



Porewater CO₂–carbonic acid system chemistry in permeable carbonate reef sands



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ABSTRACT

Porewater was collected from highly permeable, carbonate-rich, sandy sediments at two locations on Oahu, Hawai'i, CRIMP-2 on the Kaneohe Bay barrier reef and Ala Wai on a fringing coral reef nearshore to the Ala Wai canal and urban Honolulu. Samples were collected at the sediment–water interface and from porewater wells installed at sediment depths of 2, 4, 6, 8, 12, 16, 20, 30, 40, and 60 cm. Total alkalinity and dissolved inorganic carbon were enriched, relative to the overlying water column, and ratios of TA:DIC at the two sites (0.80 and 0.93) suggest that aerobic respiration and sulfate reduction – both coupled with carbonate mineral dissolution – in the oxic and anoxic layers, respectively, are the major controls on the biogeochemistry of the sediment–porewater system. The porewater was approaching thermodynamic saturation with respect to aragonite with increasing depth ($\Omega = 1.2$ –3.5) and was found to be undersaturated with respect to all phases of magnesian calcite ($\Omega = 0.3$ –0.9) containing greater than 12 mol% MgCO₃. In addition to microbial controls on porewater diagenesis, transient physical events in the water column, such as swells and changing bottom current speeds, appear to exert a strong influence on the porewater chemistry due to the highly permeable and porous nature of the sediments. Profiles collected before and after swell events at each location show an apparent flushing of the porewater system, replacing low pH, high DIC interstitial waters with seawater from the overlying water column. Based partially on the results of our porewater analysis, we hypothesize that future changes in surface water DIC and pH resulting from ocean acidification (OA) could have a very significant impact on the dissolution rates of metastable skeletal and abiotic carbonate phases of varying magnesian calcite compositions (Mg-calcite) and aragonite. This is especially important in sandy reef sediments like those of this study, which are greatly influenced by the overlying water column. As the carbonate mineral saturation state of the overlying water column continues to decrease due to OA, an increase in carbonate mineral dissolution is expected and the high advective rate of water exchange between the porewater of sandy sediments and the overlying water column, as observed in this study and others, along with increased rates of dissolution of metastable carbonate phases, could lead to significantly higher future rates of mass transfer of TA and DIC between the sediments and the overlying water column. This may result in a deficit of the CaCO₃ balance in some reef ecosystems and a decrease in accretion rates. Analysis of our porewater work in conjunction with previous studies of the porewater chemistry of Kaneohe Bay, Oahu in both siliciclastic-rich and siliciclastic-poor carbonate sediments leads to the conclusion that the porewaters of the former are more strongly buffered with respect to pH than those of the latter due to reverse weathering reactions. Thus carbonate-rich sandy sediments of reefs with little terrestrial influence and aluminosilicate detritus may become more susceptible to calcium carbonate loss due to the enhanced environmental and microbial dissolution of carbonate substrates expected due to OA.

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1. Introduction

Permeable sandy carbonate sediments can constitute up to 90% of the calcium carbonate (CaCO₃) found on coral reefs (e.g., Cyronak et al., 2013b; Gattuso et al., 1998), but despite their ubiquitous presence in reef ecosystems, they were largely ignored in terms of porewater studies prior to the 1980's (Boudreau et al., 2001; Jahnke et al., 2005; Janssen et al., 2005). These sands are composed primarily of skeletal

reef material from the aragonitic and magnesian-calcitic skeletons, shells and tests of many organisms (e.g., Chave, 1954; Morse et al., 1985; Morse and Mackenzie, 1990). Despite the high concentrations of these metastable carbonate mineral phases, it was believed that these sandy sediments were biogeochemically unimportant reservoirs in terms of mineral–water reactions and early diagenetic processes were insignificant due to the lack of organic matter, whose abundance in sediments generally decreases with increasing mineral particle grain size (Janssen et al., 2005). Given their larger grain size, permeability (measured in Darcys, 1 D = 10⁻⁸ cm²) can be orders of magnitude higher in sands (7–455 D) than in silts (0.0026–3.4 D) (Burdige,

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2006). The higher permeability in sandy sediments is one factor that leads to the increased relative importance of advective solute fluxes, which are driven by changes in pressure gradients, as opposed to fine-grained sediments where diffusive solute fluxes, driven by molecular diffusion, are the main drivers of solute transport. (e.g., Huettel and Gust, 1992; Shum, 1993; Boudreau, 1997; Precht and Huettel, 2004; Jahnke et al., 2005; Janssen et al., 2005). Surface waves, topographical sediment features such as ripples, tidal pumping, changes in near-bed current velocities, and temperature and salinity gradients can all alter pressure gradients and drive advection within highly permeable sediments (Huettel and Webster, 2001).

Differences in the physical properties between permeable sands and fine-grained sediments require that very different sampling methods be used when studying biogeochemical reactions and solute mass transfer in the two media (Jahnke et al., 2005). Although possible – with vibracores and to some extent, manual push cores – obtaining a permeable (e.g., sandy) sediment core and its interstitial waters without disrupting the physical structure of the sediment and its porewater gradient (or losing porewater) is more difficult than with fine-grained sediments. Yamamoto et al. (2015) were only able to measure porewater chemistry in very shallow cores (~2–3 cm). In addition, it is difficult to bring a permeable sediment core back to the laboratory and recreate the process of advection, driven by currents and pressure gradient forces, in a laboratory environment during the incubation of a sandy core. Thus, studies of solute fluxes in sands, including total alkalinity (TA) and dissolved inorganic carbon (DIC), are often limited to interpretations based on diffusive transport, oversimplifying the processes occurring in these systems (Huettel et al., 1996; Janssen et al., 2005). As a result, *in-situ* studies of permeable sediments are highly desirable, if not necessary.

The use of annular-flow benthic chambers has been one approach to study sandy sediment/water column fluxes because the chambers represent more accurately the circulation patterns of water movement in the natural environment than do laboratory core incubations. Once the chamber is anchored in the sediment, a stirring disc produces water flow within the chamber that mimics turbulent motion in the overlying water and induces more natural advection of porewater (Huettel and Rusch, 2000). Annular-flow benthic chambers have been employed in a wide variety of studies to measure solute fluxes in sandy sediments, including studies involving calcium carbonate (CaCO_3) dissolution and TA fluxes (Huettel and Rusch, 2000; Rao et al., 2012; Cyronak et al., 2013a,b). Nevertheless, while chamber studies can provide valuable data for determining solute fluxes and can reasonably simulate natural conditions, these experiments do not provide detailed porewater solute concentration profiles extending into the sediments.

The only reasonably reliable method for measuring the depth concentration profiles of biogeochemically important solutes in porewater under natural conditions is via direct *in situ* sample collection (e.g., Sansone et al., 1988a,b; Tribble et al., 1988; Falter and Sansone, 2000b; Burdige et al., 2008; Burdige et al., 2010; Fogaren et al., 2013). Morse et al. (1987) made use of a harpoon sampler (“sand sucker”) to extract interstitial water directly from permeable sediments, and Burdige and colleagues have employed porewater “sippers” designed to be inserted directly into the sediment (Burdige and Zimmerman, 2002). Sippers are extremely valuable because they can collect water samples from multiple locations down to a depth of ~20 cm in the sediment column. This technique has been utilized with great success in determining the role of seagrass beds in carbonate dissolution processes (Burdige and Zimmerman, 2002; Burdige et al., 2010, 2008). Sansone et al. (1988a, 1988b) developed another method of collecting shallow (<1 m) porewater from permeable sandy sediments. Initially they found that the approach for sampling porewater from consolidated dense reef frameworks using cased wells did not work in unconsolidated sediments, so they utilized pseudo-permanently installed stainless steel, porewater wells (e.g., Sansone et al., 1988a, 1988b). Eventually

PVC wells were used to eliminate metal contamination and corrosion (Falter and Sansone, 2000b). These wells allowed relatively easy sampling at a fine vertical spatial resolution in the sediment (see Section 2.2). More recently, Fogaren et al. (2013) measured oxygen penetration and nutrient remineralization employing porewater wells deployed on the south shore of Oahu near one of the locations of the present study.

In this paper, we present the first quantitative temporal study of TA and pH as a function of depth in sediment interstitial water of highly permeable, carbonate reef sands using a well-point methodology down to a depth of 60 cm. The study primarily focuses on the high temporal and spatial variability of the porewater CO_2 –carbonic acid system chemistry in this type of sediment facies and its relationship to the carbon chemistry of the overlying water column. We investigate how microbial activity affects DIC, TA, and carbonate mineral saturation states (Ω) under oxic and anoxic conditions. In addition, we hypothesize that the highly permeable nature of sandy carbonate reef sediments will have a significant effect on the sediment porewater geochemistry response to increasing OA. Changes in porewater CO_2 –carbonic acid system chemistry due to both natural processes and ocean acidification, combined with the expected decreases in coral and coralline algae calcification rates under increasing OA and temperature, make it probable that many coral reefs will experience a net deficit in their CaCO_3 budget, potentially leading to a switch from net accretion to net erosion of some reef ecosystems (Andersson, 2015; Andersson et al., 2009, 2006, 2005; Eyre et al., 2014; Kleypas et al., 1999; Mackenzie and Andersson, 2013; Silverman et al., 2009). Thus, it is critical that we investigate and understand the complex processes and multiple mechanistic factors that contribute to the biogeochemistry of the highly permeable, sandy sediment–porewater CO_2 –carbonic acid system.

2. Methodology

2.1. Study sites

Sampling was performed at two main locations around Oahu, Hawai'i: the CRIMP-2 and Ala Wai buoys (Fig. 1) from 08/23/2012 through 07/30/2014. Both buoys have been deployed since June 2008 and are part of the NOAA/PMEL (Pacific Marine Environmental Laboratory) carbon program. The buoys contain MAPCO2 systems (Moored Autonomous pCO_2) that measure atmospheric and seawater CO_2 every three hours, along with a complement of ancillary data. Data are transmitted to PMEL servers once per day via Iridium satellite and can be viewed on the internet in near-real time at <http://pmel.noaa.gov/co2/story/Coral+Reef+Moorings>. Details of the measurement technique and buoy schematics can be found in Massaro et al. (2012) and Drupp et al. (2013). In addition to the CO_2 measurements, each buoy serves as a platform for various other instruments and experimental work. These locations, described in the following sections, serve as central hubs for the porewater work described here and provide continuous data about the overlying water physical, chemical, and biological conditions.

2.1.1. Kaneohe Bay barrier reef

Kaneohe Bay, the site of the CRIMP-2 buoy, is the largest semi-enclosed bay in Hawai'i and located on the northeast (windward) coast of the island of Oahu. The bay is home to a large barrier reef, approximately 2 km wide and 5 km in length. The CRIMP-2 buoy is moored over a sand patch, in ~3.5 m of water, immediately adjacent to the leeward back edge of the barrier reef (see Fig. 1). The mean depth across the reef is ~2 m, but varies from <1 m to 4 m. Tradewinds blow from the northeast ~80% of the year, resulting in a nearly linear flow of water across the reef flat (Drupp et al., 2013; Giambelluca et al., 1986; Lowe et al., 2009a; Massaro et al., 2012). Water chemistry is biogeochemically altered in transit across the reef (4–24 h residence time), resulting in decreased alkalinity and pH of reef surface water

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