process before the equilibrium is reached in this system. On the other hand the SI values for all experiments were calculated to be −0.14 for aragonite, which means that aragonite will never precipitate in these experiments. It can be seen from Table 2 that for all experiments, actual pH at equilibrium is more acidic than calculated from the model, and more calcite was dissolved than calculated from PHREEQC.

4. Discussion

Based on our results, increasing pCO_2 in air will not only increase the acidity of aqueous solution and decrease its pH level but will also increase the dissolution rate of $CaCO_3$. This experimental result also coincides with PHREEQC model (see Table 2).

No discrepancies in the pattern of decreasing pH as result of increasing pCO2 between our experimental results and the data obtained from the model. The pH level of the reaction solution near equilibrium is ~7.8 when pCO_2 is 400 ppm. The actual oceanic pH is ~8.1, with the present atmospheric CO_2 value of 420–430 ppm. The buffer capacity of the ocean is considerably higher and more complex than a simple chemical setup. The ocean is a huge system with a complex biogeochemistry cycles and biological productivity that are directly related to CO_2 concentrations.

Although only ~4% of calcite was dissolved in the experiment (1), dissolution occurs without isotope fractionation or Ca isotope composition in calcite similar to that in aqueous solution as a result of dissolution. We speculate that calcite used in this study is completely homogeneous in its Ca isotopic composition, from its surface to the inner core of the crystals. Whatever the mechanism of dissolution (diffusion or surface control), the activation energies of dissolution of the different Ca isotopes are equal, because dissolution occurs without Ca isotope fractionation. The activation energy (Ea) for the calcite formation is ranging between 114 and 155 kJ/mol depending on the experimental setup (Alkhatib and Eisenhauer, 2017a), and is about 100 kJ/mol higher than that of calcite dissolution. Since Ea of calcite dissolution ranges between

Table 2
A comparison between experimental result and PHREEQC model.

Reaction	Experimental pH at equilibrium	pH calculated from PHREEQC	[Ca^{2+}]/mM In solution at equilibrium experimentally	[Ca^{2+}]/mM In solution at equilibrium from PHREEQC	Mass /g of calcite at equilibrium experimentally	Mass/g of calcite calcite at equilibrium from PHREEQC
1	8.040	9.937	0.752	0.1209	0.9624	0.9879
2	7.791	8.603	11.86	11.08	0.952	0.9822
3	7.775	9.913	0.599	0.1215	0.9720	0.9878
4	7.710	8.590	11.86	11.08	0.952	0.9821

Table 3
Data of reaction **1** in which 1.0 g calcite was suspended and stirred (320 rpm) into 500 ml pure water, while bubbled (60 ml/min) with air rich in (400 ppm) CO_2 g. Time of sampling, concentration of dissolved [Ca^{2+}] in ppm and mM respectively, pH, % remaining of undissolved calcite, isotope composition of [Ca^{2+}] in aqueous solution ($\delta^{44/40}$Ca‰) and calcium isotope fractionation $\Delta^{44/40}$Ca‰. SEM is the standard error of the mean.

sample	Time (h)	[Ca] (ppm)	[Ca] (mM)	pH	% Remaining calcite	$\delta^{44/40}$Ca‰ (‰ SRM915a)	±(2SEM)	$\Delta^{44/40}$Ca‰	±(2SEM)
1	0.20	5.07	0.127	9.291	99.37	1.13	0.08	0.07	0.13
2	1.00	5.14	0.129	9.240	99.36				
3	2.57	6.21	0.155	9.130	99.23				
4	4.08	7.20	0.180	9.051	99.10	1.07	0.13	0.02	0.17
5	7.72	8.09	0.202	8.821	98.99				
6	12.55	10.32	0.258	8.610	98.71				
7	19.50	11.55	0.289	8.422	98.56	1.07	0.07	0.01	0.13
8	29.72	15.12	0.378	8.240	98.11				
9	45.34	18.91	0.473	8.070	97.64				
10	67.95	22.92	0.573	7.981	97.14	1.05	0.19	−0.01	0.22
11	93.75	23.14	0.579	7.971	97.11				
12	117.57	25.30	0.633	7.970	96.84				
13	141.57	25.54	0.639	7.971	96.81				
14	165.54	26.86	0.672	7.970	96.64				
15	190.02	27.86	0.697	7.980	96.52				
16	239.00	29.52	0.737	7.981	96.32	1.06	0.11	0.00	0.15
17	285.48	30.18	0.75	8.031	96.25				
18	333.75	30.04	0.751	8.032	96.25				
19	383.08	30.04	0.751	8.030	96.25				
20	430.75	30.08	0.752	8.041	96.24	1.09	0.16	0.04	0.19

42 and 54 kJ/mol depending on pCO_2 (Oleg et al., 2009), we speculate that this gap of energy is not enough to discriminate between heavy and light Ca isotopes.

Turchyn and DePaolo (2011), studied pore fluid calcium isotope composition from ocean drilling, in order to measure the rates of diagenetic dissolution and precipitation of calcite in deep-sea sediments containing abundant clay and organic material. They found that $\delta^{44/40}$Ca of pore fluid was very close to seawater values and different from $\delta^{44/40}$Ca of carbonate solids. This finding was due to the slow dissolution rate of carbonate minerals. Clay and other organic matters, protect carbonate minerals from being dissolved. Their conclusion fits well with different numerical models. According to the numerical model of Turchyn and DePaolo (2011), there is no Ca isotope fractionation in the pore fluid occurred during calcite dissolution, as a result of the limited and slow dissolution process. This finding is consistent with our results.

This result confirms the usage of different isotope compositions of elements in the aqueous solutions to identify their original solid sources. This technique has a wide range of applications, especially in environmental studies, to determine the sources of soluble contaminants in aqueous solutions.

The Ca isotope composition of the aqueous solution of reaction (2) remains almost constant and equal to the isotope composition of the original artificial seawater (0.92‰ ± 0.17‰) as shown in Fig. 6. This phenomenon is due to the fact that the change in Ca ion concentration is limited (does not exceed 10% of the original concentration), and the isotope composition of the solid calcite used in this study is indistinguishable (1.06‰ ± 0.11‰) from that of the aqueous Ca ions in the artificial seawater (the opposite of the natural samples). Moreover, the most important finding of this study reveals that the isotope composition of the dissolved Ca ions from calcite is identical to the Ca isotope composition in the solid calcite. Hence, dissolution of calcite occurs without Ca isotope fractionation and is independent of the dissolution rate, because the Ca isotope composition of different samples from the aqueous solution of reaction (1) are identical. However, the samples are collected at different intervals of time with different dissolution rates, as shown in Fig. 3A.

It should be noted that the large error bars (2σ) in measuring Ca isotope composition, which is at least 10 times larger than that of Sr as shown in Alkhatib and Eisenhauer (2017a, 2017b) due to the following reasons:

1. Ca is lighter than Sr, so Ca is easier to be kicked off from the trajectory of the mass spectrometer, resulting in a wider spread of ionic beam.
2. We measure the ratio of $^{40}Ca/^{44}Ca$, the mass difference of 40 to 44 is 10%, which is the maximum mass spread of a mass spectrometer. So 40 and 44 are measured at the outer cups.
3. ^{43}Ca and ^{48}Ca are the spike isotopes. ^{48}Ca is not measured in the same time with 40, because the mass spread is >10%. So we need two jumps: 40, 42,43, 48 are measured simultaneously in the first jump. In the second jump we measure 43, 44, 48. For the spike correction we use the ratio 43(jump 1) and 48 (jump2). These two isotopes are thus not measured simultaneously and their ratio 43/48 can't be estimated as precise as if they were measured in one jump.
4. All Sr isotopes are measured simultaneously and they are double as heavy

   as Ca. They are not kicked off as easy from their trajectory, and are not measured at the outer cups.

PHRQEEC modeling calculations have shown that the system is undersaturated with Ca-bearing mineral phases, because all calculated results have shown negative SI values with respect to calcite in all experiments. Hence, dissolution is the predominant process over precipitation.

In this study, we focused only on the effect of chemical process, although other biogenic factors and biogeochemical cycles also contribute to the isotope composition of different elements in the ocean.

In general, Ca isotopic composition of the inorganic and marine skeletal carbonates is lighter than the Ca isotopic composition of seawater (Steuber and Buhl, 2006). Contrary to $CaCO_3$ dissolution, as precipitation rate increases and as temperature decreases, Ca isotopic composition in $CaCO_3$ becomes lighter (Tang et al., 2008a, 2008b). Increasing pCO_2 from 400 ppm [reactions (1) and (2)] to 500 ppm [reactions (3) and (4)] not only will increase water acidity (decreasing pH) but also the dissolution rate of $CaCO_3$ (Table 1). As a consequence, we believe that increasing pCO_2 will rise the Z_{sat} and CCD of different $CaCO_3$ minerals. Given that the dissolution of $CaCO_3$ will change the Ca isotopic composition of seawater to be lighter, we speculate that the Ca isotope composition of the water column of oceans can be used to determine the lysocline and CCD. We expect the depth between the lysocline and CCD should be lighter in the calcium isotope composition.

Although Oelkers et al. (2019) has studied the Ca isotopic fractionation during dissolution and reprecipitation of the dissolved calcium

Table 4
Data of reaction **2** in which 1.0 g calcite was suspended and stirred (320 rpm) into 500 ml carbonate free artificial seawater, while bubbled (60 ml/min) with air rich in (400 ppm) CO_2 g. Time of sampling, concentration of dissolved [Ca^{2+}] in ppm and mM respectively, pH, % remaining of undissolved calcite, isotope composition of [Ca^{2+}] in aqueous solution ($\delta^{44/40}$Ca‰). SEM is the standard error of the mean.

Sample	Time (h)	[Ca] (ppm)	[Ca] (mM)	pH	% remaining	[Ca] (mM)	$\delta^{44/40}$Ca‰ (SRM915a)	±(2SEM)
					calcite	From dissolved calcite		
1	0.00	436.0	10.90	5.970	100.00	0.00	0.92	0.17
2	0.50	437.2	10.93	8.383	99.85	0.03	0.93	0.18
3	1.50	442.0	11.05	8.390	99.25	0.15		
4	2.50	440.0	11.00	8.373	99.50	0.10	0.89	0.20
5	4.30	444.0	11.10	8.338	99.00	0.20		
6	6.30	444.4	11.11	8.297	98.95	0.21		
7	10.70	444.8	11.12	8.194	98.90	0.22		
8	14.70	447.2	11.18	8.130	98.60	0.28	0.86	0.22
9	23.80	451.2	11.28	8.018	98.10	0.38		
10	30.80	452.0	11.30	7.955	98.00	0.40		
11	38.00	454.8	11.37	7.910	97.65	0.47		
12	47.70	461.2	11.53	7.868	96.85	0.63	0.87	0.07
13	55.8	462.0	11.55	7.840	96.75	0.65	1.04	0.13
14	61.70	463.2	11.58	7.832	96.60	0.68		
15	71.60	466.4	11.66	7.805	96.20	0.76	0.80	0.11
16	79.60	468.8	11.72	7.797	95.90	0.82		
17	95.80	471.2	11.78	7.788	95.60	0.88		
18	120.50	472.0	11.80	7.791	95.50	0.90		
19	143.60	473.6	11.84	7.790	95.30	0.94		
20	167.70	474.0	11.85	7.791	95.25	0.95		
21	191.80	474.4	11.86	7.791	95.20	0.96		

Table 5
Data of reaction **3** in which 1.0 g calcite was suspended and stirred (320 rpm) into 500 ml pure water, while bubbled (60 ml/min) with air rich in (500 ppm) CO_2 g. Time of sampling, concentration of dissolved [Ca^{2+}] in ppm and mM respectively and pH.

Sample	Time (h)	[Ca] (ppm)	[Ca] (mM)	pH
1	0.25	5.04	0.126	9.095
2	1.00	6.16	0.154	9.000
3	2.25	7.00	0.175	8.860
4	3.50	6.92	0.173	8.740
5	5.00	8.00	0.200	8.628
6	7.12	8.64	0.216	8.503
7	12.00	11.24	0.281	8.300
8	24.15	15.72	0.393	8.027
9	34.55	18.32	0.458	7.922
10	48.83	21.32	0.533	7.830
11	59.38	22.20	0.555	7.786
12	72.22	23.36	0.584	7.778
13	84.03	23.96	0.599	7.775

ions of calcite, many differences are found between our chemical setup and that of Oelkers et al. (2019). In the study of Oelkers et al. they used NaCl from 1% to 0.008% and pure CO_2 gas to reach a pH level of 6.2. Their result showed isotope fractionation, and the aqueous solution became heavier in the Ca isotope composition. We obtained contrasting findings in the present study because Ca isotope fractionation is largely dependent on the rate and extent of dissolution of $CaCO_3$ as explained by Turchyn and DePaolo (2011).

5. Conclusion

The Ca^{2+} ions in the aqueous solution produced by partial calcite dissolution have the same Ca isotope composition of calcite. Thus, the partial dissolution of calcite occurs without Ca isotope fractionation. No differences in the dissolution activation energies are found in the different Ca isotopes in calcite. Thus, the different elemental isotope compositions as calcite in aqueous solutions can be used as robust tracers for their solid origin.

Table 6
Data of reaction **4** in which 1.0 g calcite was suspended and stirred (320 rpm) into 500 ml carbonate free artificial seawater, while bubbled (60 ml/min) with air rich in (500 ppm) CO_2 g. Time of sampling, concentration of dissolved [Ca^{2+}] in ppm and mM respectively and pH.

Sample	Time (h)	[Ca] (ppm)	[Ca] (mM)	pH
1	0.00	436.0	10.90	5.970
2	2.00	447.6	11.19	8.263
3	3.00	452.4	11.31	8.227
4	4.00	449.6	11.24	8.199
5	5.00	452.4	11.31	8.170
6	6.50	452.0	11.30	8.129
7	8.10	450.4	11.26	8.078
8	12.30	452.0	11.30	7.983
9	16.20	458.4	11.46	7.925
10	25.20	461.6	11.54	7.829
11	36.50	468.0	11.70	7.762
12	50.10	468.8	11.72	7.726
13	62.00	470.8	11.77	7.712
14	74.00	471.6	11.79	7.705
15	146.50	474.4	11.86	7.710

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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Data availability

No data was used for the research described in the article.

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Appendix A. Appendix

All the Data and the informations conserning reactions 1,2,3 and 4 are presented in Table 3, Table 4, Table 5 and Table 6 respectively.

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