

2013

## Determination of in-situ Dissolved Inorganic Carbon and Alkalinity in Marine Sedimentary Interstitial Water

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**DETERMINATION OF IN-SITU  
DISSOLVED INORGANIC CARBON AND ALKALINITY IN MARINE  
SEDIMENTARY INTERSTITIAL WATER**

**BY**

**JUSTINE SAUVAGE**

**A DISSERTATION SUBMITTED IN PARTIAL FULFILLMENT OF THE  
REQUIREMENTS FOR THE DEGREE OF**

**MASTER OF SCIENCE**

**IN**

**OCEANOGRAPHY**

**UNIVERSITY OF RHODE ISLAND**

**2013**

MASTER OF OCEANOGRAPHY THESIS  
OF  
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2013

## ABSTRACT

Porewater inorganic carbon concentration and total alkalinity from deeply buried marine sediment reflect biological activity, mineral diagenesis, sedimentary processes and past bottom ocean water composition. Reliable interpretation of these data is often complicated and/or limited due to (i) major physical environment changes taking place during sediment core retrieval, and (ii) the resulting precipitation of calcium carbonate ( $\text{CaCO}_3$ ) in the course of sample collection, processing and storage. Here we describe a robust method for quantifying the in-situ porewater carbonate system chemistry in deepsea sediment cores. The method relies on the over-determination of the dissolved carbonate system by measuring three of its parameters, and explicitly assumes  $\text{CaCO}_3$  saturation in the sediment and equilibrium conditions in-situ. The principles of the method are presented.

We experimentally test the proposed approach using concentration profiles of dissolved carbonate system components collected from the Integrated Ocean Drilling Program (IODP) Site U1368 in the Southern Pacific. Our results show that this method can be used to accurately reproduce the in-situ aqueous carbonate system chemistry if dissolved inorganic carbon, total alkalinity and calcium concentration are measured simultaneously. The method is well suited for use over a broad range of porewater chemistry and applicable for sediment over ca. 50% of the seafloor.

## ACKNOWLEDGMENTS

Firstly, I would like to thank my adviser Steven D'Hondt for his guidance and continual support during the accomplishment of this Master thesis. I'm very grateful that this originally planned 2-week-project turned out to be a two-year Master thesis (and I hope my first of many more contributions to the field of Oceanography), as it gave me the opportunity to familiarize myself with many important concepts of geochemistry in marine sediment.

Secondly, I greatly thank Arthur Spivack, who played a central scientific role in advising this project. He showed a lot of patience and enabled me to expand my understanding in many aspects of marine biogeochemistry.

I greatly thank IODP Expedition 329 Science party, which graciously provided all the data this project is based on. Without their hard work and dedicated effort this project wouldn't have been possible.

I warmly thank all the members of the D'Hondt and Spivack lab: Emily Walsh, Mary Dzaugis, John Kirkpatrick, Anne Hartwell, Yiya Huang, Leah Lewis, Dennis Graham, and Rob Pockalny, whom not only have been very helpful and supportive throughout this process but more importantly are great colleagues to work with.

I would like to thank my committee member Thomas Boving, for his collaboration on the project and enthusiasm.

I would like to thank Guizhi Wang, who I haven't had the pleasure to meet in person, but whose earlier work on the same subject formed the onset of this Master's thesis.

Last but not least, I would like to acknowledge my friends and family.

## PREFACE

This master thesis is written in manuscript format as I intend to submit this work to the scientific journal Elsevier. Following authors are involved in the publication of the manuscript: Justine Sauvage<sup>a</sup>, Arthur J. Spivack<sup>a</sup>, Richard W. Murray<sup>b</sup> and Steven D'Hondt<sup>a</sup>.

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The manuscript is currently being reviewed by co-authors involved in the project. Submission of the manuscript to the journal is estimated by summer 2013.

An appendix was added next to the manuscript and should provide the reader with all information required to get a thorough understanding of the project. The Matlab code associated with the method we developed in this project is planned to be accessible online in the form of an electronic annex upon acceptance of the manuscript.

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**“Determination of In-situ Dissolved Inorganic Carbon Concentration and Alkalinity in Marine Sedimentary Interstitial Water”**

by

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is in review for submission to *Geochimica et Cosmica Acta*

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## INTRODUCTION

Throughout the past 50 years of scientific ocean drilling, profiles of many dissolved chemicals derived from extraction and analysis of sedimentary interstitial water on deepsea drilling expeditions have significantly contributed to major advances in climatic and oceanographic sciences (Gieskis, 1975). The marine carbonate system was and remains an extensively studied subject that will bring new insights into a wide range of oceanographic disciplines. Two new areas that the study of dissolved inorganic carbon (DIC) and total alkalinity (TA), two major parameters of the carbonate system, can contribute to are (i) secular changes in the carbonate system of ocean bottom waters, and (ii) subseafloor microbial activity.

The marine carbonate system is a crucial component in controlling the pH of the world's oceans and reflects the variable distribution of CO<sub>2</sub> between the ocean and the atmosphere (Sigman and Boyle, 2000; Elderfield, 2002; Yu et al., 2010). DIC and TA reconstructions in deep subseafloor sediment have the potential to supply fundamental information for our understanding of the ocean's role in the global carbon cycle and climate. Particularly interesting in this respect is the reconstruction of past preformed carbonate ( $[\text{CO}_3^{2-}]_{\text{PF}}$ ) of the ocean's interior. Preformed nutrients represent that fraction of unutilized nutrients in surface waters that gets transported into the interior ocean (Ito and Follows, 2005). Because of the generally inverse relationship between preformed carbonate ( $[\text{CO}_3^{2-}]_{\text{PF}}$ ) and the surface seawater CO<sub>2</sub> content, reconstruction of past preformed carbonate through the Last Glacial Maximum (LGM) [24 to 18 thousand years ago] can help to constrain the CO<sub>2</sub> equilibration history of the ocean

and the atmosphere and hence provide clues to the causes of atmospheric CO<sub>2</sub> concentration variations on these time scales. Stephens and Keeling (2000) suggested that low glacial atmospheric CO<sub>2</sub> levels resulted from reduced air-sea gas exchange due to increased sea-ice cover at high southern latitudes. If true, glacial [CO<sub>3</sub><sup>2-</sup>]<sub>PF</sub> should be lower compared to modern equivalents. In contrast, assuming that atmosphere and surface oceans could equilibrate during glacial periods, we expect higher preformed CO<sub>3</sub><sup>2-</sup> concentrations. Highly important in this matter is the precision and accuracy of the measurements involved in the reconstruction of preformed nutrients. Assuming equilibrium between surface oceans and atmosphere, Yu and colleagues (2010) calculated that the change in [CO<sub>3</sub><sup>2-</sup>]<sub>PF</sub> during the LGM should be on the order of 60 μmol kg<sup>-1</sup> higher compared to modern equivalents (i.e. ca. 250 μmol kg<sup>-1</sup>) (Yu et al., 2010; Williams and Follows, 2011). Therefore, in the endeavor of reconstructing past [CO<sub>3</sub><sup>2-</sup>]<sub>PF</sub> using pore fluid chemistry, precise measurements of carbonate-related chemicals are necessary because the expected changes in [CO<sub>3</sub><sup>2-</sup>]<sub>PF</sub> are subtle and thus prone to lie within the analytical uncertainty margin of the reconstructed preformed nutrients.

Also, DIC (CO<sub>2</sub> + HCO<sub>3</sub><sup>-</sup> + CO<sub>3</sub><sup>2-</sup>) is a major metabolic product of microbial respiration, and quantification of its abundance in deepsea sediment is essential to understand the metabolic activities and biogeochemistry of the marine sedimentary biosphere (D'Hondt et al., 2002; D'Hondt et al., 2004; D'Hondt et al., 2009).

Shipboard measured values of TA and DIC of the interstitial water using standard techniques often do not match actual in-situ abundances (Sayles and Manheim, 1975;

Berner, 1980). Pioneering work of the Ocean Drilling Program showed the occurrence of significant variation in the abundance of DIC, TA and other related constituents in interstitial water [e.g. calcium ( $\text{Ca}^{2+}$ ), phosphate ( $\text{PO}_4^{3-}$ ), magnesium ( $\text{Mg}^{2+}$ ) and sulfate ( $\text{SO}_4^{2-}$ )] with varying storage time prior to analysis (Paull et al., 1996). This change in pore fluid composition is attributed to drastic modification of the physical environment during core retrieval and storage. Decompression and warming of the sediment during core recovery, followed by core handling on deck and storage, induces precipitation of carbonate due to pressure and temperature dependent solubility of carbonate minerals (Paull et al., 1996). Therefore, shipboard measured DIC and TA are commonly lower than in-situ values. In general, the longer it takes for interstitial water samples to be extracted and analyzed post-core recovery, the more offset from in-situ values are the measurements. The sample-handling-and-processing routine on scientific drilling vessels frequently results in samples being stored for hours (sometimes days) prior to analysis, leaving ample time for carbonate precipitation. Consequently, for accurate use of carbonate-related interstitial water chemistry data, it is critical to develop a method for correcting the measured abundances to in-situ values.

Here, we present a rigorous technique to quantify the in-situ dissolved inorganic carbon system chemistry in subseafloor marine sediment. This technique does not require significant additional drilling and processing time. We provide experimental validation of the proposed approach using sedimentary pore fluid concentration profiles of DIC, TA, calcium, and other dissolved species collected during Integrated Ocean Drilling Program (IODP) Expedition 329 to the South Pacific Gyre.

## THEORY OF THE METHOD

### Conceptual framework

The central concept upon which this method is built is that by measuring three parameters of the carbonate system (i.e. DIC, TA and  $\text{Ca}^{2+}$ ) in the porewater we mathematically over-determine that system which allow us to solve for the amount carbonate precipitation taking place during the sample recovery process, and thus determine the complete set of in-situ carbonate system parameters (Park, 1969). This reasoning is only valid if carbonate is saturated throughout the sediment and the dissolved carbonate system is at equilibrium in-situ. In other words, at equilibrium, if the concentrations of DIC, TA, and  $\text{Ca}^{2+}$  are measured, in-situ pH, total un-ionized dissolved carbon ( $\text{CO}_2(aq)$ ), bicarbonate ( $\text{HCO}_3^-$ ), and carbonate ( $\text{CO}_3^{2-}$ ) concentrations are mathematically over-determined if carbonate is saturated in-situ. Over-determination of the carbonate system allows the amount of carbonate precipitated during core recovery, sampling, and storage to be uniquely determined. By calculating the amount of carbonate lost during sample recovery from the seafloor, we can correct the measured dissolved [DIC] and [TA] (with [ ] denoting the concentration of the referred species) to actual in-situ values. Once in-situ [DIC] and [TA] are known, in-situ pH, in-situ concentrations of the remaining carbon system components (i.e.  $[\text{CO}_2(aq)]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ , etc.) and in-situ concentrations of the pH-dependent minor species included in the alkalinity term (i.e.  $\text{B(OH)}_4^-$ ,  $\text{SiO(OH)}_3^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{HSO}_4^-$  etc.) can be quantified. The fundamentals of this approach were first put forward by Wang et al. (2010); they are revisited, revised and tested in this study.



### Iteration process

Based on measured [TA], [DIC] and [Ca<sup>2+</sup>] (i.e. [TA]<sub>measured</sub>, [DIC]<sub>measured</sub> and [Ca<sup>2+</sup>]<sub>measured</sub>, respectively) we solve for the amount of carbonate, referred to as X<sub>CaCO<sub>3</sub></sub> (in the case of a calcitic phase) in moles per mass of pore fluid, that precipitated during core recovery and handling, together with the complete in-situ aqueous carbonate system chemistry and related chemical species. While there is more than one way to solve this set of simultaneous equations we use a simple iterative method. A combination of mass balance relationships, equilibrium reactions between species in solution, and thermodynamics relationships forms the core of the iteration algorithm.

Mass balance relationships for DIC and TA:

$$[\text{DIC}] \equiv [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (1)$$

$$\begin{aligned} [\text{TA}] \equiv & [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] \\ & + [\text{NH}_3] + [\text{HS}^-] + \dots - [\text{H}^+]_f - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \end{aligned} \quad (2)$$

For algebraic simplicity we combine all the components of minor contribution to the DIC and TA mass balance relative to that of HCO<sub>3</sub><sup>-</sup>, CO<sub>3</sub><sup>2-</sup> and B(OH)<sub>4</sub><sup>-</sup> into a fictitious species, labeled minor species:

$$\begin{aligned} [\text{minor species}] = & [\text{H}_2\text{CO}_3] - [\text{OH}^-] - [\text{HPO}_4^{2-}] - 2[\text{PO}_4^{3-}] - [\text{SiO}(\text{OH})_3^-] - [\text{NH}_3] - [\text{HS}^-] \\ & + [\text{H}^+]_f + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] \end{aligned} \quad (3)$$

In-situ abundances of the three measured components (i.e.  $[\text{DIC}]_{\text{in\_situ}}$ ,  $[\text{TA}]_{\text{in\_situ}}$ , and  $[\text{Ca}^{2+}]_{\text{in\_situ}}$ ) are parameterized as:

$$[\text{DIC}]_{\text{in\_situ}} = [\text{DIC}]_{\text{measured}} + X_{\text{CaCO}_3} \quad (4)$$

$$[\text{TA}]_{\text{in\_situ}} = [\text{TA}]_{\text{measured}} + 2X_{\text{CaCO}_3} \quad (5)$$

$$[\text{Ca}^{2+}]_{\text{in\_situ}} = [\text{Ca}^{2+}]_{\text{measured}} + X_{\text{CaCO}_3} \quad (6)$$

By assuming calcium carbonate ( $\text{CaCO}_3$ ) saturation in-situ and referring to Eq. (6) for the expression of in-situ calcium abundances we have:

$$[\text{CO}_3^{2-}][[\text{Ca}^{2+}]_{\text{measured}} + X_{\text{CaCO}_3}] = K_{\text{sp (calcite)}}^* \quad (7)$$

with  $K_{\text{sp (calcite)}}^*$ , the solubility product constant of calcite at in-situ temperature, salinity and pressure.

Substituting Eq. (3) through Eq. (6) into the DIC and TA mass balance expressions (i.e. Eq. (1) and Eq. (2), respectively) and subtracting  $[\text{DIC}]_{\text{in\_situ}}$  and  $[\text{TA}]_{\text{in\_situ}}$  by each other, and vice versa, we derive:

$$[\text{TA}]_{\text{measured}} - [\text{DIC}]_{\text{measured}} + X_{\text{CaCO}_3} = [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] - [\text{minor species}] \quad (8)$$

$$2[\text{DIC}]_{\text{measured}} - [\text{TA}]_{\text{measured}} = [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] - [\text{B}(\text{OH})_4^-] + [\text{minor species}] \quad (9)$$

Rearranging and combining Eq. (8), Eq. (9) and Eq. (7) we formulate a 2<sup>nd</sup> order polynomial of the form  $A(X_{\text{CaCO}_3})^2 + B(X_{\text{CaCO}_3}) + C = 0$  with following coefficients:

$$A = 1 \quad (10)$$

$$B = \alpha + [\text{Ca}^{2+}]_{\text{measured}} \quad (11)$$

$$C = -1 [(1 + [\text{B}(\text{OH})_3] K_{\text{B}}^*) / (K_2^* [\text{HCO}_3^-])] K_{\text{sp (calcite)}}^* + \alpha [\text{Ca}^{2+}]_{\text{measured}} \quad (12)$$

with:

$$\alpha = [\text{TA}]_{\text{measured}} - [\text{DIC}]_{\text{measured}} + [\text{minor species}] \quad (13)$$

and  $K_B^*$  and  $K_2^*$  equilibrium reaction constants, calculated at in-situ salinity, temperature and pressure, for the dissociation of borate and bicarbonate, respectively.

Eq. (1) through Eq. (13) form a determined system that can be solved for  $X_{\text{CaCO}_3}$  and, subsequently, the complete carbonate system chemistry based on equilibrium relationships between the concentrations of the various dissolved species. To simplify the solution, the iteration procedure neglects the minor species [i.e. Eq. (3)] for the initial iteration. In the second iteration step the minor species, determined in the first iteration, are incorporated into the equation set. The following iterations subsequently refine the calculated species concentrations until a stable solution is attained. Applying this iteration algorithm, and most importantly, explicitly solving for the carbonate and borate system in the first iteration (i.e. explicitly leaving  $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$  and  $\text{B(OH)}_4^-$  out of the minor species term), results in a stable solution for the abundance of in-situ carbonate system species and other related components regardless of the relative size of the measured [DIC] and [TA] values. Moreover, use of a 2<sup>nd</sup> order polynomial within the algorithm highly improves the efficiency of this calculation method, leading to rapid convergence (i.e. within a few iterations) of the species' concentrations to a stable solution. We give a detailed description of the method in the **Appendix**.

### **Thermodynamic considerations**

We take the aqueous chemistry of carbon dioxide, silica, boron, phosphate, and sulfate into consideration to characterize the complete carbon system in a sample of porewater at a particular temperature and pressure (Dickson, 2007). We calculate equilibrium and solubility constants for the acid dissociation reactions in the porewater at in-situ salinity, temperature and pressure to account for the change in physical environment during core retrieval. Expressions of equilibrium constants as a function of salinity and temperature, derived from the Total Hydrogen ion Scale by Millero et al. (2006) and Dickson et al. (2007), are used in this study. The effect of pressure on the equilibrium constants is taken into account (Millero, 1983; Zeebe and Wolf-Gladrow, 2001). The detail of the calculation steps for the determination of in-situ equilibrium constant is given in the **Appendix**.

## ASSESSMENT

### Conceptual reliability test

To validate the method computationally and conceptually, we applied the approach to modern water column chemistry. Concentration profiles for DIC, TA, silica, and phosphate, together with salinity and temperature data, extracted from the Hydrographic Atlas of the World Ocean Circulation Experiment, WOCE, are used (Talley, 2007). If the algorithm works properly and has correctly calculated the thermodynamic constants, then we should calculate  $X_{\text{CaCO}_3}$  to be zero mol kg<sup>-1</sup> at the carbonate saturation horizon (above this depth  $X_{\text{CaCO}_3}$  will be negative and below it positive).

For sites located near the center of the South Pacific Gyre, the algorithm correctly positioned the level of the calcite saturation horizon at a water depth of ca. 3000 m (Peterson, 1966; Williams and Follows, 2011). At that level, the variable  $X_{\text{CaCO}_3}$  reaches a value of zero mol kg<sup>-1</sup>. Water at depths above and below that level are increasingly calcite-supersaturated and calcite-undersaturated, respectively. This result agrees with the proposed conceptual framework. Samples below the calcite saturation horizon are undersaturated with respect to calcite, resulting in a positive  $X_{\text{CaCO}_3}$  value. Therefore to restore equilibrium, an a priori assumption of the approach, calcite precipitation has to take place. The inverse is true for water samples located above the calcite saturation horizon.

## **Experimental reliability test**

### *Interstitial water collection and analytical methods*

The method was tested using published data of pore fluid concentration profiles from IODP Expedition 329 to the South Pacific Gyre (Expedition 329 scientists, 2011). The data we used was collected at IODP Site U1368, located near the center of the gyre (27°55'S, 123°10'W) in water of 3740 m depth (**Figure 1**). This site is within a region of seamount topography, where there is some possible evidence of original abyssal hill seafloor fabric. It is located within magnetic polarity Chron 5ABn, resulting in a basement age of ca. 13.36-13.0 Ma (Gradstein et al., 2012). The slowly deposited sediment (i.e. 0.1 to 1 meter per million years) at Site U1368 consists of a 16-m sequence of calcareous ooze, pelagic clay and lithic sand (D'Hondt et al. 2009). Smear slide analysis revealed nannofossils, together with red-brownish semi-opaque oxides and foraminifers, as the principal components of the ooze. The clay-rich and sandy intervals contain a wide variety of minerals (e.g. albite, anorthite, calcite and hematite). The sediment sequence is differentiated into three lithologic units based on compositional and textural characteristics: (i) an upper nannofossil-rich ooze and marl unit, (ii) a middle dark color nannofossil-bearing clay unit and (iii) a hematitic nannofossil-bearing clay unit intercalated with sandy intervals in the lowermost part of the sequence (Expedition 329 scientists, 2011). Calcium carbonate is abundant throughout the site.

Interstitial water of the Site U1368 sediment was extracted by squeezing ca. 10-cm long whole-core rounds using Manheim squeezers (Manheim, 1966). For the purpose of this study, two core handling-and-storage procedures were adopted. In one

method we did not try to minimize storage and handling time of whole-round samples before interstitial water extraction. We refer to this as the ‘conventional process’. In contrast, we designed the second method to minimize the time between core retrieval and interstitial water extraction. The goal was to minimize the lapse of time during which carbonate precipitation might occur. We refer to this as the ‘rapid process’.

Time records of the consecutive steps of sample storage and handling for each whole-core round sample were documented. Sample handling and laboratory storage time for the conventional processed samples varied from a couple of hours to as long as seven hours. The rapid process samples were stored for less than 2 hours before extraction (**Figure 2A**; Expedition 329 scientists, 2011). For both procedures, sedimentary core samples that couldn’t be processed by the biogeochemistry laboratory right away were stored in a 4°C refrigerator until they could be squeezed and analyzed. Characteristic prevailing temperature, pressure and salinity laboratory conditions were 20°C, 1 Atm and 34.7 ppt, respectively.

Interstitial waters from 33 whole-round samples from Site U1368, Hole C, were collected and analyzed by the shipboard scientific party. The samples were obtained at a spatial resolution of approximately one sample every 50 cm. Eleven of the whole-round samples taken for interstitial water chemistry were rapid process samples (Expedition 329 scientists, 2011).

Interstitial water analyses that were key for this study included concentration measurements of DIC, TA and calcium, chloride, sulfate, phosphate, silica and  $Mg^{2+}$  along with other cations (**Table 1-2**). A glass electrode was used for pH measurement,

total alkalinity was determined by Gran titration utilizing an autotitrator (Metrohm 809 Titrando), and DIC was measured with an Aurora 1030 total organic carbon analyzer. Sulfate and chloride concentrations were quantified with a Metrohm 861 Advanced Compact ion chromatograph, and phosphate and dissolved silica concentrations were determined using an OI analytical discrete analyzer (DA3500) spectrophotometer. Cation concentrations in the pore fluid were obtained by inductively coupled plasma-emission spectrometry (ICP-AES) with a Teledyne Prodigy high-dispersion ICP spectrometer.

The standard deviation of alkalinity measurements on standard seawater (i.e. CRM94, with TA = 2.3 mM) was 0.018 mM, resulting in a 0.78% precision for the measured TA. The average standard deviation of triplicate DIC measurements of samples at Site U1368 was 0.015mM, resulting in a 0.59% precision for the measured DIC. The standard error on chloride and sulfate measurements was 0.09% and 0.05%, respectively, as estimated based on duplicate analyses of all samples involved in the study. The precision of the cation measurements were: 0.6% of the measured Ca value, 0.7% of the measured Mg value, 0.5% of the measured Na value and 0.6% of the measured K value, as quantified by triplicate analyses of the IAPSO standard seawater and other internal matrix matched standards (Shipboard Scientific Party, 2011). A detailed description of the shipboard pore fluid geochemical campaign, including details of the method is found in the *Proceedings of IODP*, Volume 329 (2011).

We used the measured in-situ bottom water temperature and thermal gradient of Site U1368 (i.e. 1.6 °C and 113 °C km<sup>-1</sup>, respectively) to calculate in-situ



temperature. We assumed the in-situ pressure to be hydrostatic and it was calculated from the water and sediment depth, considering average ocean water density.

Downhole salinity was inferred based on measured interstitial water chloride (**Table 3-4**). Equilibrium and solubility constants for the acid dissociation reactions in the porewater are calculated for in-situ temperature and salinity and are corrected for in-situ pressure conditions (**Table 5-8**).

#### *Data description*

**Figure 2 (B through D)** illustrates the shipboard measured [DIC], [TA] and [Ca<sup>2+</sup>] data for the studied site (conventionally and rapidly processed samples). Total alkalinity and dissolved inorganic carbon in the interstitial water exhibit similar behavior with depth, starting at 2.682 and 2.553 mmol kg<sup>-1</sup>, respectively, and gradually decreasing with depth to a value of ca. 2.427 and 2.373 mmol kg<sup>-1</sup>, respectively, at the bottom of the sequence. The general downhole pattern of the DIC and TA profile for the conventional samples at Site U1368 clearly deviates from the smooth profile generated by diffusive transport you would expect for sediment of that age and characterized by equilibrium conditions in-situ. The presence of multiple and irregular offsets in the carbonate chemistry profiles for conventional samples emphasize the significant impact of alteration on the measured chemistry and thus the need to correct these biased measurements for accurate use of this data. In contrast, the DIC and TA profile resulting from the rapid sampling process more closely leans toward a smooth diffusive downhole profile.

We assessed the impact of storage time by comparing catwalk versus conventional porewater chemistry data throughout the analyzed sequence. TA and DIC abundances of core samples that were handled with the conventional process were consistently lower compared to the rapidly processed samples (i.e. 0.172 mmol kg<sup>-1</sup> and 0.126 mmol kg<sup>-1</sup> lower concentration, respectively, as averaged over the entire sequence). These differences reflect more important carbonate precipitation in sediment before interstitial water squeezing in the case of conventionally handled samples.

Alteration of interstitial water chemistry was not uniformly distributed throughout the cored sequence. [DIC] is strongly altered in the interval between 8 and 11 meter below seafloor (mbsf), where [DIC] from rapidly processed samples is ca. 0.215 mmol kg<sup>-1</sup> higher than [DIC] from conventionally processed samples. A local minimum (i.e. 0.075 mmol kg<sup>-1</sup> higher [DIC]<sub>rapid</sub> compared to [DIC]<sub>conventional</sub>) and a local maximum (i.e. 0.208 mmol kg<sup>-1</sup> higher [DIC]<sub>rapid</sub> compared to [DIC]<sub>conventional</sub>) in alteration occur at 12.2 mbsf and 14 mbsf, respectively. Chemical alteration of [TA] due to storage time is variable throughout the sequence, with pronounced minima in alteration at 7.8 and 15.5 mbsf, characterized by a ca. 0.028 and 0.016 mmol kg<sup>-1</sup>, respectively, higher TA for rapidly processed samples compared to the conventionally processed samples. Storage effects on the measured calcium abundances are unclear given the precision of the available measurements (i.e. the Ca<sup>2+</sup> concentration difference between rapidly and conventionally processed samples lies within the analytical uncertainty margin of the calcium measurement). Abundances of other dissolved species, including the remaining cations (i.e. magnesium, sodium and

potassium), silica, chloride, sulfate and phosphate, do not visibly differ between rapidly squeezed samples and conventionally processed ones. The occurrence and variability of storage effects on [DIC] and [TA] illustrates the need to quantify these effects by performing post-expedition thermodynamic calculations.

#### Method validation strategy

Calcium carbonate is present throughout the core and is between 61.3 and 87.4 wt% (**Figure 3**). Also, calcareous microfossils, including planktonic foraminiferal assemblages, have been observed throughout the sequence (Shipboard Scientific Party, 2011). The lack of Mg variation between rapidly and conventionally processed samples implies that dolomite formation isn't significant during core recovery and interstitial water extraction (given the precision of the measurement). Other carbonate phases of importance in this study (e.g. SrCO<sub>3</sub>) are unstable throughout the range of conditions considered and thus do not need to be accounted for. Therefore, the carbonate formed at Site U1368 is presumed to be predominantly calcitic and consistent with the thermodynamic stability of calcite relative to aragonite in-situ and during core recovery. This supports our assumption of calcite saturation in-situ.

If our methodology and assumptions for correcting for carbonate precipitation are valid, calculated in-situ [DIC], [TA], and [Ca<sup>2+</sup>] of the conventionally processed samples (long storage time) and rapidly processed samples (short storage time), are expected to be indistinguishable and to produce a smooth depth profile due to diffusion. Corrected DIC and TA abundances for rapid process and conventional interstitial water samples that are indistinguishable would imply that the variance

between these samples is due to greater extent of carbonate precipitation following recovery and prior analysis. The availability of both sample types at a relatively high resolution throughout a deep sediment column that is dominated by carbonate-rich material and characterized by equilibrium conditions in-situ makes Site U1368 an ideal test for the application and validation of the proposed method.

### Experimental assessment results

Based on the in-situ temperature and pressure and dissolved chemical concentration data measured shipboard for Site U1368, we calculate the in-situ abundances of the measured components (i.e. DIC, TA, and  $\text{Ca}^{2+}$ , **Figure 4, Table 10 & 12**) together with the complete set of associated species involved in the carbonate system and in-situ pH that weren't measured shipboard (i.e.,  $\text{CO}_3^{2-}$ ,  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{HCO}_3^-$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{B}(\text{OH})_4^-$ ,  $\text{HPO}_4^{2-}$ , etc.). Averaged  $X_{\text{CaCO}_3}$  values for conventionally and rapidly processed samples are on the order of  $0.109 \text{ mmol kg}^{-1}$  and  $0.060 \text{ mmol kg}^{-1}$ , respectively (**Table 9**). More precisely this figure shows that, on average, ca. 4.4% of the measured [DIC] and [TA] was lost to calcium carbonate precipitation in conventionally sampled interstitial water, relative to ca. 2.4% in the case of the rapidly processed samples.

To place the obtained results by this newly developed method into a concrete evaluation context we performed a full error analysis of the reconstructed in-situ chemistry parameters. This was done in two distinct steps: (i) characterization of the analytical precision associated with the reconstructed parameters of the carbonate

system, followed by (ii) a statistical assessment of the precision with which we can reconstruct the in-situ carbonate chemistry.

The analytical error on the measured DIC, TA and  $\text{Ca}^{2+}$  was propagated on the calculated  $X_{\text{CaCO}_3}$  by taking the sum of the squares of the analytical error on each measurement:

$$\sigma_{X_{\text{CaCO}_3}}^2 = (\partial f / \partial \text{TA})^2 \sigma_{\text{TA}}^2 + (\partial f / \partial \text{DIC})^2 \sigma_{\text{DIC}}^2 + (\partial f / \partial \text{Ca})^2 \sigma_{\text{Ca}}^2 \quad (14)$$

Where  $f$  represents a function to quantify  $X_{\text{CaCO}_3}$  based on the three measured parameters (i.e.  $X_{\text{CaCO}_3} = f[\text{TA}, \text{DIC}, \text{Ca}]$ ) and  $\sigma$ , the precision of the considered measurement:

$$\sigma_{\text{TA}} (\%) = 0.78\% \text{ of the measured value}$$

$$\sigma_{\text{DIC}} (\%) = 0.59\% \text{ of the measured value}$$

$$\sigma_{\text{Ca}} (\%) = 0.60\% \text{ of the measured value}$$

We solve equation (14) numerically:

$$\sigma_{X_{\text{CaCO}_3}}^2 = (\Delta X_{\text{CaCO}_3} / \Delta \text{TA})^2 \sigma_{\text{TA}}^2 + (\Delta X_{\text{CaCO}_3} / \Delta \text{DIC})^2 \sigma_{\text{DIC}}^2 + (\Delta X_{\text{CaCO}_3} / \Delta \text{Ca})^2 \sigma_{\text{Ca}}^2 \quad (15)$$

We further propagate the analytical uncertainties (i.e. associated with the measured parameters and the calculated  $X_{\text{CaCO}_3}$ ) on the reconstructed in-situ DIC, TA and  $\text{Ca}^{2+}$ :

$$\sigma_{\text{DIC}_{\text{reconstructed\_in\_situ}}}^2 = [1 + 2(\partial f / \partial \text{DIC})] * \sigma_{\text{DIC}_{\text{measured}}}^2 + \sigma_{X_{\text{CaCO}_3}}^2 \quad (16)$$

$$\sigma_{\text{TA}_{\text{reconstructed\_in\_situ}}}^2 = [1 + 4(\partial f / \partial \text{TA})] * \sigma_{\text{TA}_{\text{measured}}}^2 + 2 * \sigma_{X_{\text{CaCO}_3}}^2 \quad (17)$$

$$\sigma_{\text{Ca\_reconstructed\_in\_situ}}^2 = [1 + 2(\partial f/\partial \text{Ca})]^* \sigma_{\text{Ca\_measured}}^2 + \sigma_{\text{X\_CaCO}_3}^2 \quad (18)$$

The error propagation analysis resulted in analytical uncertainty estimates ( $1\sigma$ ) on the order of  $2.195\text{E-}2 \text{ mmol kg}^{-1}$ ,  $1.811\text{E-}2 \text{ mmol kg}^{-1}$ ,  $6.239\text{E-}2 \text{ mmol kg}^{-1}$ , and  $6.551\text{E-}2 \text{ mmol kg}^{-1}$  for calculated  $\text{X}_{\text{CaCO}_3}$  and in-situ DIC, TA, and  $\text{Ca}^{2+}$  abundances, respectively (**Figure 4, Table 11 & 13**).

The precision with which we can reconstruct in-situ parameters of the carbonate system using the proposed method was quantified based on pooled standard deviations calculations for so called ‘duplicate runs’. In this study we consider (1) the reconstructed conventional samples results and (2) the reconstructed rapid process samples results as duplicates runs of the in-situ carbonate chemistry. The pooled standard deviation for each species considered (i.e. DIC, TA and calcium) was estimated using equation (McNaught and Wilkinson, 1997):

$$S_p = [(x_{i1}-x_{i2})^2/2k]^{1/2} \quad (19)$$

Where  $S_p$  is the pooled standard deviation,  $x_{i1}$  and  $x_{i2}$  duplicate measurement (with  $i = \text{DIC, TA, or calcium}$ ) and  $k$  the number of series of measurement.

Performing the calculation for Site U1368, eleven (i.e. coinciding with the number of rapid process samples) measurement series were delineated. For this end, each rapid process sample (i.e.  $x_{i1}$  in Eq. 19) was bracketed by its surrounding conventionally measured samples (i.e. conventional interstitial water sample taken above and below the rapid process one). The average of the two conventional sample values that bracket each rapid process sample was used as  $x_{i2}$ .

Applying this approach we obtained a pooled standard deviation of  $8.427\text{E-}2$   $\text{mmol kg}^{-1}$ ,  $7.952\text{E-}2$   $\text{mmol kg}^{-1}$  and  $0.160$   $\text{mmol kg}^{-1}$  for the in-situ [DIC], [TA], and  $[\text{Ca}^{2+}]$  calculations, respectively (**Table 14**). The pooled standard deviation between reconstructed in-situ DIC, TA and  $\text{Ca}^{2+}$  for conventionally and rapidly processed samples exceeds the analytical error associated with each of the reconstructed DIC, TA and  $\text{Ca}^{2+}$ , respectively. These results provide quantitative evidence that our approach is reasonable for the quantification of the in-situ interstitial water carbonate chemistry throughout deeply buried sediment given the analytical precision of the available measured parameters.

We ultimately quantify the uncertainty associated with the application of the proposed approach by subtracting the pooled standard deviation estimate of a species by the propagated analytical uncertainty associated with the reconstructed in-situ concentration of that species. This uncertainty estimate is thus purely methodological and separate from the source of uncertainty due to the analytical precision limitations of the available measurements. The methodological uncertainty amounts  $6.617\text{E-}02$   $\text{mmol kg}^{-1}$ ,  $1.713\text{E-}02$   $\text{mmol kg}^{-1}$ , and  $9.509\text{E-}02$   $\text{mmol kg}^{-1}$  for the reconstruction of DIC, TA, and  $\text{Ca}^{2+}$  respectively. These uncertainties encompass possible gas exchange during the core retrieval process, impact of processes affecting alteration intensity unaccounted in this method, etc. We argue that by increasing the number of samples analyzed we could improve these statistics by averaging out the remaining offsets found in the reconstructed carbonate chemistry (e.g. between 6-11 mbsf for reconstructed [TA]).

## APPLICATION OF THE APPROACH

The method that we describe is applicable for measurements that span a broad range of interstitial water chemistries and environments. The requirements are that there is carbonate saturation in-situ, that [DIC], [TA] and [Ca<sup>2+</sup>] are measured and that temperature is known. We performed iteration stability experiments of the method by applying it to minimum and maximum interstitial water DIC and TA abundances, as encountered throughout the marine seafloor. Results show that the simple algorithm we developed for calculating the extent of precipitation is stable for any expected range of DIC, TA and Ca<sup>2+</sup>. This constitutes a major improvement over the method by Wang et al. (2010), which is unstable in many situations, for example when [TA]<sub>measured</sub> <= [DIC]<sub>measured</sub>. Our technique is also widely applicable: it requires only limited calculation time and requires no additional shipboard and/or drilling for its application. Finally, our results clearly demonstrate that use of routinely generated shipboard carbonate-system chemical data must take alteration into account to avoid a biased view of in-situ DIC, TA, pH and Ca<sup>2+</sup> concentration. For example, we show that in the case of Site U1368 the measured DIC and TA abundances were offset by up to four percent from in-situ values by adopting a conventional sampling protocol. Such bias has the potential to strongly lower estimates of seafloor metabolic activities or provide poor constraints for the reconstruction of past deep ocean chemistry.

Application of the approach at Site U1368 didn't generate the smooth profile you observe in other sedimentary environment where you don't have to cope with these alteration issues. However, application of the approach visibly diminished



downhole offsets is carbonate chemistry and the variability between rapid and conventional process samples, providing a less biased representation of the in-situ chemistry. Remaining offsets in the reconstructed DIC, TA and calcium can be partly justified by the analytical uncertainty associated with the measured parameters this reconstructed carbonate chemistry is based on. We argue that application of the proposed approach generates a much more accurate view of the in-situ chemistry relative to the measured one. Correcting for alteration is rather straightforward if [DIC], [TA] and  $[Ca^{2+}]$  are measured for the same sample, and both equilibrium and calcium carbonate saturation conditions prevail in-situ. Because carbonate-bearing sediment characterizes about 50% of the seafloor (Schulz, 2000), we argue that this method is widely applicable.

An indirect application of the approach involves the detection of minor traces of calcium carbonate. Detection of low concentrations of  $CaCO_3$  is often challenging with routinely used instruments. Downhole calcium saturation being a critical requirement for the successful application of the approach, we suggest that this method could be used to effectively evaluate the carbonate content of sediment cores. For carbonate under-saturated sediment, application of the approach will result in the development of many method related artifacts downhole (i.e. profile obviously deviating from a smooth trend) as the basic requirement for the correct development of the iteration won't be fulfilled. In contrary, for carbonate-saturated columns like Site U1368, application of the method will result in an improvement of the measured downhole chemistry profiles by smoothening out possible offsets in the measured carbonate chemistry.

## COMMENTS AND RECOMMENDATIONS ON THE METHOD

Our method calculates in-situ carbonate system porewater chemistry in deeply buried marine sediment. For this end it assumes a priori calcium carbonate saturation in the sediment and equilibrium in-situ. The method successfully deals with any relative size of [DIC] and [TA] input values and incorporates physical environment information that affect the carbonate-related porewater chemistry upon core retrieval.

Although our approach has the potential to effectively quantify the complete in-situ dissolved carbon system of deeply buried marine sediment, it has limitations. The first limitation is the assumption that the calcite is the dominant carbonate phase. In the case of a different carbonate phase or the co-occurrence of multiple phases throughout the sediment, the iteration algorithm would have to be adapted to incorporate this more complex carbonate speciation. A second limitation is that roughly half of the seafloor is not characterized by carbonate-bearing sediment. Alteration effects in carbonate-free sediment are unclear and further experiments are required to explore the influence of these effects. Finally, our approach assumes a priori equilibrium conditions in-situ. This is generally true but close scrutiny should be applied to this assumption in high sedimentation environments, and other subseafloor environments characterized by not fully equilibrated systems.

## CONCLUSION

Our approach successfully quantifies the in-situ dissolved carbonate system chemistry of subseafloor sediment based on measured concentrations of dissolved carbonate system constituents that have been altered by core recovery and handling.

The method accounts for variations in temperature, chemical gradients, and physical context during the core retrieval and sample handling process. We illustrate the use of our method by applying it to IODP Site U1368. The results quantitatively demonstrate that chemical alteration associated with the core retrieval and handling processes can be significant, especially in low sedimentation rate environments like the South Pacific Gyre. For correct use of this data the method described here should therefore be implemented when the necessary interstitial water chemistry data is available and the two requirements for the application of the method are fulfilled.

Our example of Site U1368 illustrates that this approach is also an effective tool for inferring concentration profiles of dissolved carbonate-related chemicals that have not been measured on the ship.

Application of our approach will contribute to a better assessment of microbial metabolic activity rates in subseafloor environments and improve quantitative reconstructions of deep ocean chemistry through the last glacial-interglacial cycle.

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## FIGURES

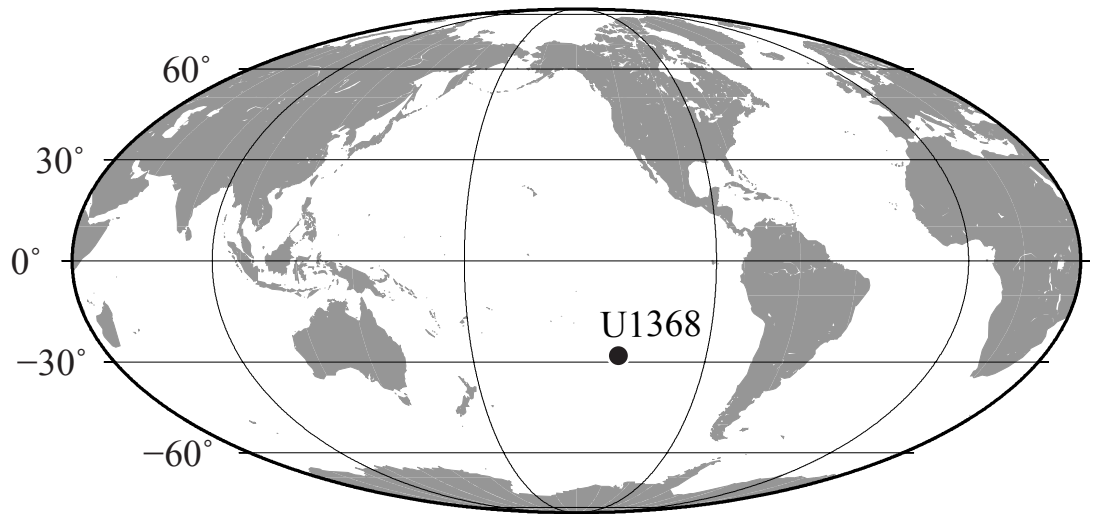


Figure 1. Location of IODP Site U1368 in the South Pacific Gyre.



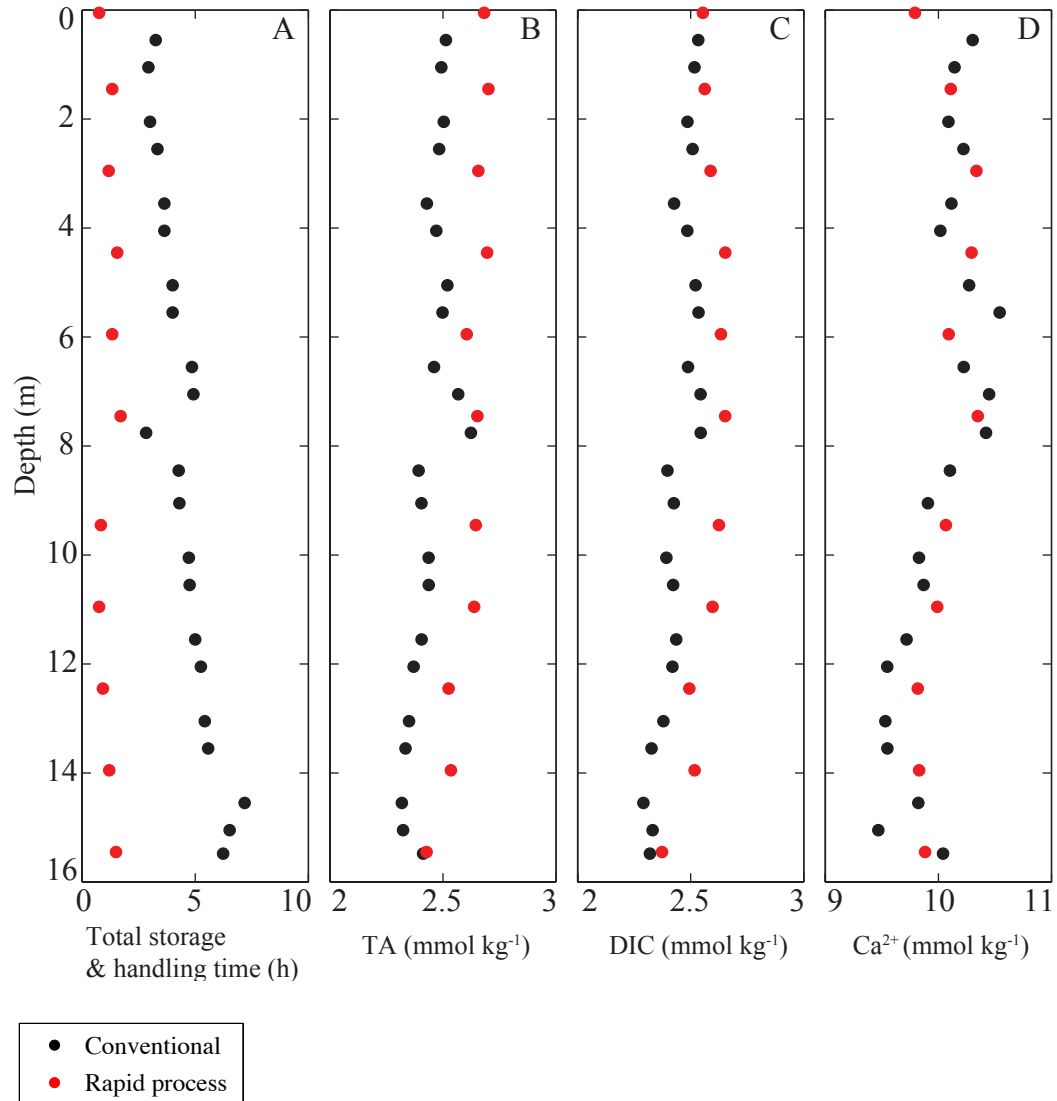


Figure 2. Depth profiles of measured pore water chemical concentrations related to the carbonate system at Site U1368. Total time span for each sample from Hole U1368 C to get from sample recovery stage to squeezing and analysis stage for conventionally processed samples (•) and rapid process samples (•) (A). Depth is in units of meters below seafloor (mbsf). Depth profiles of measured total alkalinity (B), dissolved inorganic carbon (C), and calcium abundances (D) at Site U1368, for conventional samples (•) and rapid process samples (•). Measurement data are from Expedition 329 Shipboard Scientific party (2010).

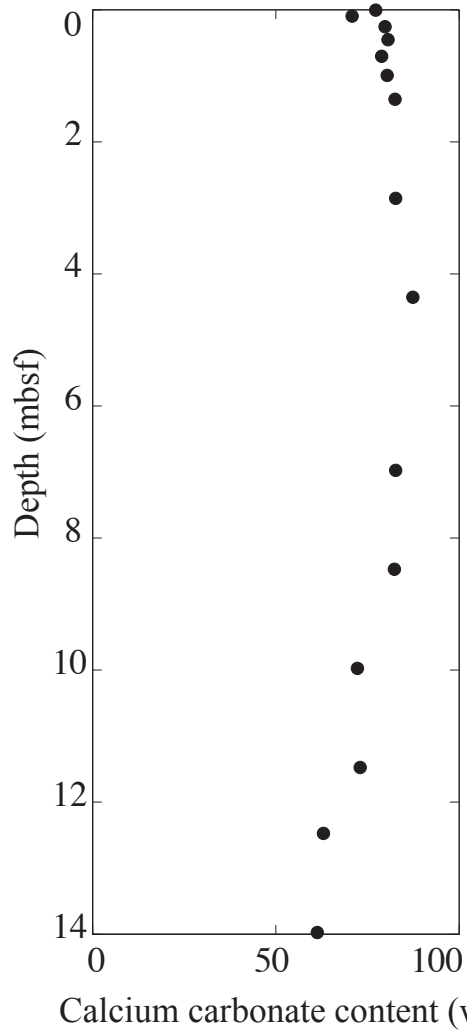


Figure 3. Solid phase analysis of the sediment at site U1368, hole B. Calcium carbonate content, expressed as weight percent (wt%). Measurement data are from Expedition 329 Shipboard Scientific party (2010).

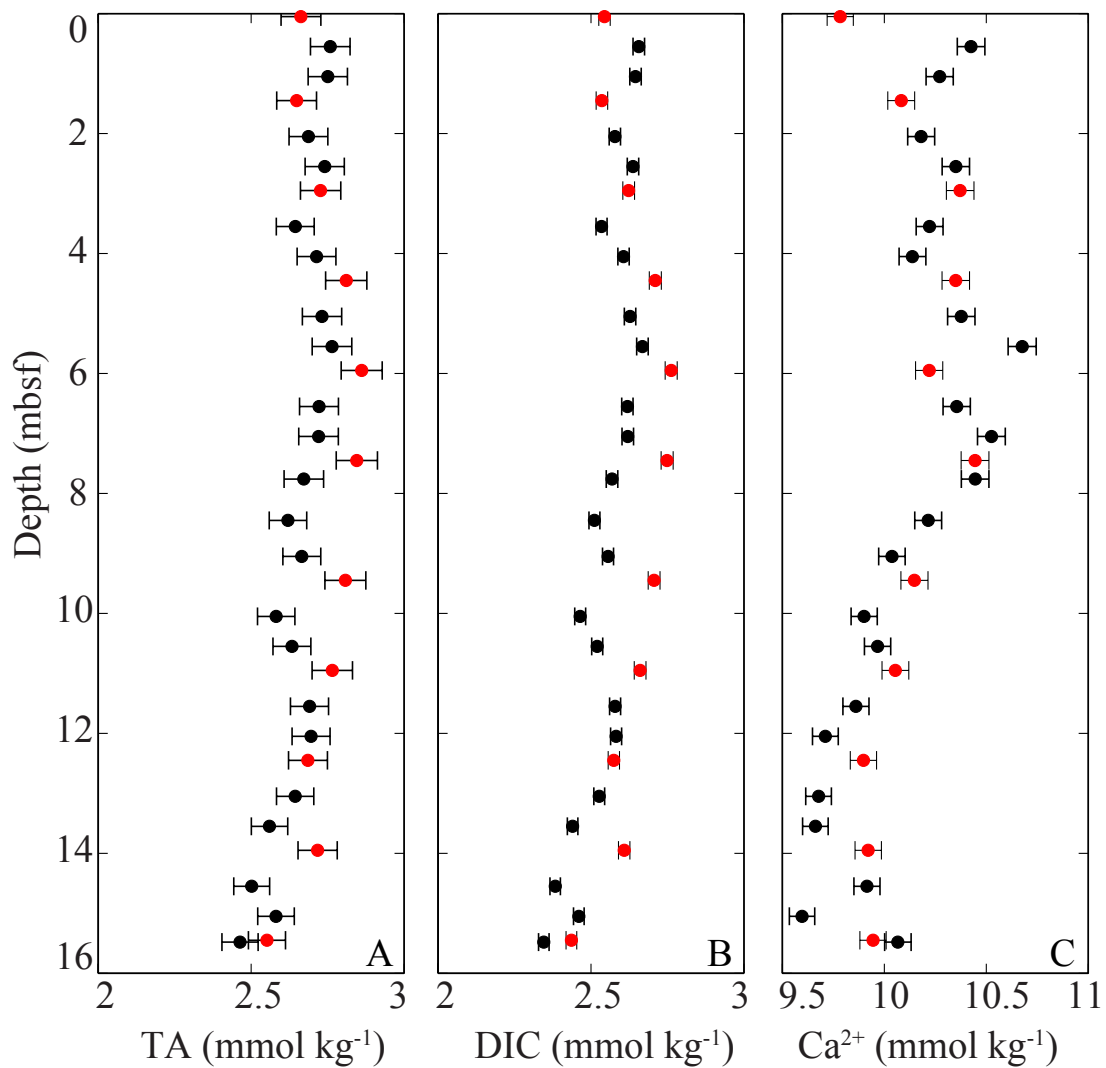


Figure 4. Depth profiles of calculated in-situ TA, DIC and  $\text{Ca}^{2+}$  abundances with error analysis ( $1\sigma$ ) for conventional (•) and rapid process (•) sampling procedures at Site U1368, hole C.

## TABLES

Depth (mbsf)	TA (mol/kg)	DIC (mol/kg)	pH	Cl <sup>-</sup> (mol/kg)	SO <sub>4</sub> <sup>2-</sup> (mol/kg)	Tot P (mol/kg)
0.55	2.513E-03	2.534E-03	7.76	5.405E-01	2.796E-02	1.741E-06
1.05	2.493E-03	2.516E-03	7.77	5.409E-01	2.798E-02	1.728E-06
2.05	2.503E-03	2.486E-03	7.75	5.413E-01	2.800E-02	1.387E-06
2.55	2.483E-03	2.509E-03	7.77	5.400E-01	2.793E-02	1.286E-06
3.55	2.429E-03	2.427E-03	7.95	5.420E-01	2.803E-02	1.144E-06
4.05	2.471E-03	2.485E-03	7.75	5.402E-01	2.794E-02	1.021E-06
5.05	2.520E-03	2.522E-03	7.76	5.417E-01	2.802E-02	1.691E-06
5.55	2.498E-03	2.535E-03	7.76	5.412E-01	2.799E-02	9.032E-07
6.55	2.460E-03	2.488E-03	7.78	5.406E-01	2.796E-02	9.579E-07
7.05	2.567E-03	2.544E-03	7.75	5.411E-01	2.799E-02	9.579E-07
7.76	2.624E-03	2.544E-03	7.74	5.411E-01	2.799E-02	9.453E-07
8.45	2.392E-03	2.397E-03	7.76	5.406E-01	2.796E-02	7.685E-07
9.05	2.405E-03	2.426E-03	7.74	5.407E-01	2.797E-02	8.173E-07
10.05	2.437E-03	2.392E-03	7.76	5.424E-01	2.806E-02	1.203E-06
10.55	2.437E-03	2.422E-03	7.77	5.425E-01	2.806E-02	8.147E-07
11.55	2.405E-03	2.436E-03	7.72	5.410E-01	2.798E-02	9.926E-07
12.05	2.370E-03	2.419E-03	7.80	5.409E-01	2.798E-02	7.666E-07
13.05	2.349E-03	2.380E-03	7.77	5.418E-01	2.803E-02	1.014E-06
13.55	2.334E-03	2.327E-03	7.78	5.396E-01	2.791E-02	8.764E-07
14.55	2.318E-03	2.291E-03	7.80	5.417E-01	2.802E-02	1.025E-06
15.05	2.324E-03	2.332E-03	7.81	5.408E-01	2.798E-02	1.210E-06
15.48	2.412E-03	2.320E-03	7.92	5.416E-01	2.801E-02	1.569E-06

Table 1. Measurement data of pore water chemical concentrations at Site U1368, hole C for **conventionally handled pore water samples**. Dissolved chemical concentrations are from Expedition 329 Shipboard Scientific Party (2010).

Depth (mbsf)	Tot Si (mol/kg)	Ca <sup>2+</sup> (mol/kg)	Na <sup>+</sup> (mol/kg)	K <sup>+</sup> (mol/kg)	Mg <sup>2+</sup> (mol/kg)
0.55	2.198E-04	1.030E-02	4.647E-01	1.075E-02	4.954E-02
1.05	2.354E-04	1.014E-02	4.592E-01	1.054E-02	4.949E-02
2.05	2.451E-04	1.009E-02	4.582E-01	1.028E-02	4.982E-02
2.55	2.381E-04	1.022E-02	4.609E-01	1.060E-02	4.936E-02
3.55	2.118E-04	1.011E-02	4.612E-01	1.038E-02	5.146E-02
4.05	2.248E-04	1.002E-02	4.589E-01	1.030E-02	5.038E-02
5.05	2.826E-04	1.027E-02	4.632E-01	1.050E-02	4.950E-02
5.55	2.510E-04	1.054E-02	4.613E-01	1.063E-02	4.943E-02
6.55	2.453E-04	1.022E-02	4.635E-01	1.082E-02	4.987E-02
7.05	2.479E-04	1.045E-02	4.617E-01	1.077E-02	4.901E-02
7.76	2.512E-04	1.042E-02	4.610E-01	1.068E-02	4.962E-02
8.45	2.272E-04	1.010E-02	4.635E-01	1.044E-02	5.129E-02
9.05	2.165E-04	9.907E-03	4.582E-01	1.024E-02	5.076E-02
10.05	2.421E-04	9.829E-03	4.585E-01	1.039E-02	5.138E-02
10.55	2.343E-04	9.869E-03	4.619E-01	1.036E-02	5.108E-02
11.55	2.610E-04	9.718E-03	4.590E-01	1.041E-02	5.060E-02
12.05	2.229E-04	9.548E-03	4.595E-01	1.034E-02	5.056E-02
13.05	2.209E-04	9.530E-03	4.569E-01	1.026E-02	5.066E-02
13.55	2.344E-04	9.549E-03	4.576E-01	1.016E-02	5.098E-02
14.55	2.169E-04	9.823E-03	4.596E-01	1.051E-02	5.159E-02
15.05	2.363E-04	9.468E-03	4.583E-01	1.026E-02	4.998E-02
15.48	1.964E-04	1.004E-02	4.604E-01	1.027E-02	5.145E-02

Table 1. (continued).

Depth (mbsf)	TA (mol/kg)	DIC (mol/kg)	pH	Cl <sup>-</sup> (mol/kg)	SO <sub>4</sub> <sup>2-</sup> (mol/kg)	Tot P (mol/kg)
0.05	2.682E-03	2.554E-03	7.67	5.411E-01	2.799E-02	2.236E-06
1.45	2.701E-03	2.562E-03	7.61	5.406E-01	2.796E-02	1.759E-06
2.95	2.656E-03	2.588E-03	7.69	5.407E-01	2.797E-02	1.425E-06
4.45	2.696E-03	2.653E-03	7.67	5.412E-01	2.799E-02	1.625E-06
5.95	2.605E-03	2.634E-03	7.74	5.415E-01	2.801E-02	8.722E-07
7.45	2.652E-03	2.652E-03	7.77	5.407E-01	2.797E-02	1.313E-06
9.45	2.645E-03	2.625E-03	7.73	5.405E-01	2.796E-02	8.933E-07
10.95	2.638E-03	2.597E-03	7.71	5.398E-01	2.792E-02	9.566E-07
12.45	2.525E-03	2.494E-03	7.76	5.407E-01	2.797E-02	9.482E-07
13.95	2.535E-03	2.517E-03	7.74	5.403E-01	2.795E-02	9.958E-07
15.45	2.427E-03	2.374E-03	7.82	5.416E-01	2.802E-02	1.236E-06
15.48	2.682E-03	2.554E-03	7.92	5.411E-01	2.799E-02	2.236E-06

Table 2. Measurement data of pore water chemical concentrations at Site U1368, hole C for **rapidly handled pore water samples**. Dissolved chemical concentrations are from Expedition 329 Shipboard Scientific Party (2010).

<b>Depth</b> (mbsf)	<b>Tot Si</b> (mol/kg)	<b>Ca<sup>2+</sup></b> (mol/kg)	<b>Na<sup>+</sup></b> (mol/kg)	<b>K<sup>+</sup></b> (mol/kg)	<b>Mg<sup>2+</sup></b> (mol/kg)
0.05	2.317E-04	9.793E-03	4.626E-01	1.099E-02	4.983E-02
1.45	2.310E-04	1.011E-02	4.572E-01	1.044E-02	4.979E-02
2.95	2.421E-04	1.034E-02	4.613E-01	1.060E-02	4.933E-02
4.45	2.825E-04	1.029E-02	4.617E-01	1.044E-02	5.020E-02
5.95	2.501E-04	1.009E-02	4.601E-01	1.045E-02	4.983E-02
7.45	3.121E-04	1.035E-02	4.598E-01	1.049E-02	4.869E-02
9.45	2.536E-04	1.007E-02	4.600E-01	1.035E-02	5.048E-02
10.95	2.480E-04	9.991E-03	4.584E-01	1.031E-02	5.110E-02
12.45	2.533E-04	9.817E-03	4.577E-01	1.013E-02	5.103E-02
13.95	2.497E-04	9.830E-03	4.607E-01	1.033E-02	5.145E-02
15.45	2.270E-04	9.883E-03	4.571E-01	1.017E-02	5.107E-02
15.48	2.317E-04	9.793E-03	4.626E-01	1.099E-02	4.983E-02

Table 2. (continued).

<b>Depth</b> (mbsf)	<b>Temperature</b> (°C)	<b>Salinity</b> (ppt)	<b>Density</b> (kg m <sup>-3</sup> )	<b>Pressure</b> (Bar)
0.55	1.60	34.52	1027.61	378.77
1.05	1.72	34.54	1027.62	378.82
2.05	1.83	34.57	1027.64	378.92
2.55	1.89	34.49	1027.57	378.97
3.55	2.00	34.61	1027.66	379.07
4.05	2.06	34.50	1027.57	379.12
5.05	2.17	34.59	1027.63	379.22
5.55	2.23	34.56	1027.60	379.27
6.55	2.34	34.52	1027.56	379.37
7.05	2.40	34.55	1027.58	379.42
7.76	2.48	34.55	1027.57	379.49
8.45	2.55	34.52	1027.54	379.56
9.05	2.62	34.53	1027.54	379.62
10.05	2.74	34.64	1027.62	379.73
10.55	2.79	34.64	1027.62	379.78
11.55	2.91	34.55	1027.53	379.88
12.05	2.96	34.54	1027.52	379.93
13.05	3.07	34.60	1027.56	380.03
13.55	3.13	34.46	1027.45	380.08
14.55	3.24	34.60	1027.54	380.18
15.05	3.30	34.54	1027.49	380.23
15.48	3.35	34.59	1027.52	380.27

Table 3. The in situ condition and density of the **conventionally** sampled pore waters at Site U1368.

Depth (mbsf)	Temperature (°C)	Salinity (ppt)	Density (kg m <sup>-3</sup> )	Pressure (Bar)
0.05	1.60	34.55	1027.64	378.72
1.45	1.76	34.52	1027.60	378.86
2.95	1.93	34.52	1027.60	379.01
4.45	2.10	34.56	1027.61	379.16
5.95	2.27	34.58	1027.61	379.31
7.45	2.44	34.53	1027.56	379.46
9.45	2.67	34.52	1027.53	379.66
10.95	2.84	34.48	1027.48	379.82
12.45	3.01	34.53	1027.51	379.97
13.95	3.18	34.51	1027.47	380.12
15.45	3.35	34.59	1027.53	380.27

Table 4. The in situ condition and density of the **rapidly** sampled pore waters at Site U1368.

Depth	K <sub>1</sub>	K <sub>2</sub>	K <sub>w</sub>	K <sub>B</sub>	K <sub>P1</sub>
0.55	8.019E-07	4.319E-10	5.866E-15	1.279E-09	2.473E-02
1.05	8.048E-07	4.342E-10	5.945E-15	1.284E-09	2.474E-02
2.05	8.077E-07	4.365E-10	6.022E-15	1.289E-09	2.475E-02
2.55	8.085E-07	4.367E-10	6.053E-15	1.290E-09	2.474E-02
3.55	8.121E-07	4.400E-10	6.139E-15	1.297E-09	2.476E-02
4.05	8.127E-07	4.399E-10	6.168E-15	1.297E-09	2.475E-02
5.05	8.160E-07	4.428E-10	6.253E-15	1.303E-09	2.476E-02
5.55	8.172E-07	4.435E-10	6.289E-15	1.305E-09	2.476E-02
6.55	8.196E-07	4.452E-10	6.365E-15	1.309E-09	2.476E-02
7.05	8.212E-07	4.465E-10	6.407E-15	1.312E-09	2.477E-02
7.76	8.231E-07	4.480E-10	6.464E-15	1.316E-09	2.477E-02
8.45	8.248E-07	4.491E-10	6.516E-15	1.318E-09	2.477E-02
9.05	8.265E-07	4.505E-10	6.566E-15	1.321E-09	2.478E-02
10.05	8.300E-07	4.537E-10	6.657E-15	1.328E-09	2.480E-02
10.55	8.314E-07	4.548E-10	6.699E-15	1.330E-09	2.480E-02
11.55	8.335E-07	4.559E-10	6.774E-15	1.333E-09	2.479E-02
12.05	8.348E-07	4.569E-10	6.815E-15	1.336E-09	2.479E-02
13.05	8.379E-07	4.596E-10	6.905E-15	1.341E-09	2.481E-02
13.55	8.384E-07	4.592E-10	6.934E-15	1.342E-09	2.479E-02
14.55	8.420E-07	4.627E-10	7.033E-15	1.348E-09	2.481E-02
15.05	8.430E-07	4.632E-10	7.071E-15	1.350E-09	2.481E-02
15.48	8.445E-07	4.646E-10	7.113E-15	1.353E-09	2.482E-02

Table 5. Thermodynamic constants calculated at standard Temperature (20°C), salinity (34.7 ppt) and pressure (1 Atm) for the **conventional samples** (Equilibrium constants are expressed on the *Total Hydrogen Scale*).

Depth	K <sub>P2</sub>	K <sub>P3</sub>	K <sub>Si</sub>	K <sub>1S</sub>	K <sub>Sp</sub>
0.55	6.577E-07	4.479E-10	1.461E-10	2.619E-01	4.227E-07
1.05	6.600E-07	4.509E-10	1.470E-10	2.606E-01	4.231E-07
2.05	6.622E-07	4.537E-10	1.479E-10	2.594E-01	4.236E-07
2.55	6.627E-07	4.559E-10	1.482E-10	2.581E-01	4.224E-07
3.55	6.655E-07	4.580E-10	1.492E-10	2.576E-01	4.242E-07
4.05	6.659E-07	4.605E-10	1.495E-10	2.561E-01	4.227E-07
5.05	6.685E-07	4.628E-10	1.504E-10	2.554E-01	4.240E-07
5.55	6.693E-07	4.646E-10	1.509E-10	2.545E-01	4.236E-07
6.55	6.711E-07	4.681E-10	1.517E-10	2.529E-01	4.231E-07
7.05	6.724E-07	4.694E-10	1.521E-10	2.524E-01	4.236E-07
7.76	6.738E-07	4.717E-10	1.528E-10	2.515E-01	4.236E-07
8.45	6.750E-07	4.741E-10	1.533E-10	2.504E-01	4.232E-07
9.05	6.763E-07	4.760E-10	1.539E-10	2.496E-01	4.233E-07
10.05	6.791E-07	4.782E-10	1.548E-10	2.490E-01	4.249E-07
10.55	6.801E-07	4.798E-10	1.553E-10	2.484E-01	4.250E-07
11.55	6.816E-07	4.839E-10	1.561E-10	2.465E-01	4.237E-07
12.05	6.826E-07	4.855E-10	1.565E-10	2.458E-01	4.236E-07
13.05	6.850E-07	4.883E-10	1.575E-10	2.449E-01	4.245E-07
13.55	6.851E-07	4.911E-10	1.578E-10	2.433E-01	4.225E-07
14.55	6.881E-07	4.933E-10	1.588E-10	2.429E-01	4.245E-07
15.05	6.887E-07	4.954E-10	1.592E-10	2.419E-01	4.237E-07
15.48	6.899E-07	4.964E-10	1.596E-10	2.416E-01	4.244E-07

Table 5. (continued).

Depth	K <sub>1</sub>	K <sub>2</sub>	K <sub>w</sub>	K <sub>B</sub>	K <sub>P1</sub>
0.05	8.021E-07	4.323E-10	5.869E-15	1.279E-09	2.473E-02
1.45	8.058E-07	4.348E-10	5.973E-15	1.286E-09	2.474E-02
2.95	8.099E-07	4.379E-10	6.086E-15	1.293E-09	2.475E-02
4.45	8.142E-07	4.413E-10	6.204E-15	1.300E-09	2.476E-02
5.95	8.184E-07	4.446E-10	6.322E-15	1.307E-09	2.477E-02
7.45	8.222E-07	4.472E-10	6.437E-15	1.314E-09	2.477E-02
9.45	8.275E-07	4.511E-10	6.597E-15	1.323E-09	2.478E-02
10.95	8.313E-07	4.538E-10	6.717E-15	1.329E-09	2.478E-02
12.45	8.358E-07	4.576E-10	6.848E-15	1.337E-09	2.480E-02
13.95	8.398E-07	4.605E-10	6.973E-15	1.344E-09	2.480E-02
15.45	8.445E-07	4.645E-10	7.111E-15	1.353E-09	2.482E-02

Table 6. Thermodynamic constants calculated at in-situ temperature and salinity for the **rapidly processed samples** (Equilibrium constants are expressed on the *Total Hydrogen Scale*).



Depth	$K_{P2}$	$K_{P3}$	$K_{Si}$	$K_{IS}$	$K_{sp}$
0.05	6.580E-07	4.476E-10	1.461E-10	2.622E-01	4.233E-07
1.45	6.607E-07	4.523E-10	1.473E-10	2.599E-01	4.228E-07
2.95	6.638E-07	4.568E-10	1.486E-10	2.579E-01	4.230E-07
4.45	6.671E-07	4.612E-10	1.499E-10	2.560E-01	4.236E-07
5.95	6.703E-07	4.657E-10	1.512E-10	2.541E-01	4.239E-07
7.45	6.730E-07	4.709E-10	1.525E-10	2.518E-01	4.233E-07
9.45	6.771E-07	4.774E-10	1.542E-10	2.490E-01	4.231E-07
10.95	6.799E-07	4.826E-10	1.555E-10	2.467E-01	4.226E-07
12.45	6.833E-07	4.869E-10	1.569E-10	2.452E-01	4.235E-07
13.95	6.862E-07	4.921E-10	1.582E-10	2.431E-01	4.231E-07
15.45	6.899E-07	4.963E-10	1.596E-10	2.417E-01	4.244E-07

Table 6. (continued).

Depth	$K^*_1$	$K^*_2$	$K^*_w$	$K^*_B$	$K^*_{PI}$
0.55	1.207E-06	5.629E-10	8.766E-15	2.055E-09	3.108E-02
1.05	1.211E-06	5.659E-10	8.880E-15	2.062E-09	3.108E-02
2.05	1.215E-06	5.689E-10	8.991E-15	2.070E-09	3.109E-02
2.55	1.216E-06	5.691E-10	9.035E-15	2.071E-09	3.107E-02
3.55	1.221E-06	5.733E-10	9.159E-15	2.081E-09	3.109E-02
4.05	1.222E-06	5.732E-10	9.201E-15	2.081E-09	3.107E-02
5.05	1.227E-06	5.770E-10	9.323E-15	2.090E-09	3.109E-02
5.55	1.228E-06	5.779E-10	9.375E-15	2.093E-09	3.108E-02
6.55	1.232E-06	5.801E-10	9.483E-15	2.098E-09	3.107E-02
7.05	1.234E-06	5.818E-10	9.544E-15	2.102E-09	3.108E-02
7.76	1.237E-06	5.837E-10	9.626E-15	2.107E-09	3.108E-02
8.45	1.239E-06	5.851E-10	9.701E-15	2.111E-09	3.107E-02
9.05	1.241E-06	5.868E-10	9.772E-15	2.115E-09	3.107E-02
10.05	1.246E-06	5.910E-10	9.904E-15	2.125E-09	3.109E-02
10.55	1.248E-06	5.924E-10	9.964E-15	2.128E-09	3.109E-02
11.55	1.251E-06	5.938E-10	1.007E-14	2.133E-09	3.107E-02
12.05	1.253E-06	5.951E-10	1.013E-14	2.136E-09	3.107E-02
13.05	1.257E-06	5.986E-10	1.026E-14	2.144E-09	3.108E-02
13.55	1.258E-06	5.981E-10	1.030E-14	2.144E-09	3.106E-02
14.55	1.263E-06	6.026E-10	1.044E-14	2.154E-09	3.108E-02
15.05	1.264E-06	6.032E-10	1.050E-14	2.156E-09	3.107E-02
15.48	1.266E-06	6.051E-10	1.056E-14	2.160E-09	3.107E-02

Table 7. In-situ apparent thermodynamic constants for the **conventional samples** (Equilibrium constants are expressed on the *Total Hydrogen Scale*).

Depth	$K_{P2}^*$	$K_{P3}^*$	$K_{Si}^*$	$K_{IS}^*$	$K_{sp}^*$
0.55	9.448E-07	6.829E-10	1.684E-10	3.476E-01	9.016E-07
1.05	9.477E-07	6.872E-10	1.694E-10	3.459E-01	9.014E-07
2.05	9.505E-07	6.912E-10	1.704E-10	3.442E-01	9.015E-07
2.55	9.511E-07	6.944E-10	1.708E-10	3.425E-01	8.986E-07
3.55	9.548E-07	6.973E-10	1.719E-10	3.418E-01	9.015E-07
4.05	9.551E-07	7.009E-10	1.723E-10	3.399E-01	8.978E-07
5.05	9.586E-07	7.042E-10	1.734E-10	3.388E-01	8.997E-07
5.55	9.596E-07	7.068E-10	1.739E-10	3.377E-01	8.985E-07
6.55	9.619E-07	7.118E-10	1.748E-10	3.355E-01	8.965E-07
7.05	9.635E-07	7.137E-10	1.754E-10	3.348E-01	8.970E-07
7.76	9.653E-07	7.169E-10	1.761E-10	3.336E-01	8.965E-07
8.45	9.669E-07	7.204E-10	1.768E-10	3.320E-01	8.950E-07
9.05	9.685E-07	7.231E-10	1.774E-10	3.310E-01	8.948E-07
10.05	9.722E-07	7.262E-10	1.785E-10	3.302E-01	8.973E-07
10.55	9.735E-07	7.284E-10	1.790E-10	3.294E-01	8.971E-07
11.55	9.753E-07	7.344E-10	1.800E-10	3.267E-01	8.934E-07
12.05	9.765E-07	7.367E-10	1.805E-10	3.258E-01	8.929E-07
13.05	9.797E-07	7.407E-10	1.815E-10	3.246E-01	8.938E-07
13.55	9.797E-07	7.448E-10	1.819E-10	3.225E-01	8.892E-07
14.55	9.836E-07	7.478E-10	1.831E-10	3.219E-01	8.924E-07
15.05	9.844E-07	7.509E-10	1.836E-10	3.206E-01	8.904E-07
15.48	9.860E-07	7.523E-10	1.841E-10	3.202E-01	8.914E-07

Table 7. (continued).

Depth	$K_1^*$	$K_2^*$	$K_w^*$	$K_B^*$	$K_{P1}^*$
0.05	1.208E-06	5.634E-10	8.770E-15	2.056E-09	3.108E-02
1.45	1.213E-06	5.667E-10	8.920E-15	2.064E-09	3.108E-02
2.95	1.218E-06	5.707E-10	9.083E-15	2.075E-09	3.108E-02
4.45	1.224E-06	5.751E-10	9.253E-15	2.085E-09	3.108E-02
5.95	1.230E-06	5.793E-10	9.423E-15	2.096E-09	3.108E-02
7.45	1.235E-06	5.826E-10	9.587E-15	2.105E-09	3.108E-02
9.45	1.243E-06	5.877E-10	9.817E-15	2.118E-09	3.107E-02
10.95	1.248E-06	5.912E-10	9.989E-15	2.127E-09	3.106E-02
12.45	1.254E-06	5.960E-10	1.018E-14	2.138E-09	3.107E-02
13.95	1.259E-06	5.997E-10	1.036E-14	2.148E-09	3.106E-02
15.45	1.266E-06	6.050E-10	1.055E-14	2.160E-09	3.107E-02

Table 8. In-situ apparent thermodynamic constants for the **rapidly processed samples** (Equilibrium constants are expressed on the *Total Hydrogen Scale*).

<b>Depth</b>	<b>K<sub>p2</sub>*</b>	<b>K<sub>p3</sub>*</b>	<b>K<sub>Si</sub>*</b>	<b>K<sub>IS</sub>*</b>	<b>K<sub>sp</sub>*</b>
0.05	9.451E-07	6.824E-10	1.684E-10	3.480E-01	9.027E-07
1.45	9.485E-07	6.892E-10	1.698E-10	3.449E-01	9.004E-07
2.95	9.525E-07	6.957E-10	1.713E-10	3.422E-01	8.995E-07
4.45	9.567E-07	7.019E-10	1.728E-10	3.397E-01	8.994E-07
5.95	9.608E-07	7.084E-10	1.743E-10	3.371E-01	8.987E-07
7.45	9.643E-07	7.158E-10	1.758E-10	3.339E-01	8.961E-07
9.45	9.695E-07	7.251E-10	1.778E-10	3.302E-01	8.941E-07
10.95	9.730E-07	7.326E-10	1.793E-10	3.271E-01	8.916E-07
12.45	9.775E-07	7.388E-10	1.809E-10	3.250E-01	8.922E-07
13.95	9.812E-07	7.462E-10	1.824E-10	3.222E-01	8.902E-07
15.45	9.859E-07	7.521E-10	1.840E-10	3.203E-01	8.915E-07

Table 8. (continued).

<u>Conventional process samples</u>		<u>Rapid process samples</u>	
<b>Depth (mbsf)</b>	<b>X<sub>CaCO<sub>3</sub></sub> (mol kg<sup>-1</sup>)</b>	<b>Depth (mbsf)</b>	<b>X<sub>CaCO<sub>3</sub></sub> (mol kg<sup>-1</sup>)</b>
0.55	1.227E-04	0.05	-9.629E-06
1.05	1.290E-04	1.45	-2.640E-05
2.05	9.194E-05	2.95	3.551E-05
2.55	1.286E-04	4.45	5.762E-05
3.55	1.078E-04	5.95	1.281E-04
4.05	1.215E-04	7.45	9.670E-05
5.05	1.059E-04	9.45	8.132E-05
5.55	1.332E-04	10.95	6.369E-05
6.55	1.308E-04	12.45	8.038E-05
7.05	7.662E-05	13.95	9.114E-05
7.76	2.430E-05	15.45	6.216E-05
8.45	1.140E-04		
9.05	1.302E-04		
10.05	7.246E-05		
10.55	9.799E-05		
11.55	1.427E-04		
12.05	1.628E-04		
13.05	1.472E-04		
13.55	1.129E-04		
14.55	9.184E-05		
15.05	1.286E-04		
15.48	2.601E-05		

Table 9. Amount of calcium carbonate precipitation post sample recovery for conventionally and rapidly sampled pore waters.

Depth (mbsf)	X <sub>CaCO<sub>3</sub></sub> (mol/kg)	TA (mol/kg)	DIC (mol/kg)	Ca <sup>2+</sup> (mol/kg)	H <sub>2</sub> CO <sub>3</sub> (mol/kg)
0.55	1.227E-04	2.759E-03	2.656E-03	1.043E-02	3.465E-05
1.05	1.290E-04	2.751E-03	2.645E-03	1.027E-02	3.391E-05
2.05	9.194E-05	2.687E-03	2.578E-03	1.018E-02	3.193E-05
2.55	1.286E-04	2.741E-03	2.637E-03	1.035E-02	3.413E-05
3.55	1.078E-04	2.644E-03	2.535E-03	1.022E-02	3.105E-05
4.05	1.215E-04	2.714E-03	2.606E-03	1.014E-02	3.271E-05
5.05	1.059E-04	2.732E-03	2.628E-03	1.038E-02	3.409E-05
5.55	1.332E-04	2.764E-03	2.668E-03	1.068E-02	3.629E-05
6.55	1.308E-04	2.722E-03	2.619E-03	1.035E-02	3.395E-05
7.05	7.662E-05	2.720E-03	2.620E-03	1.053E-02	3.459E-05
7.76	2.430E-05	2.672E-03	2.569E-03	1.045E-02	3.301E-05
8.45	1.140E-04	2.620E-03	2.511E-03	1.022E-02	3.086E-05
9.05	1.302E-04	2.666E-03	2.556E-03	1.004E-02	3.145E-05
10.05	7.246E-05	2.582E-03	2.465E-03	9.901E-03	2.878E-05
10.55	9.799E-05	2.633E-03	2.520E-03	9.967E-03	3.038E-05
11.55	1.427E-04	2.691E-03	2.579E-03	9.861E-03	3.162E-05
12.05	1.628E-04	2.696E-03	2.582E-03	9.711E-03	3.124E-05
13.05	1.472E-04	2.644E-03	2.527E-03	9.678E-03	2.982E-05
13.55	1.129E-04	2.560E-03	2.440E-03	9.662E-03	2.782E-05
14.55	9.184E-05	2.502E-03	2.383E-03	9.915E-03	2.722E-05
15.05	1.286E-04	2.581E-03	2.460E-03	9.597E-03	2.815E-05
15.48	2.601E-05	2.464E-03	2.346E-03	1.007E-02	2.685E-05

Table 10. Results of the calculated in situ pore water chemical concentration at Site U1368 for the **conventionally handled samples**. The amount of precipitation of calcium carbonate (X<sub>CaCO<sub>3</sub></sub>) we had to correct for to reconstruct in-situ abundances is also reported.

<b>Depth</b> (mbsf)	<b>HCO<sub>3</sub><sup>-</sup></b> (mol/kg)	<b>CO<sub>3</sub><sup>2-</sup></b> (mol/kg)	<b>OH<sup>-</sup></b> (mol/kg)	<b>H<sup>+</sup></b> (mol/kg)	<b>pH</b>
0.55	2.535E-03	8.648E-05	5.312E-07	1.650E-08	7.782
1.05	2.524E-03	8.776E-05	5.456E-07	1.627E-08	7.788
2.05	2.458E-03	8.855E-05	5.694E-07	1.579E-08	7.802
2.55	2.516E-03	8.681E-05	5.477E-07	1.650E-08	7.783
3.55	2.415E-03	8.819E-05	5.833E-07	1.570E-08	7.804
4.05	2.485E-03	8.856E-05	5.720E-07	1.609E-08	7.794
5.05	2.507E-03	8.670E-05	5.588E-07	1.668E-08	7.778
5.55	2.548E-03	8.416E-05	5.359E-07	1.750E-08	7.757
6.55	2.498E-03	8.658E-05	5.665E-07	1.674E-08	7.776
7.05	2.500E-03	8.523E-05	5.591E-07	1.707E-08	7.768
7.76	2.450E-03	8.582E-05	5.777E-07	1.666E-08	7.778
8.45	2.393E-03	8.762E-05	6.071E-07	1.598E-08	7.796
9.05	2.435E-03	8.915E-05	6.096E-07	1.603E-08	7.795
10.05	2.345E-03	9.063E-05	6.476E-07	1.529E-08	7.815
10.55	2.400E-03	9.001E-05	6.308E-07	1.580E-08	7.801
11.55	2.457E-03	9.060E-05	6.255E-07	1.610E-08	7.793
12.05	2.459E-03	9.194E-05	6.365E-07	1.592E-08	7.798
13.05	2.405E-03	9.235E-05	6.582E-07	1.559E-08	7.807
13.55	2.320E-03	9.203E-05	6.832E-07	1.508E-08	7.822
14.55	2.266E-03	9.001E-05	6.885E-07	1.517E-08	7.819
15.05	2.339E-03	9.278E-05	6.902E-07	1.521E-08	7.818
15.48	2.230E-03	8.855E-05	6.928E-07	1.524E-08	7.817

Table 10. (continued).

Depth (mbsf)	H <sub>3</sub> PO <sub>4</sub> (mol/kg)	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (mol/kg)	HPO <sub>4</sub> <sup>2-</sup> (mol/kg)	PO <sub>4</sub> <sup>3-</sup> (mol/kg)	B(OH) <sub>4</sub> <sup>-</sup> (mol/kg)	SiO(OH) <sub>3</sub> <sup>-</sup> (mol/kg)
0.55	1.525E-14	2.871E-08	1.644E-06	6.804E-08	4.597E-05	2.220E-06
1.05	1.467E-14	2.801E-08	1.631E-06	6.887E-08	4.668E-05	2.425E-06
2.05	1.104E-14	2.173E-08	1.308E-06	5.727E-08	4.811E-05	2.617E-06
2.55	1.118E-14	2.105E-08	1.214E-06	5.110E-08	4.630E-05	2.440E-06
3.55	8.958E-15	1.774E-08	1.079E-06	4.790E-08	4.857E-05	2.294E-06
4.05	8.393E-15	1.621E-08	9.628E-07	4.195E-08	4.755E-05	2.383E-06
5.05	1.491E-14	2.778E-08	1.596E-06	6.737E-08	4.621E-05	2.907E-06
5.55	8.756E-15	1.555E-08	8.531E-07	3.447E-08	4.435E-05	2.469E-06
6.55	8.472E-15	1.573E-08	9.037E-07	3.843E-08	4.624E-05	2.536E-06
7.05	8.798E-15	1.602E-08	9.041E-07	3.780E-08	4.552E-05	2.521E-06
7.76	8.249E-15	1.539E-08	8.915E-07	3.836E-08	4.661E-05	2.628E-06
8.45	6.152E-15	1.196E-08	7.239E-07	3.264E-08	4.844E-05	2.486E-06
9.05	6.573E-15	1.274E-08	7.698E-07	3.473E-08	4.839E-05	2.369E-06
10.05	8.759E-15	1.781E-08	1.132E-06	5.374E-08	5.063E-05	2.792E-06
10.55	6.323E-15	1.244E-08	7.669E-07	3.536E-08	4.929E-05	2.626E-06
11.55	7.995E-15	1.543E-08	9.345E-07	4.262E-08	4.855E-05	2.884E-06
12.05	6.024E-15	1.176E-08	7.215E-07	3.340E-08	4.911E-05	2.499E-06
13.05	7.607E-15	1.517E-08	9.534E-07	4.530E-08	5.019E-05	2.543E-06
13.55	6.149E-15	1.267E-08	8.231E-07	4.066E-08	5.168E-05	2.795E-06
14.55	7.248E-15	1.485E-08	9.629E-07	4.747E-08	5.161E-05	2.586E-06
15.05	8.599E-15	1.756E-08	1.137E-06	5.612E-08	5.153E-05	2.818E-06
15.48	1.117E-14	2.277E-08	1.473E-06	7.273E-08	5.153E-05	2.344E-06

Table 10. (continued).

<b>Depth</b> (mbsf)	<b>X<sub>CaCO3</sub></b> (mol/kg)	<b>TA</b> (mol/kg)	<b>DIC</b> (mol/kg)	<b>Ca<sup>2+</sup></b> (mol/kg)
0.55	2.298E-05	6.466E-05	1.882E-05	6.751E-05
1.05	2.281E-05	6.427E-05	1.869E-05	6.659E-05
2.05	2.265E-05	6.345E-05	1.841E-05	6.603E-05
2.55	2.273E-05	6.405E-05	1.864E-05	6.700E-05
3.55	2.207E-05	6.202E-05	1.800E-05	6.606E-05
4.05	2.255E-05	6.348E-05	1.844E-05	6.575E-05
5.05	2.292E-05	6.431E-05	1.870E-05	6.722E-05
5.55	2.294E-05	6.464E-05	1.884E-05	6.890E-05
6.55	2.253E-05	6.354E-05	1.849E-05	6.696E-05
7.05	2.320E-05	6.475E-05	1.883E-05	6.814E-05
7.76	2.338E-05	6.466E-05	1.879E-05	6.776E-05
8.45	2.177E-05	6.128E-05	1.778E-05	6.591E-05
9.05	2.198E-05	6.204E-05	1.801E-05	6.499E-05
10.05	2.186E-05	6.110E-05	1.768E-05	6.419E-05
10.55	2.205E-05	6.189E-05	1.794E-05	6.462E-05
11.55	2.203E-05	6.234E-05	1.810E-05	6.402E-05
12.05	2.183E-05	6.200E-05	1.800E-05	6.311E-05
13.05	2.152E-05	6.099E-05	1.768E-05	6.281E-05
13.55	2.114E-05	5.960E-05	1.724E-05	6.260E-05
14.55	2.088E-05	5.864E-05	1.695E-05	6.393E-05
15.05	2.114E-05	5.976E-05	1.729E-05	6.223E-05
15.48	2.135E-05	5.918E-05	1.711E-05	6.494E-05

Table 11. Analytical uncertainty estimates ( $1\sigma$ ) associated with the calculated in situ pore water chemical concentration at Site U1368 for the **conventionally handled samples**.



Depth (mbsf)	$X_{CaCO_3}$ (mol/kg)	TA (mol/kg)	DIC (mol/kg)	$Ca^{2+}$ (mol/kg)	$H_2CO_3$ (mol/kg)
0.05	-9.629E-06	2.663E-03	2.544E-03	9.784E-03	2.967E-05
1.45	-2.640E-05	2.649E-03	2.536E-03	1.008E-02	3.054E-05
2.95	3.551E-05	2.727E-03	2.623E-03	1.037E-02	3.383E-05
4.45	5.762E-05	2.811E-03	2.710E-03	1.035E-02	3.618E-05
5.95	1.281E-04	2.861E-03	2.762E-03	1.022E-02	3.724E-05
7.45	9.670E-05	2.845E-03	2.749E-03	1.045E-02	3.789E-05
9.45	8.132E-05	2.808E-03	2.706E-03	1.015E-02	3.580E-05
10.95	6.369E-05	2.765E-03	2.660E-03	1.005E-02	3.440E-05
12.45	8.038E-05	2.686E-03	2.575E-03	9.898E-03	3.172E-05
13.95	9.114E-05	2.717E-03	2.609E-03	9.921E-03	3.280E-05
15.45	6.216E-05	2.552E-03	2.436E-03	9.945E-03	2.863E-05

Table 12. Results of the calculated in situ pore water chemical concentration at Site U1368 for the **rapidly handled samples**. The amount of precipitation of calcium carbonate ( $X_{CaCO_3}$ ) we had to correct for to reconstruct in-situ abundances is also reported.

Depth (mbsf)	$HCO_3^-$ (mol/kg)	$CO_3^{2-}$ (mol/kg)	$OH^-$ (mol/kg)	$H^+$ (mol/kg)	pH
0.05	2.422E-03	9.227E-05	5.930E-07	1.479E-08	7.830
1.45	2.416E-03	8.930E-05	5.819E-07	1.533E-08	7.814
2.95	2.503E-03	8.672E-05	5.515E-07	1.647E-08	7.783
4.45	2.587E-03	8.689E-05	5.404E-07	1.712E-08	7.766
5.95	2.637E-03	8.794E-05	5.425E-07	1.737E-08	7.760
7.45	2.625E-03	8.579E-05	5.378E-07	1.783E-08	7.749
9.45	2.582E-03	8.810E-05	5.699E-07	1.723E-08	7.764
10.95	2.537E-03	8.868E-05	5.905E-07	1.692E-08	7.772
12.45	2.453E-03	9.014E-05	6.275E-07	1.622E-08	7.790
13.95	2.486E-03	8.972E-05	6.232E-07	1.662E-08	7.779
15.45	2.318E-03	8.965E-05	6.749E-07	1.564E-08	7.806

Table 12. (continued).

Depth (mbsf)	H <sub>3</sub> PO <sub>4</sub> (mol/kg)	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup> (mol/kg)	HPO <sub>4</sub> <sup>2-</sup> (mol/kg)	PO <sub>4</sub> <sup>3-</sup> (mol/kg)	B(OH) <sub>4</sub> <sup>-</sup> (mol/kg)	SiO(OH) <sub>3</sub> <sup>-</sup> (mol/kg)
0.05	1.568E-14	3.296E-08	2.106E-06	9.716E-08	5.065E-05	2.609E-06
1.45	1.321E-14	2.679E-08	1.658E-06	7.452E-08	4.927E-05	2.530E-06
2.95	1.233E-14	2.326E-08	1.345E-06	5.682E-08	4.644E-05	2.492E-06
4.45	1.513E-14	2.746E-08	1.534E-06	6.290E-08	4.507E-05	2.823E-06
5.95	8.321E-15	1.489E-08	8.237E-07	3.359E-08	4.469E-05	2.485E-06
7.45	1.316E-14	2.293E-08	1.241E-06	4.981E-08	4.383E-05	3.047E-06
9.45	8.304E-15	1.498E-08	8.429E-07	3.548E-08	4.544E-05	2.590E-06
10.95	8.538E-15	1.568E-08	9.019E-07	3.906E-08	4.636E-05	2.601E-06
12.45	7.732E-15	1.481E-08	8.927E-07	4.066E-08	4.835E-05	2.794E-06
13.95	8.497E-15	1.588E-08	9.378E-07	4.211E-08	4.751E-05	2.711E-06
15.45	9.273E-15	1.842E-08	1.161E-06	5.585E-08	5.037E-05	2.640E-06

Table 12. (continued).

Depth (mbsf)	X <sub>CaCO3</sub> (mol/kg)	TA (mol/kg)	DIC (mol/kg)	Ca <sup>2+</sup> (mol/kg)
0.05	2.361E-05	6.497E-05	1.882E-05	6.417E-05
1.45	2.373E-05	6.509E-05	1.888E-05	6.587E-05
2.95	2.374E-05	6.579E-05	1.912E-05	6.748E-05
4.45	2.425E-05	6.741E-05	1.961E-05	6.754E-05
5.95	2.385E-05	6.712E-05	1.956E-05	6.668E-05
7.45	2.410E-05	6.744E-05	1.965E-05	6.802E-05
9.45	2.392E-05	6.679E-05	1.943E-05	6.630E-05
10.95	2.373E-05	6.607E-05	1.920E-05	6.570E-05
12.45	2.275E-05	6.361E-05	1.845E-05	6.448E-05
13.95	2.292E-05	6.419E-05	1.863E-05	6.467E-05
15.45	2.172E-05	6.060E-05	1.753E-05	6.438E-05

Table 13. Analytical uncertainty estimates (1σ) associated with the calculated in situ pore water chemical concentration at Site U1368 for the **rapidly handled samples**.

Depth	DIC	TA	Ca <sup>2+</sup>	Brackets for pooled standard deviation	
(mbsf)	(mol/kg)	(mol/kg)	(mol/kg)		
0.05	2.544E-03	2.663E-03	9.784E-03		
0.55	2.656E-03	2.759E-03	1.043E-02		
1.05	2.645E-03	2.751E-03	1.027E-02		
1.45	2.536E-03	2.649E-03	1.008E-02		
2.05	2.578E-03	2.687E-03	1.018E-02		
2.55	2.637E-03	2.741E-03	1.035E-02		
2.95	2.623E-03	2.727E-03	1.037E-02		
3.55	2.535E-03	2.644E-03	1.022E-02		
4.05	2.606E-03	2.714E-03	1.014E-02		
4.45	2.710E-03	2.811E-03	1.035E-02		
5.05	2.628E-03	2.732E-03	1.038E-02		
5.55	2.668E-03	2.764E-03	1.068E-02		
5.95	2.762E-03	2.861E-03	1.022E-02		
6.55	2.619E-03	2.722E-03	1.035E-02		
7.05	2.620E-03	2.720E-03	1.053E-02		
7.45	2.749E-03	2.845E-03	1.045E-02		
7.76	2.569E-03	2.672E-03	1.045E-02		
8.45	2.511E-03	2.620E-03	1.022E-02		
9.05	2.556E-03	2.666E-03	1.004E-02		
9.45	2.706E-03	2.808E-03	1.015E-02		
10.05	2.465E-03	2.582E-03	9.901E-03		
10.55	2.520E-03	2.633E-03	9.967E-03		
10.95	2.660E-03	2.765E-03	1.005E-02		
11.55	2.579E-03	2.691E-03	9.861E-03		
12.05	2.582E-03	2.696E-03	9.711E-03		
12.45	2.575E-03	2.686E-03	9.898E-03		
13.05	2.527E-03	2.644E-03	9.678E-03		
13.55	2.440E-03	2.560E-03	9.662E-03		
13.95	2.609E-03	2.717E-03	9.921E-03		
14.55	2.383E-03	2.502E-03	9.915E-03		
15.05	2.460E-03	2.581E-03	9.597E-03		
15.45	2.436E-03	2.552E-03	9.945E-03		
15.48	2.346E-03	2.464E-03	1.007E-02		
<b>POOLED ST. DEV.</b>	<b>8.428E-05</b>	<b>7.953E-05</b>	<b>1.606E-04</b>		

Table 14. Results of the pooled standard deviation calculation of the in-situ calculated abundances of DIC, TA and Ca between conventionally and rapidly processed samples at Site U1368.

## APPENDIX

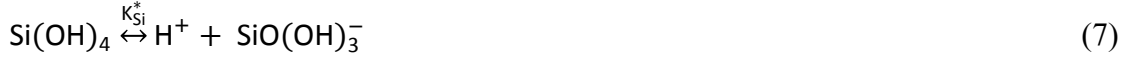
### Iteration method for the calculation of the in-situ concentration of carbonate system components

#### A.1. Conceptual Framework

An iteration method was developed to characterize the in-situ pore water carbonate system based on shipboard measured concentrations of [DIC], [TA], and  $[\text{Ca}^{2+}]$ . This iteration method is based on two assumptions: the dissolved carbonate system is at equilibrium in-situ and  $\text{CaCO}_3$  (calcite) is saturated in the sediment. The central concept upon which the method is built, is that at equilibrium, if [DIC], [TA], and  $[\text{Ca}^{2+}]$  are measured, in-situ pH,  $[\text{CO}_2(aq)]$ ,  $[\text{HCO}_3^-]$ , and  $[\text{CO}_3^{2-}]$  are mathematically over-determined if carbonate is saturated in-situ. This over-determined state of the carbonate system allows an additional variable, in this case the amount of  $\text{CaCO}_3$  precipitated during core recovery, sampling, and storage, to be uniquely determined. By calculating the amount  $\text{CaCO}_3$  lost during sample recovery from the seafloor, we can correct the measured [DIC] and [TA] to actual in-situ values. Once in-situ [DIC] and [TA] are known, in-situ pH, the remaining carbonate-system components (i.e.  $[\text{CO}_2(aq)]$ ,  $[\text{HCO}_3^-]$ ,  $[\text{CO}_3^{2-}]$ , etc.) and the pH-dependent concentrations of minor species included in the alkalinity term (i.e.  $[\text{B}(\text{OH})_4^-]$ ,  $[\text{Si}(\text{OH})_3^-]$ ,  $[\text{HSO}_4^-]$ , etc.) can be solved for.

## A.2 Method

We consider following set of chemical reactions to predominate in the porewater:



With  $\text{CO}_2^*$ , a hypothetical chemical species grouping the unionized dissolved carbon species.  $K_1^*$ ,  $K_2^*$ ,  $K_W$ ,  $K_B^*$ ,  $K_S^*$ ,  $K_{\text{Si}}^*$ ,  $K_{1\text{P}}^*$ ,  $K_{2\text{P}}^*$  and  $K_{3\text{P}}^*$  represent the apparent dissociation constants of the considered species at in-situ temperature, salinity and pressure. And  $K_{\text{sp}(\text{calcite})}^*$  is the apparent solubility constant of calcite at in-situ temperature, salinity and pressure.

By measuring three parameters of the carbonate system (i.e. [DIC], [TA], and  $[\text{Ca}^{2+}]$ ) the system is over-determined in the field, allowing a third variable ‘x’ to be uniquely determined. We define x (in moles/mass of pore fluid) as the amount of

CaCO<sub>3</sub> that precipitated during sediment recovery from the seafloor and sample handling. In that case in-situ [DIC], [TA] and [Ca<sup>2+</sup>] can be expressed as:

$$[\text{DIC}] = [\text{DIC}]_{\text{measured}} + \mathbf{x} \quad (11)$$

$$[\text{TA}] = [\text{TA}]_{\text{measured}} + 2\mathbf{x} \quad (12)$$

$$[\text{Ca}^{2+}] = [\text{Ca}^{2+}]_{\text{measured}} + \mathbf{x} \quad (13)$$

Where  $[\text{DIC}]_{\text{measured}}$ ,  $[\text{TA}]_{\text{measured}}$  and  $[\text{Ca}^{2+}]_{\text{measured}}$  represent asured values in the sample pore fluid. Additional constraints to above set of equations are provided by assuming CaCO<sub>3</sub> saturation in the sediment and equilibrium conditions in-situ:

$$[\text{CO}_3^{2-}] * ([\text{Ca}^{2+}]_{\text{measured}} + \mathbf{x}) = K_{\text{sp}}^*(\text{calcite}) \quad (14)$$

$$[\text{CO}_3^{2-}] = \frac{K_2^*[\text{HCO}_3^-]}{[\text{H}^+]} \quad (15)$$

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}^+][\text{HCO}_3^-]}{K_1^*} \quad (16)$$

$$[\text{OH}^-] = \frac{K_w^*}{[\text{H}^+]} \quad (17)$$

$$[\text{B}(\text{OH})_3] = \frac{[\text{B}]_T}{\frac{K_B^*}{[\text{H}^+]} + 1} \quad (18)$$

$$[\text{B}(\text{OH})_4^-] = [\text{B}]_T - [\text{B}(\text{OH})_3] \quad (19)$$

$$[\text{HPO}_4^{2-}] = \frac{[\text{P}]_T K_{1P}^* K_{2P}^* [\text{H}^+]}{[\text{H}^+]^3 + K_{1P}^* [\text{H}^+]^2 + K_{1P}^* K_{2P}^* [\text{H}^+] + K_{1P}^* K_{2P}^* K_{3P}^*} \quad (20)$$

$$[\text{H}_2\text{PO}_4^-] = \frac{[\text{P}]_T K_{1P}^* [\text{H}^+]^2}{[\text{H}^+]^3 + K_{1P}^* [\text{H}^+]^2 + K_{1P}^* K_{2P}^* [\text{H}^+] + K_{1P}^* K_{2P}^* K_{3P}^*} \quad (21)$$

$$[\text{H}_3\text{PO}_4] = \frac{[\text{P}]_T [\text{H}^+]^3}{[\text{H}^+]^3 + K_{1P}^* [\text{H}^+]^2 + K_{1P}^* K_{2P}^* [\text{H}^+] + K_{1P}^* K_{2P}^* K_{3P}^*} \quad (22)$$

$$[\text{PO}_4^{3-}] = \frac{[\text{P}]_T K_{1P}^* K_{2P}^* K_{3P}^*}{[\text{H}^+]^3 + K_{1P}^* [\text{H}^+]^2 + K_{1P}^* K_{2P}^* [\text{H}^+] + K_{1P}^* K_{2P}^* K_{3P}^*} \quad (23)$$

$$[\text{Si}(\text{OH})_3^-] = \frac{[\text{Si}]_T}{\left(1 + \frac{[\text{H}^+]}{K_{\text{Si}}^*}\right)} \quad (24)$$

$$[\text{HSO}_4^-] = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{K_S^*} \quad (25)$$

$$[\text{H}^+]_{\text{free}} = [\text{H}^+] - [\text{HSO}_4^-] = \frac{[\text{H}^+]}{(1 + \frac{[\text{SO}_4^{2-}]}{K_S^*})} \quad (26)$$

Where  $[B]_T$ ,  $[P]_T$  and  $[Si]_T$  represent the total concentration of boric acid, phosphate and silicic acid, respectively.

We solve for  $\mathbf{x}$  and the remaining chemical species of interest using a combination of mass balance, equilibrium reactions between species in solution and thermodynamics relationships. Following equations describing these relationships form the core upon which the iteration method is based:

Mass balance of dissolved inorganic carbon species:

$$[\text{DIC}] \equiv [\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (27)$$

Expression of total alkalinity as defined by Dickson (2007):

$$[\text{TA}] \equiv [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_4^{3-}] + [\text{SiO}(\text{OH})_3^-] + [\text{NH}_3] + [\text{HS}^-] + \dots - [\text{H}^+]_f - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4] - \dots \quad (28)$$

For ease of representation we group some of constituents of  $[\text{TA}]$  in Eq. (28) that are assumed to be of minor contribution to the total alkalinity, relative to the contribution of  $[\text{HCO}_3^-]$  and  $[\text{CO}_3^{2-}]$ , into a so-called fictitious *minor species* term:

$$[\text{minor species}] = [\text{H}_2\text{CO}_3] - [\text{OH}^-] - [\text{HPO}_4^{2-}] - 2[\text{PO}_4^{3-}] - [\text{SiO}(\text{OH})_3^-] - [\text{NH}_3] - [\text{HS}^-] + [\text{H}^+]_f + [\text{HSO}_4^-] + [\text{HF}] + [\text{H}_3\text{PO}_4] \quad (29)$$

Reorganizing Eq. (11) through Eq. (13) and Eq. (27) through Eq. (29):

$$[\text{TA}]_{\text{measured}} - [\text{DIC}]_{\text{measured}} + \mathbf{x} = [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] - [\text{minor species}] \quad (30)$$

$$2[\text{DIC}]_{\text{measured}} - [\text{TA}]_{\text{measured}} = [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3] - [\text{B}(\text{OH})_4^-] + [\text{minor species}] \quad (31)$$

Reorganizing Eq. (30):

$$\gamma = [\text{TA}]_{\text{measured}} - [\text{DIC}]_{\text{measured}} \quad (32)$$

$$\alpha = \gamma + [\text{minor species}] \quad (33)$$

$$\alpha + x = [\text{CO}_3^{2-}] + [\text{B}(\text{OH})_4^-] \quad (34)$$

$$\beta = [\text{HCO}_3^-] \quad (35)$$

$$\alpha + x = \frac{\beta K_2^*}{[\text{H}^+]} + \frac{[\text{B}(\text{OH})_3] K_B^*}{[\text{H}^+]} \quad (36)$$

Reorganizing Eq. (31):

$$\beta = 2[\text{DIC}]_{\text{measured}} - [\text{TA}]_{\text{measured}} - [\text{H}_2\text{CO}_3] + [\text{B}(\text{OH})_4^-] - [\text{minor species}] \quad (37)$$

Eliminate  $[\text{H}^+]$  in Eq. (36) and Eq. (14) and set them equal to each other:

$$([\text{Ca}^{2+}]_{\text{measured}} + x) \beta \frac{K_2^*}{K_{\text{sp}}^*(\text{calcite})} = \frac{\beta K_2^* + [\text{B}(\text{OH})_3] K_B^*}{\alpha + x} \quad (38)$$

Eq. (11) through Eq. (38) form a determined system that can be solved for  $x$ .

Reorganizing Eq. (38) results in a 2<sup>nd</sup> order polynomial of the form

$Ax(x^2) + Bx(x) + Cx = 0$  with following coefficients:

$$Ax = 1 \quad (39)$$

$$Bx = \alpha + [\text{Ca}^{2+}]_{\text{measured}} \quad (40)$$

$$Cx = -1 \left( \frac{1 + [\text{B}(\text{OH})_3] K_B^*}{K_2^* \beta} \right) K_{\text{sp}}^*(\text{calcite}) + \alpha [\text{Ca}^{2+}]_{\text{measured}} \quad (41)$$

This polynomial can be solved for  $x$ :



$$\mathbf{x} = \frac{-Bx + (Bx^2 - 4AxCx)^{1/2}}{2Ax} \quad (42)$$

To avoid enormous polynomials we develop an iteration procedure that neglects the minor species in the first iteration round. In the second iteration step, minor species determined in this first iteration will be incorporated in the equation set. The following iterations will subsequently refine the calculated species concentrations until a stable solution is attained.

*First iteration:*

- (1) An initial estimate of the in-situ hydrogen concentration is obtained by inputting a ballpark estimate of the in-situ pH:  $[H^+]_1 = 10^{-pH}$ .
- (2) Ignoring the minor species term in Eq. (31) results in a first estimate of the in-situ bicarbonate concentration:  $[HCO_3^-]_1 = 2[DIC]_{measured} - [TA]_{measured}$ .
- (3) Based on the obtained  $[H^+]_1$  and  $[HCO_3^-]_1$  we solve for the remaining species (i.e.  $[H_2CO_3]$ ,  $[OH^-]$ ,  $[B(OH)_3^-]$  etc.) using expressions that assume equilibrium between species in solution (Eq. (15) through Eq. (26)).
- (4) Adding the minor species concentrations up results in a first estimate of the minor species term (i.e.  $[minor\ species]_1$ ). In the case of Site U1368 (see manuscript) we assume  $[NH_3]$ ,  $[HF^-]$  and  $[HS]$  to be negligible and therefore not solved for.
- (5) Solve for  $[\mathbf{x}]_1$  based on Eq. (30).

*Second and subsequent iterations:*

(6) From the left hand side of Eq. (38) and from  $[\mathbf{x}]_1$  we can refine our hydrogen concentration estimate:

$$[\text{H}^+]_2 = ([\text{Ca}^{2+}]_{\text{measured}} + [\mathbf{x}]_1) \beta \frac{K_2^*}{K_{\text{sp}}^*(\text{calcite})} \quad (43)$$

(7) Solve for bicarbonate including the minor species concentrations, Eq. (37), determined in the former iteration step:

$$[\text{HCO}_3^-]_2 = 2[\text{DIC}]_{\text{measured}} - [\text{TA}]_{\text{measured}} - [\text{H}_2\text{CO}_3]_1 - [\text{minor species}]_1 \quad (44)$$

(8) Solve for remaining species as in step (3).

(9) Solve for  $[\mathbf{x}]_2$  (Eq. (30)) including the refined estimates of the minor species.

(10) Repeat steps 6 to 9 until there is convergence. We regard the obtained solution as stable as the difference in  $[\mathbf{x}]$  between former and subsequent iterations is not greater than 0.000001. Such stable solution was obtained in less than 15 iterations in the example discussed in the paper.

We validate the result of the iteration algorithm by checking that mass balance relationships for [DIC] and [TA] are conserved:

$$[\text{DIC}] = [\text{DIC}]_{\text{measured}} + [\mathbf{x}]_{\text{stable}} = [\text{H}_2\text{CO}_3]_{\text{stable}} + [\text{HCO}_3^-]_{\text{stable}} + [\text{CO}_3^{2-}]_{\text{stable}} \quad (45)$$

$$\begin{aligned} [\text{TA}] = [\text{TA}]_{\text{measured}} + 2[\mathbf{x}]_{\text{stable}} = & [\text{HCO}_3^-]_{\text{stable}} + 2[\text{CO}_3^{2-}]_{\text{stable}} + [\text{B}(\text{OH})_4^-]_{\text{stable}} + [\text{OH}^-]_{\text{stable}} \\ & + [\text{HPO}_4^{2-}]_{\text{stable}} + 2[\text{PO}_4^{3-}]_{\text{stable}} + [\text{SiO}(\text{OH})_3^-]_{\text{stable}} - [\text{H}^+]_{\text{f,stable}} - [\text{HSO}_4^-]_{\text{stable}} - \\ & [\text{H}_3\text{PO}_4]_{\text{stable}} \end{aligned} \quad (46)$$

### A.3. Data and Parameters

**Shipboard data:** pH, [DIC] (mM), [TA] (mM), [Ca<sup>2+</sup>] (mM), [Cl<sup>-</sup>] (mM), [SO<sub>4</sub><sup>2-</sup>] (mM), [P]<sub>T</sub> (μM) and [Si]<sub>T</sub> (μM) measurements are provided by the Shipboard Scientific Party (2011) of IODP Leg 329. Physical property data include bottom water temperature (°C) and the sediment thermal gradient (°C/km).

**Laboratory conditions:** We assume room temperature (~20°C), standard atmospheric pressure (~ 1 Atm) and a salinity value of 34.7 psu as characteristic laboratory conditions.

#### **In-situ temperature, density, salinity, and pressure calculation of the pore water:**

The in-situ downhole temperature (t, °C) is given by:

$$t(^{\circ}\text{C}) = t_{\text{bottomwater}}(^{\circ}\text{C}) + t_{\text{thermal\_gradient}} \left( \frac{^{\circ}\text{C}}{\text{km}} \right) * z(\text{km}) \quad (47)$$

Where z is the sediment depth in meter below seafloor (mbsf).

In-situ pressure (P) is assumed to be hydrostatic and approximated by:

$$P \text{ (Pa)} = P_{\text{atm}} + P_{\text{hydrostatic}} + g \rho_{\text{pore water}} Z \quad (48)$$

In-situ pore water salinity is approximated based on shipboard measured chloride concentration (mM) and calculated in-situ density values. Therefore, an iteration procedure was developed to simultaneously calculate the in-situ density, followed by the in-situ salinity of the porewater:

(1) Based on expressions derived by Pilson (1998) we first determine the in-situ pore water density,  $\rho(S, t, P)$  in  $\text{kg/m}^3$ , from the in situ temperature ( $t$ , °C), pressure ( $P$ , bars), and a salinity ( $S$ ) of 34.7 psu:

$$\rho(S, t, P) = \frac{\rho(S, t, 0)}{1 - \frac{P}{K(S, t, P)}} \quad (49)$$

With :

$$\begin{aligned} \rho(S, t, 0) = & 999.842594 + 6.793952 t/102 - 9.095290 t^2/103 + 1.001685 t^3/104 - \\ & 1.120083 t^4/106 + 6.536332 t^5/109 + (8.24493/10 - 4.0899 t/103 + 7.6438 t^2/105 - \\ & 8.2467 t^3/107 + 5.3875 t^4/109) S + (-5.72466/103 + 1.0227 t/104 - 1.6546 \\ & t^2/106) S^{3/2} + 4.8314 S^2/104 \end{aligned} \quad (50)$$

$$K(S, t, P) = K(S, t, 0) + AP + BP^2 \quad (51)$$

Where:

$$\begin{aligned} K(S, t, 0) = & 19652.21 + 148.4206 t - 2.327105 t^2 + 1.360477 t^3/102 - 5.155288 t^4/105 \\ & + (54.6746 - 0.603459 t + 1.09987 t^2/102 - 6.1670 t^3/105) S + (7.944/102 + 1.6483 \\ & t/102 - 5.3009 t^2/104) S^{3/2} \end{aligned} \quad (52)$$

$$\begin{aligned} A = & 3.239908 + 1.43713 t/10^3 + 1.16092 t^2/10^4 - 5.77905 t^3/10^7 + (2.2838/10^3 - \\ & 1.0981 t/10^5 - 1.6078 t^2/10^6) S + 1.91075 \end{aligned} \quad (53)$$

$$\begin{aligned} B = & 8.50935/10^5 - 6.12293 t/10^6 + 5.2787 t^2/10^8 + (-9.9348/10^7 + 2.0816 t/10^8 + \\ & 9.1697 t^2/10^{10}) S; \end{aligned} \quad (54)$$

(2) Based on the obtained in-situ density, the in-situ salinity ( $S$ ) is calculated:

$$S = 35.453[\text{Cl}^-] \frac{1000}{\rho(S, t, P)} \frac{1000}{552.94} \quad (55)$$

(3) Based on the new in-situ salinity estimate we refine the in-situ pore water density  $\rho(S, t, P)$  by substituting  $S$  into Eq. (49).

- (4) Substitute the new  $\rho(S, t, P)$  into Eq. (55) to recalculate S;
- (5) Repeat Steps (3 and 4) until  $\rho(S, t, P)$  converges, in which case the difference between  $\rho(S, t, P)$  calculated in the former and subsequent iteration is negligible ( $\sim < 1 \text{ kg m}^{-3}$ ).

### Calculation of the apparent equilibrium constants at in-situ conditions

Equilibrium constants (i.e.  $K_1$ ,  $K_2$ ,  $K_W$ ,  $K_{Sp}$ ,  $K_B$ ,  $K_S$ ,  $K_{Si}$ ,  $K_{1P}$ ,  $K_{2P}$ , and  $K_{3P}$ ) were first determined at in-situ temperature and salinity based on expressions formulated on the total hydrogen scale by Dickson (2007):

$$\ln\left(\frac{K_1}{k^0}\right) = -\frac{3633.86}{T} + 61.2172 - 9.67770 \ln(T) + 0.011555S - 0.0001152S^2 \quad (56)$$

$$\ln\left(\frac{K_2}{k^0}\right) = -\frac{471.78}{T} - 25.9290 + 3.16967 \ln(T) + 0.01781S - 0.0001122S^2 \quad (57)$$

$$\begin{aligned} \ln\left(\frac{K_W}{k^0}\right) = & \\ & -\frac{13847.26}{T} + 148.952 - 23.652 \ln(T) + \left(\frac{118.67}{T} - 5.977 + 1.0495 \ln(T)\right) S^{1/2} - \\ & 0.01615S \end{aligned} \quad (58)$$

$$\begin{aligned} \ln\left(\frac{K_B}{k^0}\right) = & \\ & \frac{-89666.90 - 2890.53S^{1/2} - 77.942S + 1.728S^{3/2} - 0.0996S^2}{T} + \left(148.0248 + 137.1942S^{\frac{1}{2}} + \right. \\ & \left. 1.62142S\right) + \left(-14.4344 - 25.08S^{\frac{1}{2}} - 0.2474S\right) \ln(T) + 0.053105S^{\frac{1}{2}} - 0.01615S \end{aligned} \quad (59)$$

$$\lg K_{\text{sp}(\text{calcite})} =$$

$$-171.9065 - 0.077993T + \frac{2839.319}{T} + 71.595 \lg(T) +$$

$$\left(-0.77712 + 0.0028426T + \frac{178.34}{T}\right) S^{0.5} - 0.07711S + 0.0041249S^{1.5} \quad (60)$$

$$\ln\left(\frac{K_{1P}}{k^0}\right) = -\frac{4576.752}{T} + 115.525 - 18.453 \ln(T) + \left(-\frac{106.736}{T} + 0.69181\right) S^{\frac{1}{2}} +$$

$$\left(-\frac{0.65643}{T} - 0.01844\right) S \quad (61)$$

$$\ln\left(\frac{K_{2P}}{k^0}\right) = -\frac{8814.715}{T} + 172.0883 - 27.927 \ln(T) + \left(-\frac{160.340}{T} + 1.3566\right) S^{\frac{1}{2}} +$$

$$\left(\frac{0.37335}{T} - 0.05778\right) S \quad (62)$$

$$\ln\left(\frac{K_{3P}}{k^0}\right) = -\frac{3070.75}{T} - 18.141 + \left(\frac{17.27039}{T} + 2.81197\right) S^{\frac{1}{2}} + \left(-\frac{44.99486}{T} + 0.09984\right) S$$

$$(63)$$

$$\ln\left(\frac{K_{Si}}{k^0}\right) = -\frac{8904.2}{T} + 117.385 - 19.334 \ln(T) + \left(-\frac{458.79}{T} + 3.5913\right) \left(\frac{I}{m^0}\right)^2 +$$

$$\ln(1 - 0.001005S) \quad (64)$$

$$\ln\left(\frac{K_{S'}}{k^0}\right) =$$

$$-\frac{4276.1}{T} + 141.328 - 23.093 \ln(T) +$$

$$\left(-\frac{13856}{T} + 324.57 - 47.986 \ln(T)\right) \left(\frac{I}{m^0}\right)^{1/2} +$$

$$\left(\frac{35474}{T} - 771.54 + 114.723 \ln(T)\right) \left(\frac{I}{m^0}\right) - \frac{2698}{T\left(\frac{I}{m^0}\right)^{\frac{3}{2}}} + \frac{1776}{T\left(\frac{I}{m^0}\right)^2} + \ln(1 - 0.001005S)$$

$$(65)$$

Secondly, apparent equilibrium constants were adapted to account for in-situ pressures using the general formulation derived by Millero (1983):

$$\ln\left(\frac{K_x^*}{K_{x,\text{ref}}}\right) = -\frac{\Delta V(T, P_{\text{ref}})}{RT} (P - P_{\text{ref}}) + \frac{0.5\Delta\kappa(T, P_{\text{ref}})}{RT} (P - P_{\text{ref}})^2 \quad (66)$$

With:

$K_x^*$ : The dissociation constant of species x at the reference pressure  $P_{ref}$  (1bar).

$K_{x,ref}$ : The dissociation constant of species x at in situ pressure P.

$\Delta V(T, P_{ref})$ : The change in partial molar volume for the reaction in seawater under the condition(T,  $P_{ref}$ ).

$\Delta \kappa(T, P_{ref})$ : The change of partial molar compressibility of the reaction in seawater under the condition(T,  $P_{ref}$ ).

R: the gas constant ( $83.144 \text{ cm}^3 \text{ bar mol}^{-1} \text{ K}^{-1}$ ).

Expressions for  $\Delta V(T, P_{ref})$  and  $\Delta \kappa(T, P_{ref})$  can be found in Millero (1983) and Zeebe and Wolf-Gladrow (2001).

#### A.4. References

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