Controlling the diffusive boundary layer thickness above the sediment–water interface in a thermostated rotating-disk reactor

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Abstract

The diffusive boundary layer (DBL) is a thin layer of fluid at the interface with a solid surface in which frictional forces cause molecular diffusion to become the dominant mode of solute transport. The thickness of the DBL is a function of the nature and roughness of sediment substrates, as well as the bottom-current speed. In low-energy natural aquatic environments, such as abyssal plains or lakes, the thickness of the DBL can reach several millimeters and significantly impede the diffusive rate of solutes through the sediment–water interface (SWI). Thus, precisely reproducing the DBL in the laboratory is required to simulate benthic diffusive fluxes similar to those encountered in situ. Yet, an experimental apparatus allowing precise control of the DBL thickness at the SWI in the laboratory has not been described in the literature. Here, we present a simple temperature-controlled rotating-disk system, which is suitable for the use with natural sediments and that is capable of generating thick DBLs. Water overlying the rotating sediment can be sampled discretely or continuously to monitor the chemical reaction progress. We tested the validity of the reactor by dissolving a foraminiferal sand bed in natural seawater. We find that (1) measured dissolution fluxes agree with those predicted by theory and (2) the dissolution of calcite in these seafloor-like hydrodynamic conditions is controlled by mass transfer across the DBL above the bed. Guidelines for best practices under various experimental conditions, possible future developments, and the theoretical equations to compute the DBL thickness and diffusive fluxes in this reactor are described.

In many situations, boundary conditions are critical in defining the hydrodynamics of natural environments. In limnology and oceanography, the bottom (or benthic) boundary layer is the part of the water column that is directly affected by the drag of currents on the sediment bed; its thickness is typically on the order of meters to tens of meters (Trowbridge and Lentz 2018). Within this bottom boundary layer, current velocities decrease toward the sediment bed, until ultimately reaching zero velocity relative to the solid boundary at the sediment–water interface (SWI) of low-permeability sediments, a concept commonly termed the no-slip condition (Day 1990). A few centimeters above the SWI, internal friction within water causes viscous transport of momentum to dominate over turbulent dispersion, in a region termed the viscous sublayer (Boudreau and Jørgensen 2001). Closer to the SWI, in a thin film of water with a thickness typically on the order of a few tens of microns (e.g., in rivers or coastal areas) to millimeters (e.g., in lakes or abyssal environments), molecular diffusion becomes the dominant mode of solute transport, rather than much faster turbulent diffusion, which dominates solute transport further away from the interface. This layer is termed the diffusive boundary layer (DBL).

Numerous investigators have reported the presence of a DBL at the SWI (Archer et al. 1989; Gundersen and Jørgensen 1990; Santschi et al. 1991; Glud et al. 1994), as well as at algal or coralline surfaces (Larkum et al. 2003; Hendriks et al. 2017; Lichtenberg et al. 2017). The thickness of this DBL depends on the nature and roughness of the substrate (Chriss and Caldwell 1982; Dade 1993; Boudreau and Jørgensen 2001; Roy et al. 2002; Han et al. 2018), as well as on the current speed of the overlying water. Slow currents generate thick DBLs, whereas fast currents cause the DBL to thin, as predicted by theory (Levich 1962; Boudreau and Guinasso 1982; Higashino and Stefan 2004) and confirmed by observations (Santschi et al. 1983; Santschi et al. 1991; Larkum et al. 2003; Lorke et al. 2003).

Across the DBL, solute transport occurs by molecular diffusion driven by a total concentration difference (gradient), $\Delta i$ (mol). The (steady state) flux of solute $i$ across the DBL, $J_i$ (mol m$^{-2}$ a$^{-1}$), is then given by (Boudreau 2013; Frank-Kamenetskii 2015):

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\[ J_i = -k^* \Delta \tau_i \] (1)

where \( k^* \) is the overall mass transfer coefficient for solute \( i \) (m a\(^{-1}\)), i.e.,

\[ k^* = (k_i \beta)(k_i + \beta)^{-1} \] (2)

where \( k_i \) is the sediment-side mass-transfer coefficient (m a\(^{-1}\)) and \( \beta \) is the water-side (DBL) mass-transfer coefficient (m a\(^{-1}\)). \( \beta \) is simply the (free solution) diffusion coefficient for solute \( i \), \( D_i \) (m\(^2\) a\(^{-1}\)), divided by the thickness of the DBL, \( \delta_i \) (m), for that solute, i.e.,

\[ \beta = D_i(\delta_i)^{-1} \] (3)

The sediment-side mass-transfer coefficient, \( k_s \), for a solid surface without porosity is the heterogeneous rate constant for reaction within that sediment. For a porous sediment, the functionality of \( k_s \) can be complex, depending on the exact form of the kinetics and the nature of transport within the pores. Nevertheless, for a linear dissolution reaction of a solid and molecular/ionic transport within the pores, such as we will consider here, \( k_s \) has the form (Boudreau and Guinasso 1982; Boudreau 2013):

\[ k_s = [\varphi(1 - \varphi)k_i D_i B]^{1/2} \] (4)

where \( \varphi \) is the porosity of the sediment, \( k_i \) is the apparent first-order rate constant for dissolution in the sediment (a\(^{-1}\)), \( D_i \) is the tortuosity-corrected diffusion coefficient of the solute of interest (m\(^2\) a\(^{-1}\)), and \( B \) is the fraction of dissolvable solid in the sediment; this \( k_s \) can be determined experimentally.

If \( k_s \ll \beta \), the diffusive flux is termed internal or sediment-side controlled, and the overall mass-transfer coefficient \( k^* \) tends toward \( k_s \). Reactions under the sediment-side-controlled regime include the dissolution of biogenic silica at the seafloor (Fanning and Pilson 1971; Schink et al. 1975) or the release of soluble reactive phosphate from lacustrine sediments (Schauer et al. 2006; Ding et al. 2016). Conversely, if \( \beta \ll k_s \), virtually the totality of the gradient in solute \( i \) is comprised within the DBL above the SWI, and the chemical flux across the DBL is termed external or water-side transport-controlled. Examples of water-side transport-controlled reaction are the dissolution of calcium carbonate at the deep-seafloor (Schink and Guinasso 1977; Santschi et al. 1991; Sulpis et al. 2017) and the accretion of manganese at the surface of deep-sea nodules (Boudreau and Scott 1978). Commonly, the diffusion through the DBL of most solutes is ruled by a combination of both regimes, termed mixed-control, e.g., dissolved oxygen (Jørgensen and Revsbech 1985; Hondzo 1998; Lorenzen et al. 1998; Rassmann et al. 2016) or radon (Homoky 2016; Cook et al. 2018), that display concentration gradients extending on both sides of the SWI. For more details on the theoretical framework of solute exchange across the SWI, we refer the reader to the comprehensive review published by Boudreau and Guinasso (1982).

The present study describes a newly developed experimental system that reproduces the DBL above the SWI over a range of thicknesses representative of various aqueous environments and, therefore, applicable to studies of external or mixed-controlled chemical exchanges through the DBL.

Reproducing natural scale DBLs at the SWI in laboratory experiments has been a long-term challenge for experimentalists. Attempts to simulate chemical boundary layers in laboratory flumes (Steinberger and Hondzo 1999; Røy et al. 2004) or stirred reactors (Keir 1983; Javadi and Khalili 2009) and benthic chambers (Santschi et al. 1983) have been less than satisfactory for several reasons: (1) In a classical linear flume (Fig. 1a), there is inevitably a leading edge of the reactive sediment on the flume floor. The chemical boundary layer does not exist until that edge is reached by the flow, and it grows downstream for a considerable length (roughly proportional to the square root of the distance); this means that a dissolution reaction, as we consider, is subject to internal control at the leading edge and can only shift to transport control somewhere downstream, where the DBL has become thick enough to exert its control. No such edge exists on the seafloor, and the water-side control always occurs for an appropriately fast reaction. Measurements in such laboratory flumes are thus compromised. (2) While stirred reactors (Fig. 1b) have been designed as an alternative to flumes, they suffer from exactly the same problem. The main flow may appear to be simply a circular flow over the bed surface, but that belies a pressure gradient created by the rotating bar or disk, which engenders a secondary flow that sweeps down the sides of the chamber and then across the sediment. The secondary flow encounters the sediment at the floor-wall intersection, where a chemical boundary layer will initiate and grow downstream across the sediment, as the flow crosses the floor. Thus, stirred reactors only hide the growing boundary layer problem; they do not eliminate it. Efforts have been made to replace rotating disks with a cone to counteract the pressure gradient (e.g., Javadi and Khalili 2009), but that has enjoyed questionable success, from a physicochemical point of view, as the angle of the cone then needs to be matched exactly to the rotation speed and that is exceedingly difficult to implement. Race-track-shaped flumes also suffer from this exact problem. (3) All these experimental systems typically fail to reproduce the slow flows encountered in low energy environments, such as abyssal plains or lakes, where the bottom currents are on the order of a few millimeters per second and the DBLs of several millimeters thick (Frenzel et al. 1990; Dade 1993; Sulpis et al. 2018). (4) Finally, measurements of fluxes from benthic chambers cannot be compared with any expected theoretical values, as no theory of mass transfer for such chambers currently exists. The solution for the flux with a growing laminar boundary layer in a flume does exist (e.g., Apelblat 1980), but it is not in closed form, making it inconvenient to use;
unfortunately, flows under deep-sea environmental conditions are usually turbulent in such flumes, making that solution approximate.

As a viable alternative, we build upon the development of rotating-disk reactors (Fig. 1c) that have been used extensively to study single crystal dissolution and precipitation kinetics (Tomlan and Hudson 1971; Sjöberg and Rickard 1983; Alkatant et al. 1998; Fredd and Fogler 1998; Gautelier et al. 1999; Chang and Abbad 2011) and which have a well-defined hydrodynamic (Schlichting 1968, pp. 93–99, 232–235, 508–509, 606–610) and mass transfer theory (Levich 1962, pp. 157–159). We adapt this approach for use with a (non-cohesive) sediment, where the sediment disk is mounted at the bottom of the reactor, rather than suspended upside down in the reactor.

**Materials and procedures**

**Experimental design**

The design and technical description of the rotating disk reactor are presented in Fig. 2. This reactor was designed to simulate slow flow in a reaction chamber containing a rotating-sediment disk, where the entire water velocity gradient is reproduced, from zero velocity at the SWI (no-slip condition) to constant full velocity at the top of the water level. The reactor can be thermally controlled, and the overlying water can be sampled without disturbing the flow.

A cylindrical polyvinyl chloride (PVC) disk support—the sediment container Fig. 2f,g—is screwed atop a stainless-steel shaft (Fig. 2l) driven by a high-torque motor (Fig. 2p) through a belt-and-pulley system (Fig. 2m,o). The shaft is maintained in its vertical axis by two ball bearings (Fig. 2j), located on either side of the height-adjustable belt drive (Fig. 2m). A nitrile seal (Fig. 2h) was placed around the shaft at the base of the reactor chamber, which holds the experimental solution and contains the rotating sediment disk, to prevent fluid leaks. The shaft height-adjustable pulley was connected to a motor with a rubber belt to mitigate the propagation of motor vibrations to the reactor chamber and prevent disruption of the DBL or flow. The motor was fixed vertically and powered by 12 V power supply through a variable potentiometer with digital power display (not shown), to precisely control the rotation speed. The reactor chamber is jacketed by a ~1-cm inner diameter (ID) wall through which water can be pumped from a thermostated water-recirculating bath to control the temperature of the experimental solution and sediment disk. PVC pieces a–d and i (in Fig. 2) were glued together with methylene chloride under a fume hood. Finally, the reactor was wrapped in an opaque and thermally insulating material, e.g., aluminum.
foil paper, to maintain a temperature-controlled environment and prevent light penetration; the latter is needed to curb the proliferation of photosynthetic organisms during week-to-month-long experiments.

During the experiment, the water in the reactor can be continuously or discretely analyzed to follow the evolution of the reaction. In the present study, we tested the reactor by measuring the dissolution kinetics of a CaCO₃-rich sediment. In this flow-through experiment, an undersaturated solution is introduced in the reactor, driving the solution to a new steady state controlled by the rate of introduction of the inlet solution and the rate of dissolution of the CaCO₃ in the sediment. The input solution was injected into the reactor chamber at a constant rate through a 0.51-mm ID Tygon PVC tube, using a multi-channel peristaltic pump (Gilson’s Minipuls™ 3 Peristaltic Pump). The pumping rate was determined for each setting in each experiment by weighing the amount of solution pumped out of the reactor over a fixed period of time. To keep a constant volume of solution in the reactor, the solution was withdrawn from the reactor by the same pump through a 0.76-mm ID tube fixed at the surface of the solution, as shown in Fig. 3. For users carrying out experiments on water containing suspended particles, a filter should be mounted at the mouth of the output tube to avoid clogging or modifying the solid:solution ratio. Sensors (e.g., pH electrode) should not be inserted directly within the reactor chamber, to avoid disrupting the DBL. Alternatively, discrete measurements should be performed in a separate vial where the outlet solution is collected or using sensors mounted within the inner wall to the reactor without altering its geometry or surface roughness. The former method.

| Pos. | Nb. | Description                  | Material           |
|------|-----|------------------------------|--------------------|
| a    | 1   | reactor top wall             | polyvinyl chloride |
| b    | 1   | thermostated bath connector  | polyvinyl chloride |
| c    | 1   | reactor external wall        | polyvinyl chloride |
| d    | 1   | reactor internal wall        | polyvinyl chloride |
| e    | 1   | Screw                        | stainless steel    |
| f    | 1   | disk wall                    | polyvinyl chloride |
| g    | 1   | disk support                 | polyvinyl chloride |
| h    | 1   | rotary shaft seal            | nitrile rubber / acrylic |
| i    | 1   | reactor bottom wall          | polyvinyl chloride |
| j    | 2   | ball bearing                 | Steel              |
| k    | 1   | ball bearing support         | stainless steel    |
| l    | 1   | rotary shaft                 | stainless steel    |
| m    | 2   | height adjustable pulley     | stainless steel    |
| n    | 1   | reactor support cylinder     | stainless steel    |
| o    | 1   | pulley belt                  | polyurethane rubber|
| p    | 1   | high torque motor            |                    |

Fig. 2. Technical drawing of the thermostated rotating-disk reactor.
could be adapted to monitor sediment diffusive fluxes by continuous flow analysis of dissolved elements or isotopic ratios (Brenna et al. 1997; Stoll et al. 2001; St-Jean 2003).

After each experiment, the upper section of the reactor (Fig. 2a–i) can be removed from its base (Fig. 2j–n) for cleaning. Under the experimental conditions tested to date, i.e., temperatures between 6°C and 25°C, rotation speeds between 1 and 10 rpm, seawater salinities between 0 and 35, the shaft can rotate for several weeks without interruption or leakage. If the seal deteriorates with time or usage, it can easily be replaced, as it is not glued to the reactor bottom wall, but simply pressure fitted. It is also preferable that the sediment disk holder rotate counterclockwise, so that it does not unscrew from the driving shaft.

Rotating disk theory

The motion of the seawater in the reactor chamber is driven by the spinning action of the immersed sediment disk, acting as a pump drawing in fluid axially and driving it away toward the outer edge of the disk in an outward spiral (von Kármán 1921; Escudier 1984; Hyun and Kim 1987). Levich (1962) modeled the rotating-disk flow system in a cylindrical coordinate system where the continuity and Navier-Stokes equations are decomposed into a radial, azimuthal, and axial component. Far above the SWI, the axial fluid velocity component is constant and downward while the other velocity components are nearly zero. In a thin layer of fluid adjacent to the SWI, the water is dragged by the rotating disk with an azimuthal velocity that increases as the surface of the disk is approached, until the azimuthal velocity of the disk is attained just above the SWI (Bircumshaw and Riddiford 1952; Levich 1962). Solutions to the equations that describe the velocity distribution throughout the body of the viscous fluid are reported in Schlichting (1968), and solutes concentration profiles, DBL thicknesses, and molecular diffusion fluxes above a rotating disk were derived and reported in the pioneering work of Levich (1962). It is not our intent here to review this theory; instead we refer the reader to the numerous previous studies in which mathematical descriptions and solutions to the rotating-disk hydrodynamics are provided (Levich 1962; Brady and Durlofsky 1987; Chang and Abbad 2011; Imayama 2012).

As noted by Levich (1962), the DBL thickness for a given species \( i \), \( \delta_i \), on a rotating disk is largely not a function of the distance from the axis of rotation, but is constant over the entire disk surface (except very close to the external edge, potentially subject to eddies), i.e., the DBL thickness can be considered as radially uniform. Assuming that the disk is sufficiently large, edge effects become negligible and, regardless of the distance from the rotation axis, the disk reactive surface is uniformly accessible from the standpoint of diffusion (Levich 1962; Frank-Kamenetskii 2015). Under this assumption, assuming laminar flow and steady state, \( \delta_i \) is a function of the (free solution) diffusion coefficient of the species, the kinematic viscosity of the fluid \( (\nu, \text{in m}^2 \text{s}^{-1}) \), and the angular velocity of the disk \( (\omega, \text{in rad s}^{-1}) \):

\[
\delta_i = 1.61\left(\frac{D_i}{\nu}\right)^{\frac{1}{4}} \sqrt{\frac{\nu}{\omega}}
\]  

(5)

This equation has been extensively and successfully applied by many experimentalists (Gregory and Riddiford 1956; Ellis-on and Cornet 1971; Lund et al. 1973; Sjöberg and Rickard 1983; Compton and Daly 1987), supporting the uniformity assumption of negligible DBL radial dependency.

The microtopography of the sediment bed can lead to small-scale horizontal variations of the DBL thickness, as documented by Gundersen and Jørgensen (1990): the DBL being thinner over the “peaks” and thicker over the “troughs.” In this study, we treat the DBL above our sediment disk as a single mean value, as we assume that the DBL negative anomalies on the micro-“peaks” approximately compensate for the positive anomalies on the micro-“troughs.” We acknowledge, however, that this treatment may oversimplify the three-dimensional structure of the DBL over rough natural sediment bed surfaces, which is not the case of the sediment used in this study, described below. To illustrate the range of DBLs achievable by the rotating-disk reactor, we report, in Fig. 4, the theoretical DBL thicknesses for \( \text{O}_2 \) \( (D_{\text{O}_2} = 1.33 \times 10^{-9} \text{ m}^2 \text{s}^{-1}) \); \( \text{CO}_2 \) \( (D_{\text{CO}_2} = 5.21 \times 10^{-10} \text{ m}^2 \text{s}^{-1}) \); \( \text{Zeebe} \) \( (11) \); and benzoic acid \( (C_7H_6O_2) \), \( D_{C_7H_6O_2} = 6.7 \times 10^{-10} \text{ m}^2 \text{s}^{-1} \); Delgado 2007) as a function of the rotating speed of the disk \( (\omega) \), for a temperature of 10°C in freshwater \( (\nu = 1.31 \times 10^{-6} \text{ m}^2 \text{s}^{-1}) \).

By adopting Eq. 5 and substituting it into Eqs. 1 and 2, the expression for the diffusive flux of the species \( i \) \( (f_i) \) across the DBL above the rotating sediment disk becomes:

\[
f_i = \frac{k_{i,x} \times 0.62}{k_{i,x} + 0.62} \left( \frac{\partial \delta_i}{\partial x} \right) \left( [i]_s - [i]_0 \right)
\]  

(6)

where \([i]_s\) is the concentration of \( i \) at or below the SWI, at the lower limit of the concentration gradient, i.e., at saturation, and \([i]_0\) is the concentration of \( i \) in the bulk water, i.e., at the
top of the water height in the reactor chamber. Note that, in our experimental apparatus, the sediment disk is placed at the bottom of the reactor chamber; thus, the diffusive flux \( j_i \) is upward.

**Method validation**

We assessed the validity of the rotating-disk reactor by measuring alkalinity fluxes resulting from \( \text{CaCO}_3 \) dissolution in a sediment disk containing natural calcitic grains (foraminifera) immersed in natural seawater and then comparing these measurements with the predicted diffusive fluxes (\( j_i \)) and DBL thicknesses (\( \delta \)) from the theory described above.

Calcite dissolution in an aqueous solution can be described by the reaction:

\[
\text{CaCO}_3(s) \rightarrow \text{Ca}^{2+}(aq) + \text{CO}_2^{−}(aq)
\]  

(7)

In seawater, at a salinity of 35, [\( \text{Ca}^{2+} \)] is about two orders of magnitude larger than [\( \text{CO}_2^{−} \)]. Given the nearly invariant [\( \text{Ca}^{2+} \)] in the deep ocean, and in our reactors, the saturation state of seawater with respect to calcite, i.e., \( \Omega_C = [\text{Ca}^{2+}][\text{CO}_2^{−}]/K^*_{sp} \), where \( K^*_{sp} \) is the stoichiometric solubility constant of calcite at in situ T, P, and S, as given in Mucci (1983) and Millero (1995), can simply be represented by the ratio of the carbonate ion concentration in the overlying water, [\( \text{CO}_2^{−} \)\(_{SW} \)], to the carbonate ion concentration at equilibrium with calcite, [\( \text{CO}_2^{−} \)\(_{eq} \)]. The quantity \[ [\text{CO}_2^{−} \]\(_{eq} \) − [\( \text{CO}_2^{−} \)\(_{SW} \)]\] is a measure of the disequilibrium and the driving force that controls the rate (\( r \)) of the calcite dissolution reaction at the SWI. Here, we consider the calcite dissolution rate at the SWI as a diffusive flux (\( j_{\text{CO}_2} \)) in response to a \( \text{CO}_2^{−} \) concentration gradient (\( \Delta[\text{CO}_2^{−}] \)), following Eq. 1.

We used a natural foraminiferal sand from the top 10 cm of a sediment gravity core sampled in the Southern Central Pacific Ocean (26°5.07’S; 146°45.01’W) at 1916 m depth in April 2010. This sediment was composed at ~ 98% of *Globigerinoides ruber* (T. de Garidel-Thoron pers. comm.). These foraminifera were rinsed with deionized water and dried at room temperature before the experiments. The foraminiferal sediment was then mixed with natural seawater collected at ~ 400 m depth in the Gulf of Saint Lawrence in May 2017. The seawater was aged for several months in polypropylene carboys before being filtered and calcite-equilibrated following the protocols described in Sulpis et al. (2017). The main criteria used to assess the suitability of the sediment was the cohesion and stability of the mixture, especially at the SWI when the beaker was moved. The fresh disks were stored in calcite-equilibrated seawater and kept in the dark to avoid the proliferation of bacteria until used within a few days. Based on weight loss upon drying at low temperature (< 50°C), a solid density of 2.71, and the salinity of the seawater, the primary porosity (\( \phi \)) of the foraminiferal sand sediment was estimated at 0.84 ± 0.03 (\( n = 3 \)).

The calcite contained in the simulated sediment, if exposed to a solution undersaturated with respect to calcite, should dissolve. In order to obtain an undersaturated solution, a fraction of the treated seawater was acidified by adding dilute hydrochloric acid (~1N) to reduce the total alkalinity (TA) from ~ 2300 to ~ 400 μmol kg\(^{-1}\) and \( \Omega_C \) from ~ 4 to ~ 0.15. Seawater acidification was performed following the protocols described in Sulpis et al. (2017). This acidified seawater served as the input solution and was pumped into the reactor, initially filled with calcite-equilibrated seawater (\( \Omega_C = 1 \)).

The evolution of the dissolution reaction was assessed by monitoring the pH\(_r\) of the experimental solution by collecting the output seawater in a separate flow-through and sealed vial at a fixed acidified seawater pumping rate. Once a steady-state pH\(_r\) was achieved, an aliquot of the output solution was collected and analyzed to determine the steady-state TA, S, and soluble reactive phosphorus (SRP) concentration. The pumping rate was then increased and, consequently, the residence time of the solution in the reactor, as well as the saturation state of the reactor solution decreased, triggering an increase in the calcite dissolution rate. Residence times of the input solution in the reactor varied between 28 and 303 h, corresponding to input flow rates between 7 and 2 g hr\(^{-1}\).

Following Sulpis et al. (2017), the dissolution rate \( r \) (mol m\(^{-2}\) a\(^{-1}\)) was determined from the difference in the composition of the input and output solutions, according to:

\[
r = \frac{m_{sw}(\text{TA}_{output} - \text{TA}_{input})}{2A \Delta t}
\]  

where \( m_{sw} \) is the mass of seawater in the reactor chamber, \( \text{TA}_{output} \) is the steady-state TA of the output solution (see Fig. 3),

![Diffusive boundary layer thickness](image)

**Fig. 4.** Predicted DBL thicknesses (\( \delta \)) as a function of the disk rotation speed (\( \omega \)) in water at 10°C for the carbonate ion (\( \text{CO}_2^{−} \), solid blue line), dissolved oxygen (\( \text{O}_2 \), dashed green line) and benzoic acid (\( \text{C}_7\text{H}_6\text{O}_2 \), dotted dashed orange line) computed using Eq. 5.
$\Delta T_{\text{input}}$ is the TA of the input solution, $A$ is the sediment surface area, and $\Delta t$ is the residence time of seawater in the reactor chamber.

Analytical procedures

The pH$_T$ of the output solution was measured in a flow-through sealed vial with a Radiometer Analytical$^{\text{®}}$ GK2401C combination glass electrode, connected to a Radiometer Analytical$^{\text{®}}$ PHM84 pH/mV-meter. Prior to each measurement, the electrode response (in mV) was calibrated against three NIST-traceable buffer solutions: pH-4.00, pH-7.00, and pH-10.00 at 25$^\circ$C, and a TRIS buffer solution with an assigned pH$_T$ of 8.100 at $S_T = 35$ and 25$^\circ$C to convert these measurements to the "total" hydrogen ion concentration scale (pH$_T$).

TA was determined by potentiometric titration of both the initial reservoir solution and subsequent steady-state solutions with a dilute hydrochloric acid solution (0.005N < [HCl] < 0.010 N, according to the TA of the sample), using an automated Radiometer (TitraLab865$^{\text{®}}$) titrator and a Red Rod$^{\text{®}}$ combination pH electrode (pHC2001). The dilute HCl titrant was calibrated prior to, during, and after each titration session, using certified reference materials (CRM Batch #140 and #154) provided by Andrew Dickson (Scripps Institute of Oceanography). The reproducibility of the method was better than 0.5%. The uncertainties presented in this study for TA, as well as steady-state pH$_T$, were estimated based on multiple replicate measurements of each sample.

The salinity of the experimental solution was monitored regularly by potentiometric titration of an aliquot of the output solution with a AgNO$_3$ solution calibrated with IAPSO standard seawater. The measurements were performed with an automated Radiometer (TTT80) titrator, a silver electrode, and a mercuric sulfate reference electrode. The reproducibility was better than 0.2%.

The SRP concentration of the initial reservoir and steady-state solutions was determined spectrophotometrically using the technique developed by Murphy and Riley (1962) and described in Grasshoff et al. (1999). The absorbance of the phosphomolybdate reaction product was measured manually at 880 nm with a Hewlett-Packard Agilent 8453 UV-visible spectrophotometer using a 10-cm cell. The detection limit was 0.01 $\mu$M and the reproducibility was better than 0.5%. Calibration curves were constructed by four successive dilutions of a 10-mM standard phosphate stock solution prepared in a 0.7 M NaCl solution to prevent salt effects and the corresponding $R^2$ values were always better than 0.999.

The Microsoft Excel version of CO2SYS (Pierrot et al. 2006), based on the original algorithm of Lewis and Wallace (1998), was used to calculate the initial reservoir and steady-state solution $p$CO$_2$, $[\text{CO}_2^{\text{eq}}]$ and $[\text{CO}_2^{\text{eq}}]$ for the steady-state pH$_T$ and TA, at in situ $T$, $S$, and [SRP]. The uncertainties on $[\text{CO}_2^{\text{eq}}]$ values reported here were computed separately and included errors of the solubility constant estimate. All calculations were carried out on the total hydrogen ion concentration scale, using the stoichiometric carbonic acid dissociation constants determined by Lueker et al. (2000), the total boron concentration [B]$_T$ value from Uppström (1974), and the standard acidity constant of the HSO$_4^-$ ion from Dickson (1990).

Results

We ran 16 distinct week-long dissolution experiments at three different disk-rotation speeds, over a range of $(\text{CO}_2^{\text{eq}}) - [\text{CO}_2^{\text{eq}}]$ values from near equilibrium $(\text{CO}_2^{\text{eq}}) - [\text{CO}_2^{\text{eq}}] = 3.4 \mu$mol kg$^{-1}$) to highly undersaturated $(\text{CO}_2^{\text{eq}}) - [\text{CO}_2^{\text{eq}}] = 28.2 \mu$mol kg$^{-1}$). The corresponding saturation states with respect to calcite ($\Omega_c$) are 0.94 and 0.33, respectively. calculated $p$CO$_2$ in steady-state aliquots varied between 382 and 790 $\mu$atm, measured salinities ranged from 34.82 to 35.90, and [SRP] was between 0.9 and 3.1 $\mu$mol kg$^{-1}$. We report the data obtained from each experiment in Table 1.

Figure 5 presents the measured calcite dissolution rates normalized by the SWI surface area, as a function of (a) calcite undersaturation state with respect to calcite $(1 - \Omega_c)$ and (b) disk rotation rate. The measured dissolution rates follow a square-root dependency on the disk-rotation rate predicted by Eq. 6 and are linearly dependent on $(1 - \Omega_c)$ over the range of undersaturation rates investigated. A comparison of the observed dissolution rates, estimated from the alkalinity fluxes, using Eq. 8, with theoretical dissolution fluxes, computed as a function of the disk rotation rate and $(\text{CO}_2^{\text{eq}}) - [\text{CO}_2^{\text{eq}}]$ from Eq. 6, is presented in Fig. 6a. Our measured dissolution rates (vertical axis in Fig. 6a) are linearly correlated with the theoretical dissolution rates (horizontal axis in Fig. 6a) with a coefficient of determination ($R^2$) of 0.96. In Fig. 6b, we compare the DBL thicknesses computed from the measured dissolution rates, using Eqs. 1–3, with the theoretical DBL thicknesses derived using Eq. 5. Note that we did not measure directly the thickness of the DBL. Instead, the values on the vertical axis of Fig. 6b are the DBL thicknesses that are required to explain our measured dissolution fluxes, as computed using Eqs. 1–3; thus, Fig. 6b compares values inferred from measurements with values from the Levich (1962) theory. A statistical analysis reveals that the inferred values are linearly correlated to the predicted values with a $R^2$ of 0.80. These results show that diffusive fluxes in the rotating-disk reactor can be successfully predicted by the Levich (1962) theory.

To interpret these results in terms of controlling mechanism for calcite dissolution at the SWI, we compared our results with theoretical sediment-side, water-side, and overall mass-transfer coefficients as a function of the disk-rotating speed. To obtain the mass-transfer coefficient for each of the data points, we divided the measured dissolution rate by the disequilibrium CO$_2$ concentration $(\text{CO}_2^{\text{eq}}) - [\text{CO}_2^{\text{eq}}]$; these experimental mass-transfer coefficients are the black circles in Fig. 7. The sediment-side mass-transfer coefficient for calcite dissolution in sediment beds ($k_s$, the dashed blue line
Table 1. Description of dissolution experiments, steady-state seawater chemistry, and experimental results for sediment disks containing foraminifera in natural seawater. \( \omega \) is the disk rotation rate, \( \Delta t \) is the residence time of water in the reactor, \( A \) is the surface area of the sediment disk, \( m_{SW} \) is the mass of water in the reactor, \( \rho_H \) is the steady-state seawater pH on the total proton concentration scale, \( T_{A_{out}} \) is the steady-state total alkalinity, \( [CO_3^{2-}]_{SW} \) is the steady-state \( CO_3^{2-} \) concentration, \( \text{[SRP]} \) is the steady-state soluble reactive phosphate concentration, \( S \) is the steady-state salinity, \( r \) is the measured calcite dissolution rate, \( \delta \) is the diffusive boundary layer thickness computed from the measured \( r \), and \( k^* \) is the overall \( CO_3^{2-} \) mass-transfer coefficient computed from the measured \( r \).

| Experiments characteristics | Steady-state seawater chemistry | Results |
|-----------------------------|---------------------------------|--------|
| \( \Delta t \) (h) | \( A \) (cm\(^2\)) | \( m_{SW} \) (g) | \( \rho_H \) | \( T_{A_{out}} \) (mol kg\(^{-1}\)) | \( [CO_3^{2-}]_{SW} \) (mol kg\(^{-1}\)) | \( \Omega_C \) | \( \text{[SRP]} \) (\( \mu \text{M} \)) | \( S \) | \( r \) (mol m\(^{-2}\) a\(^{-1}\)) | \( \delta \) (\( \mu \text{m} \)) | \( k^* \) (m a\(^{-1}\)) |
| (\( \pm 0.1 \)) | (\( \pm 3\% \)) | (\( \pm 0.1 \)) | (\( \pm 0.003 \)) | (\( \pm 0.5\% \)) |

**Disk-rotation rate (\( \omega \)) of 1 rpm**

- 27.6 35.3 212.7 7.423 523.1 ±1.8 13.4 ±1.8 0.33 ±0.05 0.9 35.12 1.3 ±0.1 486 ±69 45 ±6
- 52.9 35.3 212.7 7.471 634.4 ±2.8 18.2 ±2.9 0.45 ±0.07 1.1 35.21 1.2 ±0.1 409 ±65 52 ±8
- 80.2 35.3 212.7 7.529 1077.1 ±2.6 36.1 ±2.7 0.91 ±0.08 1.0 35.90 0.2 ±0.1 395 ±31 54 ±43
- 95.5 35.3 212.7 7.529 1110.5 ±1.1 36.6 ±3.2 0.90 ±0.09 1.0 34.99 0.3 ±0.1 322 ±24 64 ±48
- 105.4 35.3 212.7 7.532 721.2 ±2.3 23.3 ±2.4 0.58 ±0.06 0.9 35.54 0.8 ±0.1 470 ±82 47 ±8
- 198.3 35.3 212.7 7.509 1132.2 ±1.9 36.4 ±1.9 0.91 ±0.06 1.0 35.78 0.2 ±0.1 579 ±36 39 ±25

**Disk-rotation rate (\( \omega \)) of 3 rpm**

- 39.1 72.4 537.4 7.498 605.1 ±3.0 18.4 ±3.1 0.46 ±0.08 2.3 35.75 1.8 ±0.2 242 ±50 80 ±16
- 64.9 72.4 537.4 7.506 1095.0 ±2.0 34.5 ±2.0 0.85 ±0.06 1.1 35.21 0.5 ±0.3 264 ±179 75 ±51
- 75.8 72.4 537.4 7.568 740.0 ±1.8 25.9 ±1.8 0.64 ±0.05 2.0 35.00 1.5 ±0.1 191 ±36 95 ±18
- 82.7 72.4 537.4 7.524 1087.8 ±1.3 35.8 ±1.3 0.89 ±0.04 1.0 35.46 0.3 ±0.2 331 ±249 62 ±47
- 167.8 72.4 537.4 7.548 819.1 ±2.0 28.0 ±2.1 0.69 ±0.06 1.0 35.41 0.8 ±0.1 331 ±73 62 ±14
- 192.6 72.4 537.4 7.523 1172.3 ±2.0 38.3 ±2.1 0.94 ±0.07 1.4 35.09 0.3 ±0.1 221 ±196 85 ±76

**Disk-rotation rate (\( \omega \)) of 10 rpm**

- 52.4 72.4 548.5 7.758 723.2 ±0.6 25.9 ±0.6 0.64 ±0.03 1.7 35.22 2.1 ±0.2 110 ±17 136 ±21
- 115.5 72.4 548.5 7.549 1123.5 ±2.0 39.3 ±2.1 0.94 ±0.06 1.2 35.82 0.4 ±0.2 179 ±164 99 ±91
- 151.3 72.4 548.5 7.664 829.9 ±1.0 35.5 ±1.0 0.87 ±0.05 3.1 35.07 1.0 ±0.1 87 ±31 154 ±54
- 302.7 72.4 548.5 7.623 934.6 ±1.2 37.1 ±1.2 0.91 ±0.05 2.2 35.02 0.6 ±0.1 123 ±59 127 ±61

Fig. 5. (a) Measured calcite dissolution rates \( r \) as a function of the steady-state undersaturation state of seawater with respect to calcite \((1 - \Omega_C)\), for three different rotation rates \((\omega = 1, 3, \text{and } 10 \text{ rpm})\), shown in green, turquoise, and blue, respectively. Solid lines are linear regression fits to the data for each rotation-rate group, shown along with their equations and coefficients of determination \((R^2)\). (b) Measured \( r \) as a function of \( \omega \) for different groups of steady-state \( \Omega_C \). Dashed lines indicate the theoretical \( r \) values computed using Eq. 6 as a function of \( \omega \) for a range of \( \Omega_C \), for comparison with our data. Each data point is shown with an error bar that represents one standard deviation.
in Fig. 7) is from Sulpis et al. (2017), set as $k_s = 326.9 \pm 39.5 \text{ m a}^{-1}$, which is similar to the value calculated by Boudreau (2013) from the Keir (1983) data. The water-side mass-transfer coefficient ($\beta$, the dashed green line in Fig. 7) is obtained by dividing the diffusion coefficient of CO$_2$ at 25°C by the DBL thickness in our reactor, obtained from the Levich (1962) theory through Eq. 5. Finally, the overall mass-transfer coefficient ($k^*$, the solid red line in Fig. 5) was derived from Eq. 2. As can be seen in Fig. 7, our data fall on the predicted overall mass-transfer coefficients and follow a square-root dependency on the disk-rotation speed, as it should be observed for a water-side transport-controlled reaction. In addition, $\beta \ll k_s$ for the entire range of hydrodynamic conditions investigated in this study. These experimental results constitute further evidence that, in these deep-seafloor-like experimental conditions, and in the absence of respiration-driven dissolution, calcite dissolution is controlled by diffusion through the DBL above the sediment bed.

**Discussion**

We initially designed this rotating-disk reactor to reproduce well-defined hydrodynamics (flow) above a sediment bed in the laboratory, generating DBLs with thicknesses representative of most natural sedimentary aquatic environments, including very low-energy environments such as deep lakes or abyssal plains. Although experimental systems have been developed in the past to simulate benthic hydrodynamics (Keir 1983; Javadi and Khalili 2009), these systems often generate uncharacterized turbulence (Sulpis et al. 2017), spawning DBLs of unknown thicknesses. Although flumes (Steinberger and Hondzo 1999; Ray et al. 2004) seemingly offer a potential solution to this issue, as noted above, the resulting DBLs are again difficult to calculate, compromising the interpretation of experimental results.

We have adapted the rotating-disk reactors traditionally used for the study of single crystal dissolution/precipitation kinetics (Tomlan and Hudson 1971; Sjöberg and Rickard 1983; Alkattan et al. 1998; Fredd and Fogler 1998; Gautelier et al. 1999; Chang and Abbad 2011) to a (non-cohesive) sediment, placing the disk at the bottom of the reactor and inducing a rotation of the sediment through a pulley system in order to attenuate motor vibrations. Based on our experimental results, we believe that the reactor fulfills all of our initial requirements. It produces a well-defined flow of water over a sediment disk, unaffected by stirrer/motor vibrations or turbulence or by the presence of sensors, and generates diffusive fluxes and DBL thicknesses that are well predicted by theory. The latter are similar in thickness to deep lake and ocean environments.

We note that during one experiment carried out using sediment disks of pure synthetic calcite and quartz sand, i.e., with a non-cohesive texture and with grains readily movable, we observed millimeter-scaled spiraling sediment ripple marks developing at the surface of the sediment after a few weeks. These sedimentary structures are usually observed on sediment beds under low flow regimes (Boggs 2012). Thus, our system is also able to reproduce, in the laboratory, natural sedimentary structures.

In addition to its ability to successfully reproduce DBLs encountered in benthic environments, we wish to highlight a few practical benefits of this reactor. First, this reactor can be assembled at a relatively low cost. All components and materials can be purchased from traditional suppliers. With the exception of applications involving trace metals or requiring peculiar properties, engineering the different components out of PVC and stainless steel, as shown in Fig. 2, should suffice. Second, the reactor is portable and, thus, can be brought to the field to perform experiments on freshly sampled sediments, but a mobile thermostatic system and peristaltic pump
may be required. Third, the reactor can be entirely disassembled for maintenance and cleaning.

One limitation of this system is that it is difficult to place sensors into the sediment disk to follow the reaction progress (e.g., O\(_2\) or pH microelectrodes) because these would likely disrupt the flow and the DBL above the sediment disk. To remedy this issue, sensors (e.g., microelectrodes) could be inserted from below the sediment disk, instead of penetrating the sediment on the water side, or inserted in the wall of the reactor. Future work should focus on quantifying the spatial distribution of the DBL, rather than assuming its uniformity over the entire disk surface, as we did here following Levich (1962). This could be achieved with multiple microelectrode measurements or using optical methods such as particle image velocimetry. It should be noted that, although the dimensions presented in Fig. 2 are suitable for the study of water-side transport-controlled reactions, such as the dissolution of calcite, they may not be ideal to characterize sediment-side controlled fluxes. The sediment disk in Fig. 2 is only 2 cm thick and likely too thin to reproduce realistic solute concentration gradients that would develop during early diagenesis.

**Conclusion**

The thermostated rotating-disk reactor, as described in this article, can reproduce DBL thicknesses that are typically encountered at an SWI. Calcite-rich sediment dissolution experiments reveal that the DBL thickness and diffusive fluxes through the SWI can be accurately predicted using the equations also described in this communication. In particular, this reactor can reach slow flow rates and thick DBLs, representative of low-energy aquatic natural environments, such as lakes or abyssal plains. The present rotating-disk reactor is a practical and suitable alternative to other traditional experimental reactors, e.g., flumes or stirred reactors, which may be more adapted to high-energy benthic conditions.

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Conflict of Interest
None declared.

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