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Detecting the calcium carbonate saturation state under the stress of ocean acidification using saturometry technique

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Abstract. CO_2-induced ocean acidification lowers the degree of carbonate saturation state of the seawater, which affects calcification of marine organisms and influences the marine carbonate cycle, thus have negative impacts on the entire marine biogeochemical system. This study seeks to develop a rapid technique to detect carbonate saturation state of seawater based on conductivity changes. A series of batch and flow-through experiments were conducted using various $CaCO_3$ materials. Results show that the conductivity ratios of seawater with and without carbonate addition increase generally with decreasing carbonate saturation states (Ω). The relationship between conductivity ratio and $\log_{10}\Omega$ apparently follows a linear trend when $\Omega < 1$. It suggests that conductivity measurements can be used to indicate carbonate saturation state of seawater. It is expected to be deployed on CTD instrument to produce depth profiles of seawater carbonate saturation state and will be of great help to future studies on ocean acidification.

1. Introduction

Ocean acidification is the ongoing decline in ocean pH caused by absorbing anthropogenic CO_2 from atmosphere [1]. When CO_2 dissolves in seawater, it forms carbonic acid (H_2CO_3) and undergoes hydrolysis reaction, forming bicarbonate ions (HCO_3^-), carbonate ions (CO_3^{2-}) and releasing H^+ [2]. Depending on the conditions of temperature, salinity and pressure, the proportions of dissolved CO_2, HCO_3^- and CO_3^{2-} (the three major forms of inorganic carbon), as well as H^+ will reach different equilibrium states [3]. As exceeded CO_2 accumulates in the atmosphere, the amount of CO_2 absorbed by the ocean is increasing significantly, disturbing the equilibrium of the carbonate system in the seawater, resulting in the release of more H^+ and HCO_3^-, but reduce of CO_3^{2-} [1],[3].

The degree of saturation (Ω) defines the states of undersaturation, saturation, and supersaturation of the solutes. As shown in the equation below, with respect to carbonate saturation state, Ω is the ratio of the product of Ca^{2+} and CO_3^{2-} concentrations (the ion activity product should be used) to the product of those concentrations at saturation state:

$$\Omega = \frac{[Ca^{2+}][CO_3^{2-}]}{[Ca^{2+}]_{sat}[CO_3^{2-}]_{sat}} \approx \frac{[CO_3^{2-}]}{[CO_3^{2-}]_{sat}} \tag{1}$$

When $\Omega < 1$ the solute is undersaturated, i.e. seawater is undersaturated with respect to $CaCO_3$; when $\Omega = 1$, the solute is saturated; and when $\Omega > 1$, the solute is supersaturated. The equation can be simplified since the concentration of Ca^{2+} is considered to be approximately constant relative to seawater salinity. The dissolved Ca^{2+} is a major constituent in seawater with a mean concentration of

about 10.280 mmol/kg which is three orders of magnitude larger than that of CO_3^{2-}, and the observed variations of dissolved Ca^{2+} concentration in seawater are much smaller than those of CO_3^{2-} [4].

CO_2-induced ocean acidification reduces CO_3^{2-} concentration in the ocean and lowers the saturation state of carbonate [4], which is of great importance to marine calcifying organisms and the biogeochemical processes of $CaCO_3$ in the ocean [3]. Feely *et al.*[5] suggest that the saturation horizon for aragonite has already shoaled by several hundred meters in some regions. Experiments of Riebesell *et al.*[6] in the laboratory imply the calcification rate of coccolithophorids decreases as the availability of aqueous CO_2 increases. Orr *et al.*[7] suggest that key marine organisms, such as corals and some plankton, will have difficulty maintaining their external $CaCO_3$ skeletons. Reduced calcification rates for various marine calcifying organisms at high CO_2 levels are observed when $\Omega > 1$ [3].

Declining carbonate saturation states below a certain threshold will have severe consequences on the recycling of $CaCO_3$ and the survival of calcifying organisms in the ocean. The accurate estimation of $CaCO_3$ saturation state of seawater is crucial to research on the effects of ocean acidification and to identify the saturation threshold below which marine calcifying organisms will begin to suffer the adverse effects of ocean acidification. There are two approaches to measure carbonate saturation state of the seawater: calculation of carbon species concentrations [8] and *in situ* solubility tests [9].

Carbonate saturation state can be estimated based on theoretical calculation. The concentrations of the acid-base species in seawater can be inferred from measurements of salinity, temperature and two of the four CO_2-related parameters: total dissolved inorganic carbon (DIC), total alkalinity (TA), H^+ concentration and pCO_2, together with published values of various equilibrium constants and boron to salinity ratio of seawater [8]. Several programs can be used to do the calculations, such as CO2SYS [10], CSYS [11], SEACARB [12] and SWCO2 from Keith Hunter.

A carbonate saturometer designed by Weyl [13] is based on the principle that pH changes when carbonate is added to or removed from the solution. A pH-sensitive electrode and a reference electrode are used to measure the pH of the solution before and after equilibrating with solid carbonate. The output of the saturometer has been widely used as a relative evaluation for the degree of carbonate saturation and the adaptations of the saturometer were designed for oceanographic *in situ* measurements [9]. When a change in pH of 0.1 units is detected, the concentration of CO_3^{2-} has already altered more than 20%.

This study aims to test the hypothesis that dissolution of $CaCO_3$ would facilitate the release of ions (including CO_3^{2-}) which in turn would raise the conductivity in proportion to the degree of saturation state of seawater. The study aim to test that precise conductivity measurements can be used to detect the saturation state of seawater with respect to carbonate, and to develop an experimental technique that can provide rapid information about the saturation state of seawater with respect to $CaCO_3$ based on seawater conductivity changes.

2. Materials and methods

A series of batch and flow-through laboratory experiments were conducted. Seawater used for the experiments was collected in northwest European shelf seas during SOLAS cruise (D326) in February 2008 and stored at 5 °C. The samples were transferred to the laboratory (20 °C) several hours before the experiments, allowing the samples to reach room temperature. Various calcium carbonate materials were used including synthetic calcite (SOCAL® 31) and aragonite (SOCAL® 90A), marble chips (6 mm, Fisher Scientific) and oyster shells (clean and dry).

The seawater carbonate chemistry was manipulated by adding appropriate amounts of 1mol/L HCl calculated using SEACARB to achieve different carbonate saturation states. The changes of carbonate speciation and carbonate saturation state were calculated using SEACARB [12] with DIC and TA as input parameters. The DIC and TA were measured using VINDTA 3C (Versatile INstrument for the Determination of Total inorganic carbon and titration Alkalinity).

The conductivity measurements were carried out using an AUTOSAL MODEL 8400A Laboratory Salinometer. The AUTOSAL has a four-electrode cell in which the electrodes measure the conductivity of the seawater sample proportional to a standard reference seawater. The measurements

were conducted at 20 °C in a water bath cell in the AUTOSAL instrument. Each measurement takes less than half a minute and the accuracy of the instrument stated in the instructions is ± 0.00005.

2.1. Batch bottle experiments

Calcite and aragonite were used in batch bottle experiments. Acidified seawater samples at 57 different carbonate saturation states with respect to calcite and 11 to aragonite were prepared in these experiments. Each acidified seawater sample was divided into two 250 mL borosilicate glass bottles. Five grams calcite or aragonite were added into one of the two bottles while no calcite or aragonite was added into the other. The bottles were then sealed and stayed for two hours for equilibrating. After 2-hour incubation, ten replicate measurements on the sample in each bottle were achieved and the conductivity ratios of samples with and without carbonate were calculated (see Figure 1).
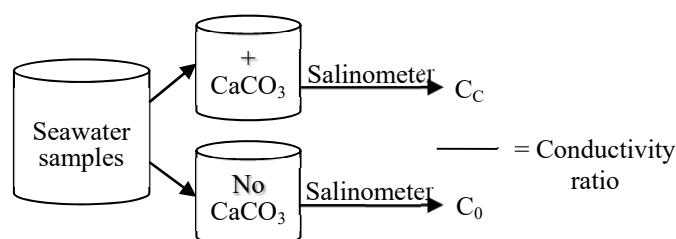

Figure 1. The procedures of the batch bottle experiments and the conductivity ratio calculation. C_C and C_0 represent conductivities of seawater with and without carbonate addition.

2.2. Flow-through experiments

Oyster shells and marble chips were used in flow-through experiments with acidified seawater samples at 4 and 5 different carbonate saturation states respectively. Two litres of each acidified seawater sample was pumped continuously to go through an approximately 600 mL watertight $CaCO_3$ container filled with 160 g (9 pieces) oyster shells or 840 g marble chips using a peristaltic pump (see Figure 2). The volume of the seawater filling the container with shells or marble was 520 mL and 280 mL respectively. The flow speed was 23 mL/min, so that the residence time of the seawater in the container with shells or marble was 23 min and 12 min respectively.

Conductivity was measured 10 times at both the inlet and the outlet sides of the container, corresponding to a pair of seawater conductivity before and after reacting with the $CaCO_3$ materials having conductivity C_0 and C_C respectively. Before the measurements of each sample, the flow-through system was flushed by 1 L of the seawater sample to be measured for about 45 minutes to ensure that the solution from last sample was removed from the container.
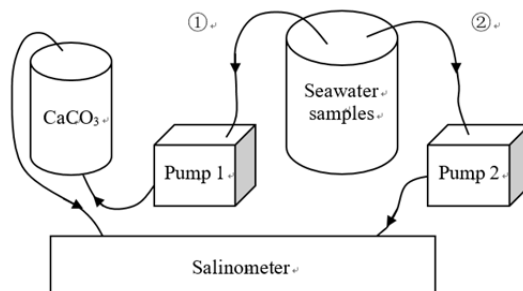

Figure 2. A schematic diagram of the flow through system. The conductivity readings for pathway ① and ② represent C_C and C_0, respectively.

3. Results and discussions

3.1. Carbonate chemistry modelling

TA and DIC of the non-treated seawater were 2.46061mmol/kg and 2.15730mmol/kg respectively, averaged from 4 replicate measurements using VINDTA 3C instrument. Based on the TA and DIC values, the changes in carbonate chemistry speciation due to acid addition were calculated using SEACARB, where about 60 different HCl volumes were calculated. Figures 3 and 4 show the carbonate speciation changes and the variations in the saturation state of seawater with respect to calcite and aragonite, respectively.
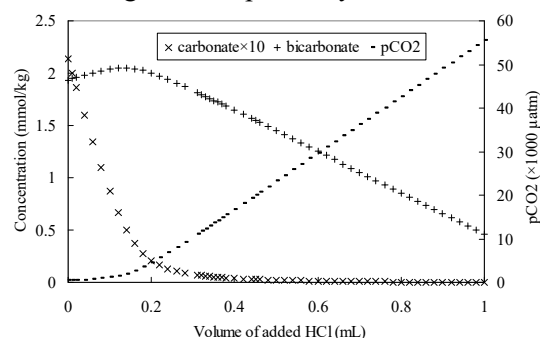
Figure 3. Theoretical inorganic carbon speciation changes with HCl addition. The x axis is volumes (mL) of 1mol/L HCl added into 500 mL seawater samples. The left y axis is the scale of CO_3^{2-} and HCO_3^- concentrations (mmol/kg). The CO_3^{2-} concentrations are multiplied by 10 to fit the axis scale. The right y axis is the scale of pCO_2 (1000atm).
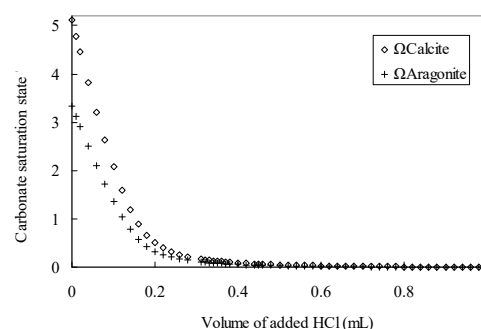
Figure 4. Carbonate saturation state variation with HCl addition. The x axis stands for the volumes (mL) of 1 mol/L HCl added into 500 mL seawater samples and the y axis is the scale of carbonate saturation state.

As shown in Figure 3, pCO_2 increases gently with initial HCl addition and then followed by a continuous rise at a constant rate. The initial pCO_2 concentration is 414µatm and the maximum value is 55600µatm after 1mL HCl addtion. HCO_3^- concentration gently raises from 1.934mmol/kg to a maximum of 2.049mmol/kg when HCl addition is 0.14mL, then decreases almost linearly to 0.458mmol/kg with further HCl addition. The initial CO_3^{2-} concentration is 0.213mmol/kg. With HCl addition, it declines significantly to nearly 0mmol/kg. The CO_3^{2-} concentration determines carbonate saturation state (Ω), thus seawater carbonate saturation state declines with HCl addition as well (shown in Figure 4). The initial values of $\Omega_{Calcite}$ and $\Omega_{Aragonite}$ of the seawater sample are 5.112 and 3.341 respectively. Rapid decreases in Ω with respect to both calcite and aragonite are observed with initial HCl addition. Then Ω values approach the minimum possible value of 0 gradually.

3.2. Theoretical link between conductivity ratios and carbonate saturation states

In Figure 5a, the conductivity ratio shows no apparent correlation with Ω in the supersaturated area ($\Omega > 1$) but it increases rapidly with Ω in part of the undersaturated region ($\Omega < 0.5$). In Figure 5b, the conductivity ratio with respect to aragonite shows dramatic increase when $\Omega < 0.3$. Although fewer points are produced in flow-through experiments, the data points in Figure 5c and d show a similar trend to those of batch bottle results (Figure 5a and b). However, the distributions of the data points are highly uneven, making the relationship between the conductivity ratios and the carbonate saturation states less clear. The results are represented on a logarithmic scale for Ω in Figure 6 to better illustrate the trend of the data points' distribution. The point distribution at $\Omega < 1$ seems to follow a linear trend in each plot of Figure 6, indicated by a trend line labelled with its equation and coefficient of determination (R^2). The trend lines are extended to supersaturated areas ($\Omega > 1$) based on extrapolation method, marked with dash line.

When seawater carbonate is undersaturated ($\Omega < 1$), the $CaCO_3$ added into the seawater is expected to dissolve, resulting in an increase of ions; the conductivity ratio with and without $CaCO_3$ addition should be higher than one. Thus, the conductivity ratios higher than 1 in Figure 6 indicate an increase of dissolved ions and the undersaturation conditions of the solutions. When seawater is supersaturated ($\Omega > 1$), $CaCO_3$ would precipitate from the solutions, resulting in ion decline in the solution; then the conductivity ratio should be lower than one. Therefore the conductivity ratios less than one in Figure 6 suggest carbonate precipitation from the supersaturated seawater. When seawater is exactly saturated ($\Omega = 1$), ideally neither dissolution nor precipitation would occur, letting the amount of ions in the seawater remain unchanged. The conductivity ratio of the seawater should remain as 1.
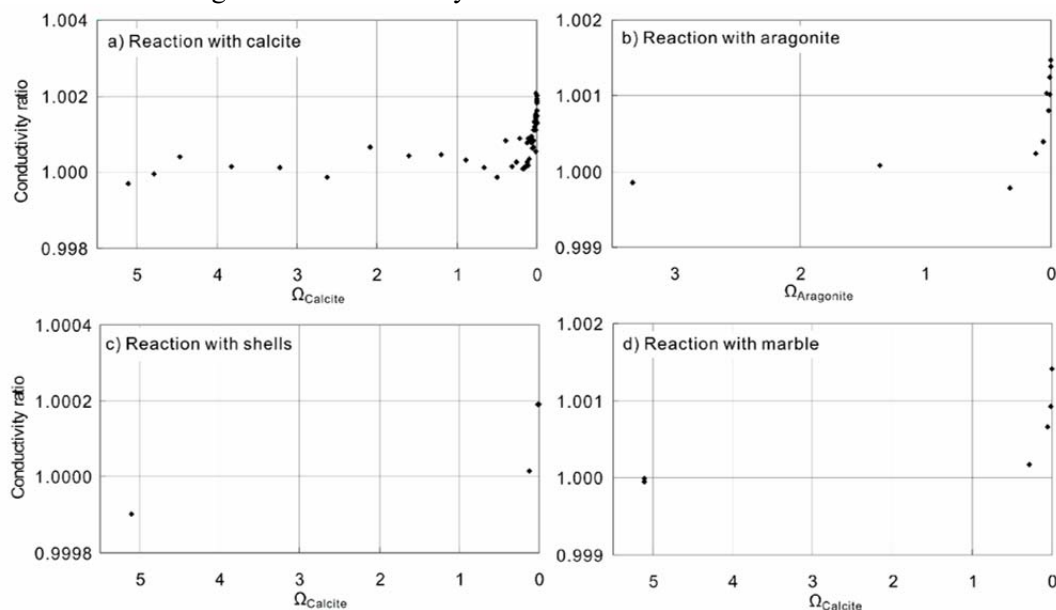

Figure 5. Conductivity ratio of seawater reacting with and without different $CaCO_3$ materials against carbonate saturation state with respect to calcite or aragonite.

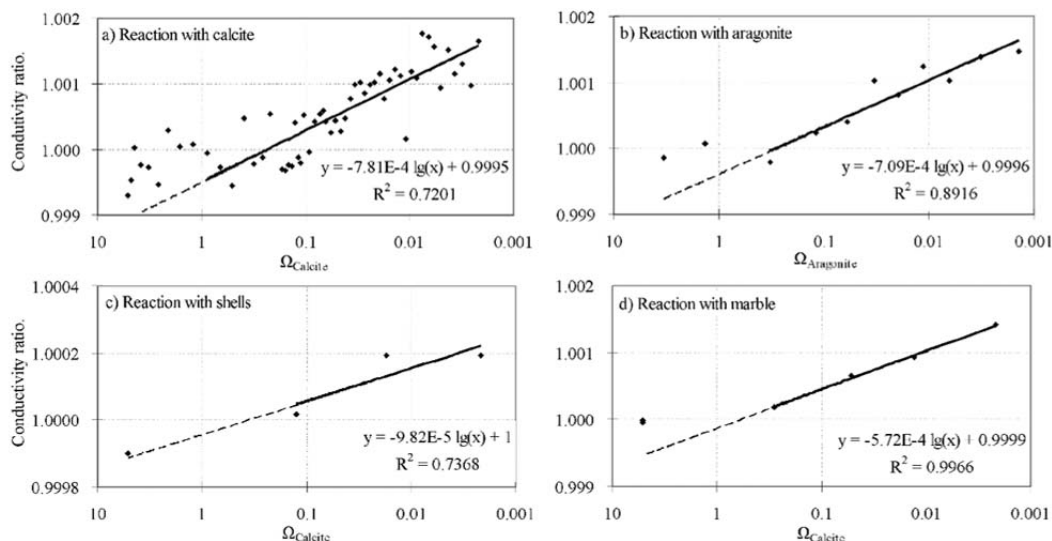**Figure 6.** Conductivity ratio of seawater reacting with and without different $CaCO_3$ materials against carbonate saturation state with respect to calcite or aragonite. The *x* axes are the carbonate saturation state on logarithmic scales and the *y* axes are the conductivity ratio on linear scales.

However, in Figure 6 abnormal precipitation in the undersaturated areas is indicated by the conductivity ratios less than one when Ω is near but lower than one. On the contrary, non-precipitation or even dissolution in the supersaturated areas is suggested by the conductivity ratios equal to or higher than one.

One explanation for the anomalies may be the transition between precipitation and dissolution in saturated area. Both dissolution and precipitation are happening at all states in the solution. When seawater is undersaturated, dissolution speed is higher than precipitation speed, therefore the overall trend is dissolution. On the contrary, at supersaturated conditions, the precipitation process exceeds dissolution, thus the overall trend is precipitation. When seawater is near exactly saturated ($\Omega \approx 1$), the dissolution and precipitation processes compete and reach a dynamic equilibrium, making the instantaneous measurements not stable.

However, it cannot explain the anomalies away from $\Omega \approx 1$ area. Another possible explanation is the inhibition of $CaCO_3$ precipitation by Mg^{2+}, PO_4^{3+} and humic substances[14],[15]. It is considered that Mg^{2+} ions in seawater have a strong retarding effect on calcite crystal growth rate. Mg^{2+} ions serve as a surface poison by inhibition the active growth sites on calcite crystal surface as magnesium hydrate. Moreover, the Mg^{2+} ions are incorporated within the crystal during growth and lead to thermodynamic destabilization, thus enhance calcite solubility even in supersaturated seawater. Therefore conductivity ratio < 1 when $\Omega < 1$ in Figure 6a may be due to Mg^{2+} adsorption rather than calcite precipitation, and conductivity ratios > 1 when $\Omega > 1$ probably due to the inhibition effect of magnesium on calcite precipitation and the formation of more soluble Mg-calcite. Moreover, the observed conductivity ratios may all result from a synergistic effect of Mg^{2+} adsorption and calcite dissolution or precipitation. Similarly, aragonite precipitation, which is unaffected by Mg^{2+}, is distinctly inhibited by low concentrations of PO_4^{3+} and humic substances in seawater. The inhibiting mechanism relies on the affinity of dissociated carboxyl groups (-COOH) or PO_4^{3-} for Ca^{2+} which would lead to adsorption of humics or PO_4^{3-} onto aragonite surface, subsequently obstructing the active growth sites on the crystal surface, and causing precipitation inhibition. This interpretation explains the conductivity ratio ≈ 1 when $\Omega > 1$, with respect to aragonite, in Figure 6b.

Furthermore, Ω of the acidified seawater samples was calculated by SEACARB based on theoretical carbonate speciation in seawaters. The theoretical calculation uncertainty ranges from 2.2 to 9.3% [8]. This could contribute to the noises in the plots.

3.3. Correlation between conductivity ratios and carbonate saturation states
The strength of relationship can be evaluated by correlation coefficient (R). Absolute R value (|R|) between 0.7 and 0.9 indicates a strong correlation of the two variables; the value between 0.9 and 1.0 indicates a very strong correlation of the two variables. In Figure 6a and c, |R|=0.8486 and 0.8584 respectively, both suggesting a strong correlation between the conductivity ratio and $log_{10}\Omega$; in Figure 6b and d |R|=0.9442 and 0.9983 respectively, both suggesting a very strong correlation between the conductivity ratio and $log_{10}\Omega$.

Table 1. Results of the correlation coefficient t-test for the correlations between conductivity ratios and $log_{10}\Omega$.

Figure	t	df [a]	$t_{0.05, df}$ [b]	p	Significance
6a	10.760	45	$t_{0.05, 40} = 2.021$ $t_{0.05, 50} = 2.009$	**p < 0.05**	**Significant**
6b	7.588	7	$t_{0.05, 7} = 2.365$	**p < 0.05**	**Significant**
6c	1.673	1	$t_{0.05, 1} = 12.706$	p > 0.05	Not significant
6d	24.212	2	$t_{0.05, 2} = 4.303$	**p < 0.05**	**Significant**

[a] The degree of freedom (df) equals to the number of points minus 2.
[b] The values of $t_{0.05, df}$ are from the t-test table, in order to convert the calculated t values to a statement about significance.

The significance of correlation is evaluated by probability (p) using correlation coefficient t-test. Table 1 shows the results of the t-test for the correlations between conductivity ratios and $\log_{10}\Omega$, demonstrating the correlations are significant except for in Figure 6c.

Combining the strength and significance analyses, the correlation between conductivity ratio and $\log_{10}\Omega$ in Figure 6a is strong and significant, those in Figure 6b and d are very strong and significant, whereas in Figure 6c the correlation is strong but not significant. The non-significance of the correlation could arise from a shortage of data points that are insufficient to shape the relationship. The best correlation occurs in Figure 6d, which is very strong and significant and has fewer noises, implying that marble may be an ideal $CaCO_3$ material for this conductivity technique and verifying the feasibility of the flow-through system to be applied to *in situ* carbonate saturation state measurements. It is supposed to be deployed with CTD (Conductance, Temperature, Depth) instrument to produce depth profiles of seawater saturation state with respect to carbonate, and hence of great help to future studies on ocean acidification.

4. Conclusions

A series of batch and flow-through experiments were conducted using various calcium carbonate materials including synthetic calcite and aragonite, and more realistically marble chips and oyster shells. The conductivity ratios of the seawater samples with and without calcium carbonate addition were obtained at various carbonate saturation states which were achieved by adding appropriate amounts of HCl into the seawater samples.

The experimental results suggest that conductivity measurements can be used to detect dissolution or precipitation of calcium carbonate in seawater. The strong and significant correlation between conductivity ratio and base 10 logarithm of carbonate saturation state implies that precise conductivity measurements could be used to provide information about the level of carbonate saturation state of seawaters. The best correlation occurred in the reaction with marble suggesting marble is an ideal calcium carbonate material for this technique. Moreover, the flow-through system can rapidly and sensitively detect the conductivity changes that are proportional to the carbonate saturation state of the seawater, which verifies the feasibility of this technique to be applied to *in situ* measurements of carbonate saturation state in the oceans and to produce depth profiles of the seawater with regard to carbonate saturation states. Hence, it will have the potential to help future research on the effects of ocean acidification on the carbonate chemistry and the biogeochemical cycle in the oceans.

5. Future work

This project provides a possible way to measure seawater carbonate saturation state based on conductivity measurements. Results of the experiments confirm the feasibility of this technique to be applied to a deployable instrument for *in situ* measurements in the oceans. While to apply this technique, further studies are required.

The correlation between conductivity ratio and carbonate saturation state is unclear when $\Omega > 1$. More experiments need to be carried out to provide sufficient data points at $\Omega > 1$ regions in the plots, to determine the relationship between the two variables under supersaturated conditions.

Among the four calcium carbonate materials used in the experiments, marble shows the best suitability to this technique. Further studies with marble on more detailed correlation between conductivity ratio and carbonate saturation state are required to provide in-between points for the plot. In addition, other calcium carbonate materials, such as limestone and chalk, can be tested during the experiments to identify the most ideal calcium carbonate material for this saturometry technique.

Further studies are required to find out the shortest time for the measurement of the flow-through system. Increasing the seawater-$CaCO_3$ interface, for example increasing the amounts and/or reducing the granule size of the calcium carbonate material, can accelerate the reaction between seawater and $CaCO_3$. The reaction between seawater and calcium carbonate materials takes place during the residence time of the seawater within the $CaCO_3$ container. Enhancing the capability of the calcium

carbonate container to hold seawater allows increasing the flow speed without shortening the residence time.

Moreover, different carbonate saturation states of the seawater were achieved by adding hydrochloric acid into the solution during the experiments. While in reality the variation of carbonate saturation state of the seawater in the oceans is due to CO_2 absorption. Therefore, CO_2 may be used in future studies to simulate this reality.

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