2014

Determination of in situ dissolved inorganic carbon concentration and alkalinity for marine sedimentary porewater

Justine Sauvage

Arthur J. Spivack
University of Rhode Island, spivack@uri.edu

See next page for additional authors

Citation/Publisher Attribution

Sauvage, J., Spivack, A. J., Murray, R. W., & D'Hondt, S. (2014). Determination of in situ dissolved inorganic carbon concentration and alkalinity for marine sedimentary porewater. *Chemical Geology*, 387, 66-73. doi: 10.1016/j.chemgeo.2014.06.010
Available at: https://doi.org/10.1016/j.chemgeo.2014.06.010

Authors
Justine Sauvage, Arthur J. Spivack, Richard W. Murray, and Steven D'Hondt

Chemical Geology 387 (2014) 66–73

Contents lists available at ScienceDirect

Chemical Geology

journal homepage: www.elsevier.com/locate/chemgeo

Determination of in situ dissolved inorganic carbon concentration and alkalinity for marine sedimentary porewater

Justine Sauvage [a],*, Arthur J. Spivack [a], Richard W. Murray [b], Steven D'Hondt [a]

[a] Graduate School of Oceanography, University of Rhode Island, Narragansett, RI 02882, USA
[b] Department of Earth and Environment, Boston University, Boston, MA 02215, USA

ARTICLE INFO

Article history:
Received 5 February 2014
Received in revised form 9 June 2014
Accepted 17 June 2014
Available online 18 July 2014

Editor: David R. Hilton

Keywords:
Carbonate system chemistry
Subseafloor sediment sampling artifact
Dissolved inorganic carbon
Total alkalinity

ABSTRACT

Dissolved inorganic carbon (DIC) concentration and total alkalinity in marine sediment vary with biological activity, mineral diagenesis and past bottom ocean water composition. Reliable interpretation of this data is often compromised due to precipitation of calcium carbonate ($CaCO_3$) during sediment recovery, processing and sample storage.

Here we present and test a method that corrects for this precipitation and consequently allows quantification of in situ carbonate system chemistry. Our method relies on the over-determination of the dissolved carbonate system by (i) measuring DIC, alkalinity and calcium, and (ii) explicitly assuming $CaCO_3$ saturation in the sediment. We experimentally tested this method using data from Integrated Ocean Drilling Program (IODP) Site U1368 in the South Pacific Gyre. Our results show that we can accurately reproduce in situ aqueous carbonate system chemistry if DIC, alkalinity and calcium concentration are measured simultaneously. At Site U1368, the correction for sampling associated precipitation is equivalent to 4.5 and 8.9% of the measured DIC and alkalinity, respectively. The method is well suited for any sediment porewater that is saturated with respect to calcium carbonate; consequently, it is applicable for approximately 50% of the global oceanic seafloor.

1. Introduction

The present-day composition of sedimentary porewater results from both ongoing sedimentary processes and past bottom water composition (Gieskes, 1975; Berner, 1980; McDuff, 1985; Adkins and Schrag, 2003). Dissolved inorganic carbon (DIC) and alkalinity measurements of pore fluid are used to understand current subseafloor microbial activity (D'Hondt et al., 2004), and could also be used to understand past changes in ocean chemistry if in situ concentrations were quantified precisely and accurately. However, measured DIC and alkalinity are often subject to post recovery artifacts due to calcium carbonate precipitation. In this paper, we present and test a method for correcting measured pore fluid DIC and alkalinity for these artifacts.

DIC ($H_2CO_3 + HCO_3^- + CO_3^{2-}$) is a major product of microbial respiration in the subseafloor biosphere (D'Hondt et al., 2002). Microbial activities in deeply buried sediment are highly diverse, occur at low rates, and are difficult to constrain with conventional radiotracer experiments (D'Hondt et al., 2004). One way to study net rates of biogeochemical reactions in subseafloor sediment is by transport-reaction modeling (e.g. Berner, 1964; Froelich et al., 1979; Schulz, 2000). A fundamental requirement of this approach is accurate knowledge of in situ dissolved concentration of metabolites.

In addition to constraining metabolic pathways and rates, pore fluid DIC and alkalinity should also reflect the CO_2 partial pressure (P_{CO2}) and carbonate (CO_3^{2-}) concentration of bottom waters. Pore fluids contain a record of past ocean salinity and have been used to reconstruct salinity distribution during the last glacial maximum (Adkins and Schrag, 2003). In principle, once effects of subseafloor respiration and carbonate dissolution have been accounted for, a similar approach can be applied to DIC and alkalinity from which P_{CO2} and CO_3^{2-} are calculated. Reconstructions of P_{CO2} and CO_3^{2-} are valuable because they would place important constraints on glacial/interglacial P_{CO2} variations in the distribution of carbon between the ocean, atmosphere and land (e.g. Yu et al., 2010). Therefore, reliable determination of past P_{CO2} in pore fluid ultimately also depends on the precise and accurate measurement of DIC and alkalinity in situ.

Measured values of alkalinity, DIC and related constituents in porewater [e.g. calcium (Ca^{2+}), phosphate (PO_4^{3-}), magnesium (Mg^{2+}) and sulfate (SO_4^{2-})] deviate from in situ abundances (Sayles and Manheim, 1975; Paull et al., 1996). Decompression and warming of the sediment during core recovery, followed by core handling and

---

* Corresponding author at: 215 S Ferry Rd, Narragansett, RI 02882, United States.
E-mail address: justine_sauvage@my.uri.edu (J. Sauvage).

http://dx.doi.org/10.1016/j.chemgeo.2014.06.010

storage, induces precipitation of calcium carbonate due to the pressure and temperature dependence of its solubility. As a result, measured DIC and alkalinity are commonly lower than in situ values. Sample handling and processing frequently results in samples being stored for hours (or even days) prior to analysis, leaving ample time for carbonate precipitation. In general, larger time intervals between fluid extraction and core recovery lead to larger deviations from in situ values. Consequently, for accurate use of carbonate-related porewater chemistry data, it is critical to have a method for correcting measured abundances to in situ values.

Here, we present a rigorous technique for quantifying in situ dissolved inorganic carbon system chemistry in subseafloor sediment. One major assumption of our method is in situ sediment porewater saturation with respect to calcium carbonate. This assumption is critical for correct application of the method and should thus be carefully evaluated before its utilization. This technique does not require additional coring and processing time. We provide experimental validation of our approach using sedimentary pore fluid concentration profiles of DIC, alkalinity, Ca^{2+}, and other dissolved species collected from Site U1368 during Integrated Ocean Drilling Program (IODP) Expedition 329.

2. Theory of the method

2.1. Conceptual framework

The central concept of our method is that measurement of three carbonate-system parameters (i.e. DIC, alkalinity and Ca^{2+}) in the porewater allows us to mathematically over-determine the carbonate system (e.g., CO_3^{2-}, bicarbonate (HCO_3^-), carbonic acid (H_2CO_3) and pH) if calcium carbonate saturation is assumed. That is, if no calcium carbonate precipitated during sample recovery or storage, there is a unique mathematical solution for the various over-determined equilibria of the in-situ carbonate system chemistry. In contrast, if the porewater re-equilibrated during core recovery (due to pressure and temperature changes), there will be no consistent mathematical solution for the in situ carbonate chemistry unless the amount of calcium carbonate precipitated is quantified. We therefore take advantage of the over-determined character of the system to calculate the amount calcium carbonate that precipitated during core recovery and sample handling.

By calculating the amount of carbonate lost during sample recovery and storage, we can correct the measured dissolved DIC concentration and alkalinity to actual in situ values. Once in situ DIC and alkalinity are known, we can quantify in situ pH, the in situ concentrations of the remaining carbon system components (i.e. H_2CO_3, HCO_3^-, CO_3^{2-}, etc.), and the in situ concentrations of the pH-dependent minor species included in total alkalinity (i.e. $B(OH)_4^-$, $SiO(OH)_3^-$, PO_4^{3-}, HSO_4^- etc.). The fundamentals of this approach were first put forward by Wang et al. (2010); we revise and test them in this study. This method is only applicable if sediment porewater is saturated with respect to calcium carbonate. In the case of saturation with respect to other carbonate phases or minerals (e.g. $FeCO_3$, $MnCO_3$, aragonite, dolomite), the method won't be as accurate because more equivalents of alkalinity will be removed through precipitation of non-calcitic phases. We therefore emphasize close scrutiny of the in situ state of the porewater chemistry before application of the method.

2.2. Iteration process

Based on measured [alkalinity], [DIC] and $[Ca^{2+}]$ (i.e., $[\text{alkalinity}]_{\text{measured}}$, $[\text{DIC}]_{\text{measured}}$ and $[Ca^{2+}]_{\text{measured}}$, respectively), we solve for the amount of carbonate precipitated (in units of moles per mass of pore fluid) during recovery and sampling, referred to as "*excess carbonate*", or X_{CaCO_3}, 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 relatively simple iterative method that avoids cubic equations. A combination of mass-balance relationships, equilibrium reactions between species in solution, and thermodynamics relationships forms the core of the iteration algorithm. As such,

$$[\text{DIC}] \equiv [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \tag{1}$$

$$\begin{aligned}[\text{alkalinity}] \equiv\, & [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] + [HPO_4^{2-}] \\ & + 2[PO_4^{3-}] + [SiO(OH)_3^-] + [NH_3] + [HS^-] \\ & + \ldots - [H^+]_f - [HSO_4^-] - [HF] - [H_3PO_4] - \ldots\end{aligned} \tag{2}$$

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

$$[\text{DIC}]_{\text{in\_situ}} = [\text{DIC}]_{\text{measured}} + X_{CaCO_3} \tag{3}$$

$$[\text{alkalinity}]_{\text{in\_situ}} = [\text{alkalinity}]_{\text{measured}} + 2X_{CaCO_3} \tag{4}$$

$$\left[Ca^{2+}\right]_{\text{in\_situ}} = \left[Ca^{2+}\right]_{\text{measured}} + X_{CaCO_3}. \tag{5}$$

By assuming calcite saturation in situ and using Eq. (5) we derive,

$$\left[{CO_3}^{2-}\right]\left(\left[Ca^{2+}\right]_{\text{measured}} + X_{CaCO_3}\right) = K^*_{sp}(T, P, S) \tag{6}$$

with $K^*_{sp}(T,P,S)$ the solubility product of calcite at in situ temperature, salinity and pressure.

For algebraic simplicity, we combine all the components of minor contribution to the DIC and alkalinity mass balance relative to HCO_3^-, CO_3^{2-} and $B(OH)_4^-$ into a grouped term, labeled "*minor species*":

$$\begin{aligned}[\text{minor species}] \equiv\, & [H_2CO_3] - [OH^-] - \left[{HPO_4}^{2-}\right] - 2\left[{PO_4}^{3-}\right] - \left[{SiO(OH)_3}^-\right] - [NH_3] - [HS^-] + \\ & \left[H^+\right]_f + \left[{HSO_4}^-\right] + [HF] + [H_3PO_4]\end{aligned} \tag{7}$$

With $[H^+]_f$ the free hydrogen concentration ($[H^+]_f = [H^+] - [HSO_4^-]$), indicating that only the hydrated forms of the ion are included.

Substituting Eq. (3) through Eq. (5) into the DIC and total alkalinity mass balance expressions (i.e. Eq. (1) and Eq. (2), respectively), we derive:

$$\begin{aligned}[\text{alkalinity}]_{\text{measured}} - [\text{DIC}] + X_{CaCO_3} = & \left[{CO_3}^{2-}\right] + \left[{B(OH)_4}^-\right] \\ & - [\text{minor species}]\end{aligned} \tag{8}$$

$$\begin{aligned}2[\text{DIC}]_{\text{measured}} - [\text{alkalinity}]_{\text{measured}} = & \left[{HCO_3}^-\right] + [H_2CO_3] - \left[{B(OH)_4}^-\right] \\ & + [\text{minor species}].\end{aligned} \tag{9}$$

Rearranging and combining Eq.(1) through Eq.(9) we derive a set of equations that form a uniquely determined system that can be solved for X_{CaCO_3} and, subsequently, the complete carbonate system chemistry. This is done through iteration of a series mass-balance and equilibrium relationships that also consider the minor species included in total alkalinity. To simplify the solution, the iteration procedure neglects the *minor species* [i.e. Eq. (7)] for the initial iteration. In the second iteration the *minor species*, determined in the first iteration, is incorporated into the equation set. The following iterations subsequently refine the calculated species concentrations until a stable solution is attained. After five iterations the difference between X_{CaCO_3} calculated in the last iteration and in the iteration to the last round is not greater than

1E-9 mol kg^{-1}. This demonstrates that the iteration scheme converges rapidly, and results in a stable solution for the abundance of in situ carbonate system species and other related components. Also, the stability of the algorithm is independent of the relative size of the measured DIC and alkalinity concentration. We give a detailed description of the method in Appendix-A1. A Matlab-code of the calculation method is also available online as an electronic supplement.

2.3. Thermodynamic constants

We calculate equilibrium and solubility constants for the acid dissociation reactions and calcium carbonate, respectively, at in situ salinity, temperature and pressure (Millero, 1983; Zeebe and Wolf-Gladrow, 2001; Dickson et al., 2007). Equilibrium constants are on the total hydrogen ion concentration scale (Millero et al., 2006; Dickson et al., 2007). The details of the calculation steps for the determination of in situ equilibrium constant are given in Appendix-A1.

3. Assessment

3.1. Application of the method using water column data

To validate the method computationally and conceptually, we apply the approach using modern water column data [concentrations of DIC, alkalinity, silica, and phosphate, together with salinity and temperature data (location 27°S 123°W)] from the Hydrographic Atlas of the World Ocean Circulation Experiment, WOCE (Talley, 2007). For this method-evaluation effort, we implicitly assume that the water-column total alkalinity and DIC concentration measurements from the WOCE Pacific Atlas are not subject to pressure and temperature artifacts. If the algorithm works properly and has correctly calculated the thermodynamic constants, “*excess carbonate*” (X_{CaCO_3}) will be zero mol kg^{-1} at the carbonate saturation horizon (above this depth, X_{CaCO_3} will be negative, and below this depth, it will be positive).

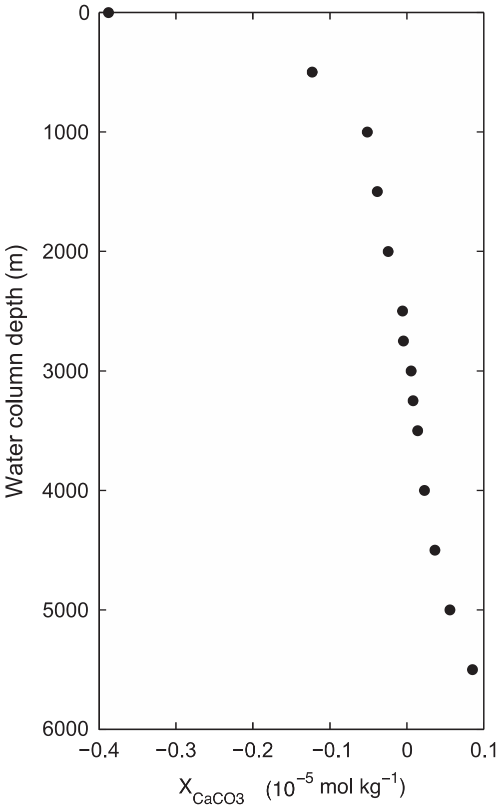

Fig. 1. Evolution of X_{CaCO_3} (excess carbonate) throughout the water-column for the region located in the heart of the South Pacific Gyre. Negative X_{CaCO_3}values point to calcite supersaturation, X_{CaCO_3} equaling zero represents the calcite saturation horizon and positive X_{CaCO_3} values point to undersaturation with respect to calcite. A value of zero mol kg^{-1} for $X_{CaCO_3}$is reached at 2875 m.

The algorithm correctly positions the level of the calcite saturation horizon at a water depth of 2785 m indistinguishable from the depth of an independent calculation of the saturation horizon (Williams and Follows, 2011). It is also consistent with in situ dissolution experiments (Peterson, 1966). X_{CaCO_3} is negative above 2875 m depth, zero at 2875 m, and positive below (where there is undersaturation, Fig. 1). A positive X_{CaCO_3} implies that to reach saturation, calcium carbonate must precipitate, while a negative X_{CaCO_3} implies calcium carbonate dissolution is required to reach saturation. This result supports the validity of the algorithm, and the proposed thermodynamic framework to describe experimentally observed calcite dissolution.

3.2. Experimental validation test

3.2.1. Porewater collection and analytical methods

We tested the method using published pore fluid concentration data from IODP Expedition 329 to the South Pacific Gyre (D'Hondt et al., 2011). The data is from IODP Site U1368, located at 3470 m water depth, near the center of the Gyre (27°55′S, 123°10′W). Site U1368 is in a region of seamount topography, within magnetic polarity Chron 5ABn [basement age of ca. 13.36–13.0 Ma (Gradstein et al., 2012)] (Fig. 2). The slowly deposited sediment (i.e. 0.1 to 1 m per million years) at Site U1368 consists of a 16-m sequence of calcareous ooze, pelagic clay and lithic sand (D'Hondt et al., 2011). Smear-slide analysis revealed nannofossils, red-brownish semi-opaque oxides and foraminifera 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 [0 to 14 m], (ii) a middle dark color nannofossil-bearing clay unit [14 to 15.5 m] and (iii) a hematitic nannofossil-bearing clay unit intercalated with sandy intervals in the lowermost part of the sequence [15.5 to 16 m] (Expedition 329 Scientists, 2011a, 2011b). Calcium carbonate is abundant throughout the sequence.

Porewater of Site U1368 sediment was extracted from 10-cm long whole-core rounds using the standard Ti IODP squeezers (Manheim, 1966). Two core handling-and-storage procedures were adopted. In one procedure, we did not minimize storage and handling time of whole-round samples before porewater extraction. We refer to this as the ‘*conventional process*’. In contrast, we designed the second procedure to minimize the time between core retrieval and porewater extraction in order to minimize carbonate precipitation. We refer to this as the ‘*rapid process*’. We recorded the amount of time between when the core was taken from the seafloor, brought to the rig floor, brought to the chemistry lab, and finally when the porewater was extracted. Sample handling and laboratory storage time for the *conventionally processed* samples varied from a couple of hours to as long as seven hours. The *rapidly processed* samples were stored for less than two hours before extraction (Fig. 3A; Expedition 329 Scientists, 2011b, 2011c). For both procedures, core samples that could not be processed right away were stored in a 4 °C refrigerator in their core liner until they could be extracted and squeezed. Characteristic prevailing temperature in the laboratory was 20 °C. After porewater extraction samples were stored in a refrigerator (4 °C) in sealed vials that minimize CO_2 loss until they could be analyzed.

Porewater was collected from 33 whole-round samples of Site U1368 Hole C. Spatial resolution was approximately one sample every 50 cm. Eleven of the whole-round samples taken for porewater chemistry analysis were *rapidly processed* samples (Expedition 329 Scientists, 2011b).

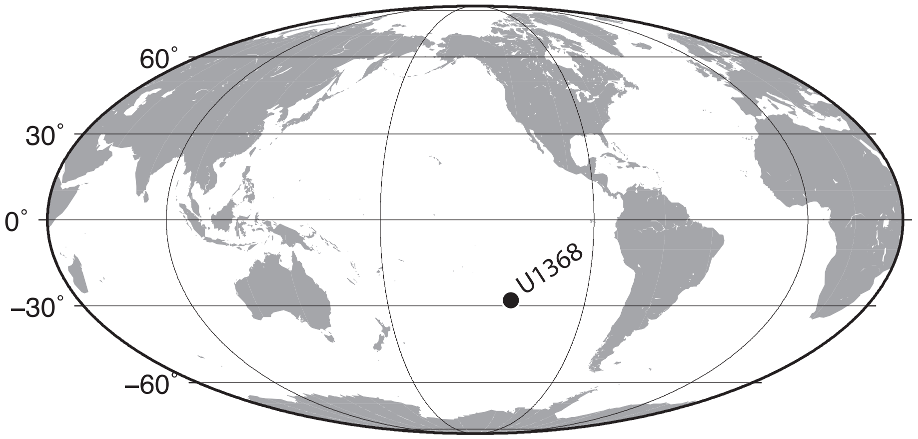

Fig. 2. IODP Expedition 329, Site U1368 location used in the evaluation of the method.

Porewater analytes that were key for this study and that are required in the iterative process include the concentrations of DIC, alkalinity, calcium, chloride, sulfate, phosphate, and silica (see Appendix-A1). Total alkalinity was determined by Gran titration utilizing an autotritrator (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. Phosphate and dissolved silica concentrations were determined using an OI analytical discrete analyzer (DA3500) spectrophotometer. Concentrations of calcium and other cations (i.e., Mg, Na and K) in the pore fluid were obtained by inductively coupled plasma-emission spectrometry (ICP-AES) with a Teledyne Prodigy high-dispersion ICP spectrometer. Detailed descriptions of the shipboard pore fluid geochemical campaign, including details of the method are in the *Proceedings of IODP*, Volume 329 (2011).

The observed relative standard deviation of alkalinity measurements on standard seawater (i.e. CRM94, with TA = 2.222 mM) was 0.80%. We assign the same relative standard deviation to our samples. The pooled relative standard deviation of triplicate DIC measurements of all the samples at Site U1368 was 0.59% uncertainty. The uncertainty for 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, 0.7% of the measured Mg value, 0.5% of the measured Na value,

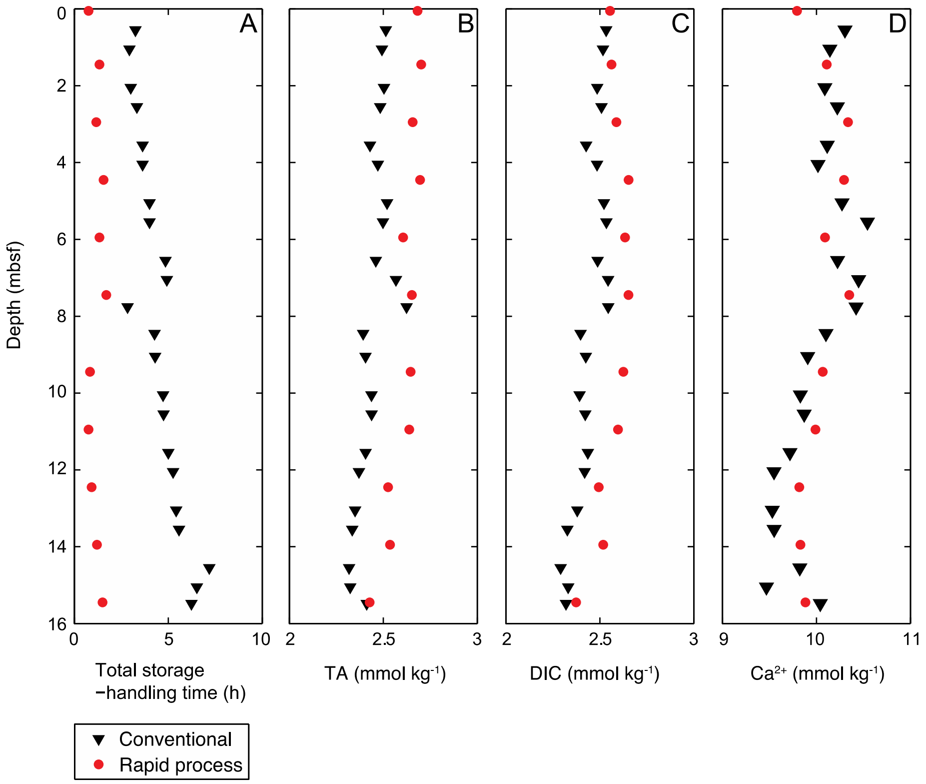

Fig. 3. (A) Total time in hours to get from the sample recovery stage to the squeezing and analysis stage for each *conventionally processed* porewater sample (▼) and *rapidly processed* sample (•) from Site U1368, Hole C. Sediment depth is in units of meters below seafloor (mbsf). (B) Depth profiles of measured total alkalinity, (C) dissolved inorganic carbon (DIC), and (D) calcium concentrations, for *conventionally processed* samples (▼) and *rapidly processed* samples (•).
Data from Expedition 329 Shipboard Scientific party (2011b).

and 0.6% of the measured K value, based on replicate analyses of the IAPSO standard seawater and other internal matrix matched standards (Shipboard Scientific Party, 2011). Lastly, the uncertainty of dissolved silica and phosphate measurements was 1.4% and 10%, as estimated from the pooled standard deviation of duplicate and triplicate measurements of each porewater sample, respectively.

We use the measured in situ bottom water temperature and thermal gradient of Site U1368 (i.e. 1.6 °C and 113 °C km^{-1}, respectively) to calculate in situ downhole temperature. We assume the in situ pressure to be hydrostatic and calculate it from water depth and sediment depth, considering average ocean water density. Downhole salinity is inferred based on measured porewater chloride, although it should be recognized that this is an approximation, as the concept of salinity usually assumes a constant proportion of dissolved constituents.

3.2.2. Data description

Total alkalinity and dissolved inorganic carbon (for both *conventionally* and *rapidly processed* samples) exhibit similar behavior with depth, starting at 2.682 and 2.553 mmol kg^{-1}, respectively, and gradually decreasing with depth to a value of 2.427 and 2.373 mmol kg^{-1}, respectively, at the bottom of the sequence (Fig. 3B–D). The general downhole pattern of the DIC and alkalinity profile for the *conventional* samples at Site U1368 clearly deviates from the smooth profile expected due to diffusion. Some fraction of this deviation is due to the analytical uncertainty of the measurement. 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 the data. In contrast to *conventional* samples, the DIC and alkalinity profile resulting from the *rapid* sampling *process* more closely tends toward a smooth diffusive profile.

We assess the impact of storage time by comparing *rapid process* versus *conventional* porewater chemistry data throughout the analyzed sequence. Alkalinity and DIC abundances in *conventionally processed* samples are consistently lower than in *rapidly processed* samples (i.e. 0.172 mmol kg^{-1} and 0.126 mmol kg^{-1} lower concentrations, respectively, averaged over the entire sequence). These differences reflect a greater extent of carbonate precipitation in the case of *conventionally processed* samples.

The deviation in DIC and alkalinity concentration between *conventionally* and *rapidly processed* samples is not uniform and is consistently larger than can be explained by analytical uncertainty. The difference in measured concentration between *rapidly* and *conventionally* processed samples downhole is unidirectional (the *conventionally processed* samples exhibit consistently lower values), suggesting that these variations are real. The occurrence and variability of storage effects on measured DIC and alkalinity illustrate the need to better quantify these effects.

Storage effects on measured calcium concentrations are unclear given the precision of the available measurements (the Ca^{2+} concentration difference between *rapidly* and *conventionally processed* samples lies within the analytical uncertainty of the measurement). Abundances of other dissolved species, including the remaining cations (magnesium, sodium and potassium), silica, chloride, sulfate and phosphate, do not significantly differ between rapidly squeezed samples and conventionally processed samples. The uniformity between *rapid* and *conventional* process concentrations for the remaining cation concentrations suggests that the porewater is not saturated with respect to other carbonate phases.

3.2.3. Method validation strategy

Solid-phase calcium carbonate is between 61.3 and 87.4 wt.% throughout the hole (Fig. 4). Other carbonate phases (e.g. $CaMg(CO_3)_2$, $SrCO_3$, $FeCO_3$) are not saturated. Under these conditions, calcite rather than aragonite is the stable calcium carbonate phase. Therefore, we presume the calcium carbonate formed during recovery and extraction at Site U1368 to be exclusively calcite. This fulfills the fundamental requirement for the correct application of the method.

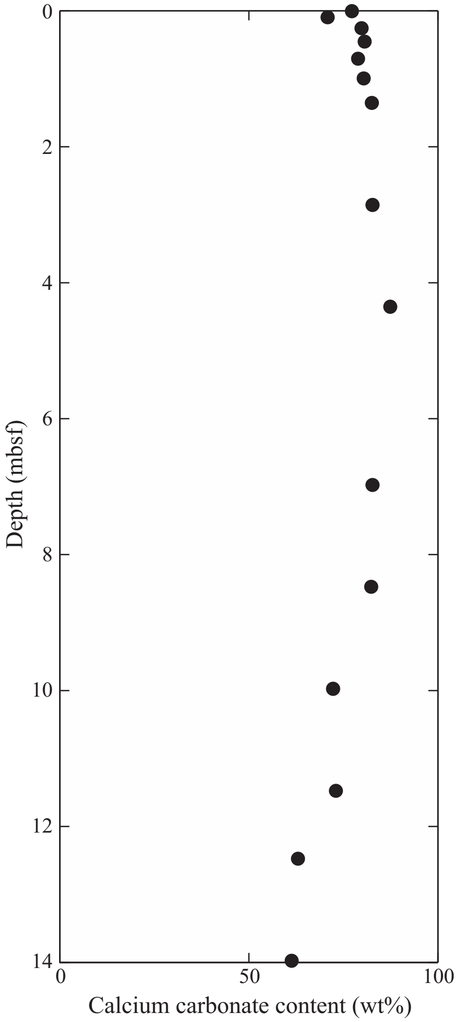

Fig. 4. Solid-phase calcium carbonate content of sediment at Site U1368 Hole B, expressed as weight percent (wt.%).
Data from Expedition 329 Shipboard Scientific party (2011b).

If our methodology and assumptions for correcting for carbonate precipitation are valid, we expect calculated in situ concentrations of DIC, alkalinity, and calcium for the *conventionally processed* samples (long storage time) and *rapidly processed* samples (short storage time), to be statistically indistinguishable and to have a smooth depth profile due to diffusion. Thus, if corrected DIC and alkalinity abundances for *rapid* and *conventional* porewater samples are identical, this observation supports the argument that the variance between these samples is due to carbonate precipitation following recovery and prior to analysis.

3.2.4. Assessment of experimental results

Calculated in situ abundances of the measured components (i.e. DIC, TA, and Ca^{2+}) are shown in Fig. 5. *Excess carbonate*, (X_{CaCO_3}), averages 0.109 mmol kg^{-1} and 0.060 mmol kg^{-1} for *conventionally* and *rapidly processed* samples, respectively (Table 1). This shows that, on average, 4.5% of the measured [DIC] and 8.9% of the measured [alkalinity] were lost to calcium carbonate precipitation in *conventionally* sampled porewater, relative to 2.4% and 4.6% in the case of the *rapidly processed* samples. Also, concentrations of calculated in situ DIC, alkalinity and calcium for *rapid* and *conventionally* processed samples fluctuate randomly downhole within a narrow range. This is in contrast to the unidirectional trend between these two sample types for the measured values,

Table 1
Amount of calcium carbonate precipitation (i.e. X_{CaCO_3}, excess carbonate) we had to account for to calculate in situ carbonate system chemistry for *conventionally* and *rapidly processed* samples.

Depth (mbsf)	X_{CaCO_3} (mol kg^{-1})
Conventionally processed samples	
0.55	1.227E−04
1.05	1.290E−04
2.05	9.194E−05
2.55	1.286E−04
3.55	1.078E−04
4.05	1.215E−04
5.05	1.059E−04
5.55	1.332E−04
6.55	1.308E−04
7.05	7.662E−05
7.76	2.430E−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
Rapidly processed samples	
0.05	9.629E−06
1.45	2.640E−05
2.95	3.551E−05
4.45	5.762E−05
5.95	1.281E−04
7.45	9.670E−05
9.45	8.132E−05
10.95	6.369E−05
12.45	8.038E−05
13.95	9.114E−05
15.45	6.216E−05

where *rapidly processed* samples are consistently higher in concentration compared to the *conventionally processed* ones.

We statistically estimate the analytical error, ε, associated with calculated values of "*excess carbonate*" ($\varepsilon_{X_{CaCO_3}}$), in situ DIC ($\varepsilon_{DIC_{in\_situ}}$), alkalinity ($\varepsilon_{Alkalinity_{in\_situ}}$) and calcium ($\varepsilon_{Ca^{2+}_{in\_situ}}$) and use these to evaluate the validation experiment and method. We assume that error due to uncertainty in the thermodynamic constants is comparatively small. We estimate $\varepsilon_{X_{CaCO_3}}$ by propagating the sum of the squares of the analytical error of each measurement used in its calculation.

$$\varepsilon^2_{X_{CaCO_3}} = \left(\frac{\partial X_{CaCO_3}}{\partial Alkalinity}\right)^2 \sigma^2_{Alkalinity} + \left(\frac{\partial X_{CaCO_3}}{\partial DIC}\right)^2 \sigma^2_{DIC} + \left(\frac{\partial X_{CaCO_3}}{\partial Ca^{2+}}\right)^2 \sigma^2_{Ca^{2+}} \tag{10}$$

where σ_i is the precision of measurement i (with i = alkalinity, DIC or Ca $^{2+}$).

We approximate $\frac{\partial X_{CaCO_3}}{\partial i}$ in Eq. (10) by numerically evaluating $\frac{\Delta X_{CaCO_3}}{\Delta i}$ for small Δi at the calculated value of X_{CaCO_3}. The analytical error for the calculated in situ values is,

$$\varepsilon^2_{DIC_{in\_situ}} = \left[1+2\left(\frac{\partial X_{CaCO_3}}{\partial DIC}\right)\right]\sigma^2_{DIC} + \varepsilon^2_{X_{CaCO_3}} \tag{11}$$

$$\varepsilon^2_{Alkalinity_{in\_situ}} = \left[1+4\left(\frac{\partial X_{CaCO_3}}{\partial Alkalinity}\right)\right]\sigma^2_{Alkalinity} + 2\varepsilon^2_{X_{CaCO_3}} \tag{12}$$

$$\varepsilon^2_{Ca^{2+}_{in\_situ}} = \left[1+2\left(\frac{\partial X_{CaCO_3}}{\partial Ca^{2+}}\right)\right]\sigma^2_{Ca^{2+}} + \varepsilon^2_{X_{CaCO_3}}. \tag{13}$$

The average analytical error estimates for calculated X_{CaCO_3} and in situ DIC, TA, and Ca^{2+} concentration are 2.20E − 2 mmol kg^{-1} [2.09E − 2–2.34E − 2 mmol kg^{-1}], 1.8E − 2 mmol kg^{-1} [1.7E − 2–1.9E − 2 mmol kg^{-1}], 5.4E − 2 mmol kg^{-1} [5.1E − 2–5.6E − 2 mmol kg^{-1}], and 6.5E − 2 mmol kg^{-1} [6.2E − 2–6.9E − 2 mmol kg^{-1}], respectively (Fig. 5). The ranges of analytical error estimates on the calculated in situ species are narrow because the ranges in measured species are similarly small.

The total uncertainty on the calculated values ($\varepsilon_{i,total}$) has multiple components: analytical uncertainty ($\varepsilon_{i,\ in\ \_\ situ}$), sampling error, errors related to the assumptions (i.e., thermodynamic equilibrium) and errors in the thermodynamic constants. We define the method-specific error as the error not associated with analytical uncertainty. To assess the extent of the method-specific error we calculate the total uncertainty ($\varepsilon^2_{i,total}$ = (method-specific error)^2 + (analytical error)^2) and compare it to the error we expect due to analytical uncertainty only.

We quantify the total methodological precision ($\varepsilon_{i,total}$) by pooling the standard deviations of the calculated in situ DIC, alkalinity and calcium for *conventionally* and *rapidly* processed samples at similar depths. In other words, we define pairs of *conventionally* and *rapidly processed* samples that consist of each *rapidly processed* sample and the average of the two *conventionally processed* samples that immediately sandwich (underlie and overlie) that *rapidly processed* sample in the stratigraphy. We calculate the pooled standard deviation of species i as follows (McNaught and Wilkinson, 1997):

$$S_p = \sum\left[\left(i_{conventional} - i_{rapid}\right)^2/2\,k\right]^{1/2} \tag{14}$$

where S_p is the pooled standard deviation, k the number of *conventional* and *rapid* pairs and $i_{conventional/rapid}$ the calculated concentration of species i for *rapidly* and *conventionally* (averaged) *processed* samples. For Site U1368, k equals 11, which is the number of *rapidly processed* samples.

The pooled standard deviations for calculated in situ DIC, alkalinity, and calcium ($\varepsilon_{i,total}$) are 8.4E − 2 mmol kg^{-1}, 7.9E − 2 mmol kg^{-1} and 0.16 mmol kg^{-1}, respectively.

Since these values are larger than the uncertainty expected due to analytical error, there is method-specific error. The methodological precision is quantified as follows,

$$\varepsilon^2_{i,method} = \varepsilon^2_{i,total} - \varepsilon^2_{i,in\_situ}. \tag{15}$$

The uncertainty introduced by the method amounts to 8.2E − 02 mmol kg^{-1}, 5.7E − 02 mmol kg^{-1}, and 1.5E − 01 mmol kg^{-1} for the calculation of in situ DIC, TA, and Ca^{2+}, respectively. This uncertainty estimate is purely methodological and separate from the uncertainty due to analytical precision of the chemical measurements. Part of the methodological error may be due to CO_2 loss during sample storage and squeezing, or due to continuous precipitation of calcium carbonate during the analysis of the different porewater solutes. The use of sealed vials that are specifically designed to minimize CO_2 loss should minimize this methodological uncertainty. This method-specific error is not a major impediment to application of the method as the correction brought by the method (4.5 and 8.9% of the measured values for DIC and alkalinity, respectively) is larger than the uncertainty introduced by the method (3.2 and 2.1% for DIC and alkalinity, respectively).

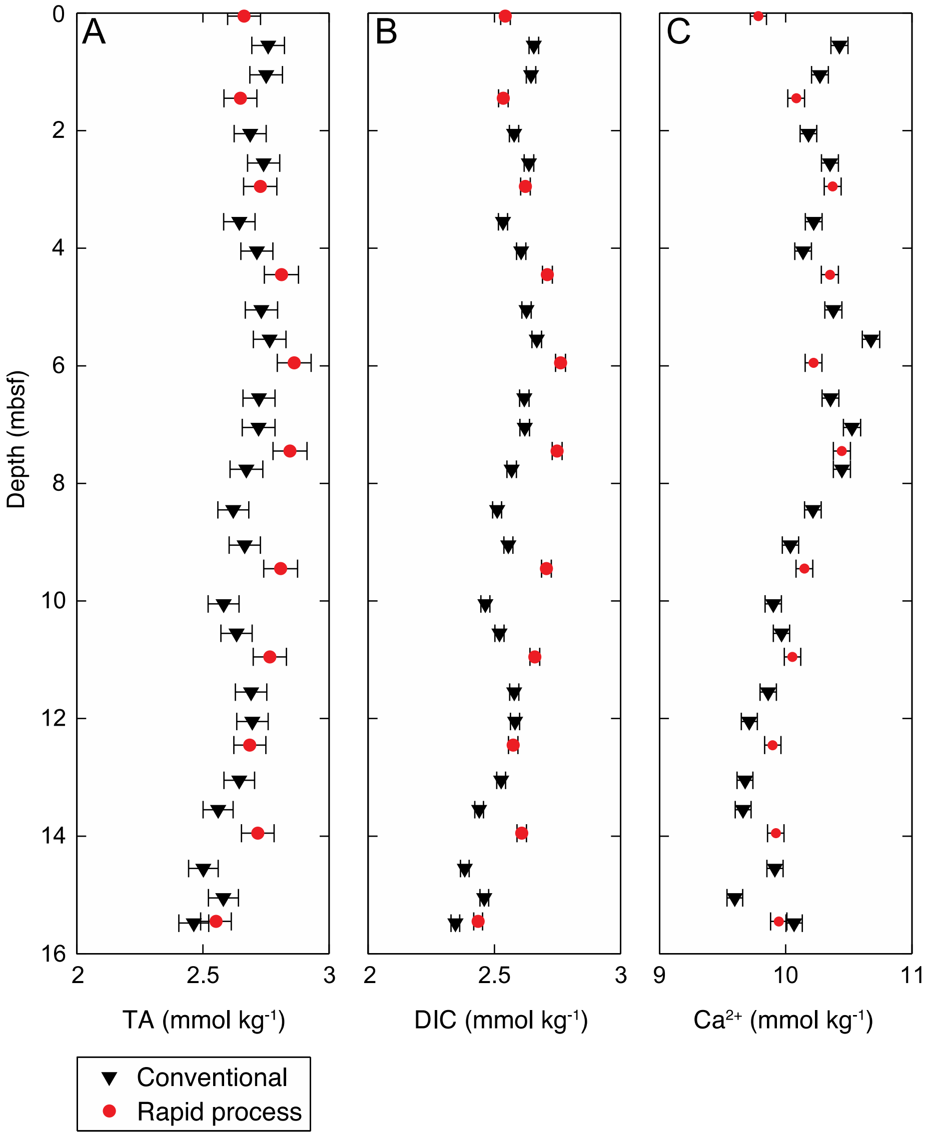

Fig. 5. Sediment depth profiles of calculated in situ TA, DIC and Ca^{2+} concentrations with analytical error analysis (1σ) for *conventionally* (▼) and *rapidly processed* (•) samples from Site U1368 Hole C.

4. Conclusion and application of the approach

We present a method that accounts for precipitation of $CaCO_3$ from porewater during sediment recovery, enabling quantification of in situ carbonate chemistry. Fundamental requirements for application of our approach are (i) in situ calcium carbonate saturation (calcitic phase) and (ii) equilibrium conditions. For the case of porewater saturation with respect to other carbonate phases, the algorithm and its equilibrium and solubility constant expressions should be adapted accordingly.

Application of our approach generates a quantitatively accurate view of the in situ dissolved carbonate system chemistry of subseafloor sediment. It is rather straightforward if porewater alkalinity, DIC and calcium concentration are measured for the same sample, and equilibrium condition prevails in situ. This method is applicable for any sediment with in situ calcium carbonate saturation. Because carbonate-bearing sediment covers about 50% of the seafloor (Schulz, 2000), the method is widely applicable.

We tested the stability and applicability of our iteration method by inserting sets of DIC and TA concentration values from the WOCE Pacific Atlas to cover the range of subseafloor environments (i.e. marginal sediments, open ocean, etc.) found beneath the global ocean. The method resulted in stable solutions for the in situ carbonate system chemistry for each of these porewater chemistry scenarios, underlining the wide applicability of the method. This constitutes a major improvement over the method by Wang et al. (2010), which is unstable in many situations (e.g., when $[\text{alkalinity}]_{\text{measured}} \leq [\text{DIC}]_{\text{measured}}$). Our method requires only limited calculation time, relatively simple spreadsheet-based calculations, and no additional shipboard time and/or drilling for its application.

We also show that this method is effective for inferring concentration profiles of dissolved carbonate-related chemicals that were not measured directly (e.g. CO_3^{2-}, H^+, OH^-, HCO_3^-, H_2CO_3, $B(OH)_4^-$, HPO_4^{2-}, etc.).

The subseafloor sedimentary environment used to illustrate the proposed method (i.e. Site U1368) is extremely poor in organic matter content and therefore did not contain any dissolved ammonia or sulfide. However, we have designed the method to also be operational in more organic-rich environments, where these solutes might be present and should thus be accounted for in the total alkalinity term.

Finally, we demonstrate quantitatively that chemical alteration associated with core retrieval and handling processes can be significant.

For example, in the case of Site U1368, the measured DIC and TA abundances were offset by up to four and eight percent from in situ values, respectively. Such bias can strongly lower estimates of subseafloor metabolic activities and provide poor constraints for reconstruction of past deep ocean chemistry.

Consequently, application of this approach will contribute to better assessment of microbial metabolic activity rates in subseafloor environments and improve quantitative reconstructions of deep ocean chemistry through the last glacial–interglacial cycle.

Acknowledgments

We greatly appreciate the thoughtful comments of David Burdige and an anonymous reviewer. They significantly improved the manuscript. We thank the Center for Dark Energy Biosphere Investigations (C-DEBI) and the National Science Foundation (grants OCE-0939564 and OCE-1130735) for funding this study. We also thank the IODP Expedition 329 Science Party, which provided all of the data for this project. Without their hard work and dedicated effort, this project wouldn't have been possible. This is C-DEBI Contribution 229.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.chemgeo.2014.06.010.

References

Adkins, J.F., Schrag, D.P., 2003. Reconstructing Last Glacial Maximum bottom water salinities from deep-sea sediment pore fluid profiles. EPSL 216, 109–123.

Berner, R.A., 1964. An idealized model of dissolved sulfate distribution in recent sediments. Geochim. Cosmochim. Acta 28, 1497–1503.

Berner, R.A., 1980. Early diagenesis: a theoretical approach. Princeton Series in Geochemistry. Princeton University Press, Princeton, NJ (241 pp.).

D'Hondt, S., Rutherford, S., Spivack, A.J., 2002. Metabolic activity of subsurface life in deep-sea sediments. Science 295, 2067–2070.

D'Hondt, S., Jørgensen, B.B., Miller, D.J., Batzke, A., Blake, R., Cragg, B.A., Cypionka, H., Dickens, G.R., Ferdelman, T., Hinrichs, K.U., Holm, N.G., Mitterer, R., Spivack, A., Wang, G., Bekins, B., Engelen, B., Ford, K., Gettemy, G., Rutherford, S.D., Sass, H., Skilbeck, C.G., Aiello, I.W., Guèrin, G., House, C., Inagaki, F., Meister, P., Naehr, T., Niitsuma, S., Parkes, R.J., Schippers, A., Smith, D.C., Teske, A., Wiegel, J., Padilla, C.N., Acosta, J.L.S., 2004. Distributions of microbial activities in deep subseafloor sediment. Science 306, 2216–2221.

D'Hondt, S., Inagaki, F., Alvarez Zarikian, C.A., Expedition 329 Scientists, 2011. South Pacific Gyre subseafloor life. Proceedings of the Integrated Ocean Drilling Program, vol. 329 (61pp.).

Dickson, A.G., Sabine, C.L., Christian, J.R., 2007. Guide to best practices for ocean CO2 measurements. PICES Spec. Publ. 3, 191.

Expedition 329 Scientists, 2011a. Expedition 329 summary. In: D'Hondt, S., Inagaki, F., Alvarez Zarikian, C.A., the Expedition 329 Scientists (Eds.), Proceedings of the Integrated Ocean Drilling Program, vol. 329. Integrated Ocean Drilling Program Management International, Inc., Tokyo.

Expedition 329 Scientists, 2011b. Site U1368. In: D'Hondt, S., Inagaki, F., Alvarez Zarikian, C.A., the Expedition 329 Scientists (Eds.), Proc. IODP, 329. Integrated Ocean Drilling Program Management International, Inc., Tokyo.

Expedition 329 Scientists, 2011c. Methods. In: D'Hondt, S., Inagaki, F., Alvarez Zarikian, C.A., the Expedition 329 Scientists (Eds.), Proc. IODP, 329. Integrated Ocean Drilling Program Management International, Inc., Tokyo.

Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedtke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., 1979. Early oxidation of organic matter in pelagic sediments of the eastern equatorial Atlantic: suboxic diagenesis. Geochim. Cosmochim. Acta 43, 1075–1090.

Gieskes, J.M., 1975. Chemistry of porewaters of marine sediment. Annu. Rev. Earth Planet. Sci. 3, 433–453.

Gradstein, F.M., Ogg, J.G., Schitz, M.D., Ogg, G.M., 2012. A Geologic Time Scale 2012. Elsevier Science Ltd, NY, USA (1176 pp).

Manheim, F.T., 1966. A hydraulic squeezer for obtaining porewaters from consolidated and unconsolidated sediments. U. S. Geol. Surv. Prof. Pap. 550-C, 256–261.

McDuff, R.E., 1985. The chemistry of porewaters, deep sea drilling project leg 86. DSDP Initial Reports 86pp. 675–687.

McNaught, A.D., Wilkinson, A. (Eds.), 1997. IUPAC Compendium of Chemical Terminology, 2nd ed. R. Soc. Chem, Cambridge.

Millero, F.J., 1983. Influence of pressure on chemical processes in the sea. In: Riley, J.P., Chester, R. (Eds.), Chemical Oceanography, Vol. 8. Academic Press, New York (88 pp).

Millero, F.J., Graham, T.B., Huang, F., Bustos-Serrano, H., Pierrot, D., 2006. Dissociation constants of carbonic acid in seawater as a function of salinity and temperature. Mar. Chem. 100, 80–94.

Paull, C.K., Matsumoto, R., Wallace, P.J., et al., 1996. Proceedings of the Integrated Ocean Drilling Program, Initial Reports, vol. 164. College Station, TX, USA.

Peterson, M.N.A., 1996. Calcite: rates of dissolution in a vertical profile in the Central Pacific. Science 154, 1542–1544.

Sayles, F.L., Manheim, F.T., 1975. Porewater solutions and diagenesis in deeply buried marine sediment: results from the Deep Sea Drilling Project. Geochim. Cosmochim. Acta 39, 103–127.

Schulz, H.D., 2000. Quantification of early diagenesis: dissolved constituents in marine pore water. In: Schulz, H.D., Zabel, M. (Eds.), Marine Geochemistry. Springer-Verlag, Berlin, pp. 85–128.

Talley, L.D., 2007. Hydrographic Atlas of the World Ocean Circulation Experiment (WOCE). In: Sparrow, M., Chapman, P., Gould, J. (Eds.), Pacific Ocean, vol. 2. International WOCE Project Office, Southampton, U.K.

Wang, G., Spivack, A.J., D'Hondt, S., 2010. Gibbs energies of reaction and microbial mutualism in anaerobic deep subseafloor sediment of ODP Site 1226. Geochim. Cosmochim. Acta 74, 3938–3947.

Williams, R.G., Follows, M.J., 2011. Ocean Dynamics and the Carbon Cycle. Cambridge University Press, USA 416 pp.

Yu, J.M., Broecker, W.S., Elderfield, H., Jin, Z.D., McManus, J., Zhang, F., 2010. Loss of carbon from the deep sea since the Last Glacial Maximum. Science 330, 1084–1087.

Zeebe, R.E., Wolf-Gladrow, D., 2001. CO2 in Seawater: Equilibrium, Kinetics, Isotopes Elsevier Oceanography Series, 65, pp. 346, Amsterdam.