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Aragonite saturation state in a monsoonal upwelling system off Java, Indonesia

Liang Xue [a,*], Huiwu Wang [a], Li-Qing Jiang [b], Wei-Jun Cai [c], Qinsheng Wei [d], Hongjun Song [d], Rita Tisiana Dwi Kuswardani [e], Widodo S. Pranowo [e], Brian Beck [b], Lin Liu [a], Weidong Yu [a]

[a] *Center for Ocean and Climate Research, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China*
[b] *Cooperative Institute for Climate and Satellites–Maryland, Earth System Science Interdisciplinary Center, University of Maryland, College Park, MD 20740, USA*
[c] *School of Marine Science and Policy, University of Delaware, Newark, DE 19716, USA*
[d] *Marine Ecology Research Center, First Institute of Oceanography, State Oceanic Administration, Qingdao 266061, China*
[e] *Research and Development Center for Marine and Coastal Resources, Agency for Marine and Fisheries Research and Development, Ministry of Marine and Fisheries Research, Indonesia*

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ABSTRACT

Aragonite saturation state (Ω_{arag}) and its influence from upwelling along the southern coast of Java, Indonesia were examined using carbonate and hydrographic data collected from 22 September to 2 October 2013. Results showed that sea surface Ω_{arag} was lower in the upwelling area (2.97–3.44) than in the nonupwelling area (3.45–3.57), with the lowest value in the eastern part of the study area. We used a two end-member mixing model to separate contributions on Ω_{arag} from two processes associated with upwelling: physical transport vs. biological production. Results indicated that physical transport induced at least a Ω_{arag} decrease of 0.8, whereas biological production caused Ω_{arag} to increase by up to 0.6. Additionally, the influence on Ω_{arag} of interannual upwelling variability modulated by the Indian Ocean Dipole (IOD), a unique climate phenomenon in the Indian Ocean, was roughly estimated. We argue that the effect of interannual upwelling variability modulated by IOD events was possibly larger than what was imposed on Ω_{arag} by increasing atmospheric CO_2 levels over the past decade.
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1. Introduction

While effectively alleviating the rise in atmospheric carbon dioxide (CO_2) concentration and global climate change (Canadell et al., 2007; Le Quéré et al., 2014), the oceanic uptake of anthropogenic CO_2 has been causing a decrease in pH, carbonate ion concentration, and carbonate mineral saturation states in the oceans, a process commonly referred to as "ocean acidification" (OA) (Caldeira and Wickett, 2003; Doney et al., 2009; Feely et al., 2004; Orr et al., 2005). OA not only leads to speciation shifts of elements in seawater (Gledhill et al., 2015), affecting their bioavailability to phytoplankton, but also impacts the ability of many marine calcifying organisms to form their calcium carbonate ($CaCO_3$) shells and skeletons (Bednarsek et al., 2012; Doney et al., 2009).

Carbonate mineral saturation state (Ω) may better represent the effect of carbonate chemistry on biologically mediated $CaCO_3$ precipitation, compared with pH and CO_2 partial pressure or other CO_2 species (Riebesell, 2004; Waldbusser et al., 2014). When $\Omega < 1.0$, waters are undersaturated with respect to carbonate minerals, causing shells and skeletons made of $CaCO_3$ to become susceptible to dissolution without protection from, e.g., organic coatings (Doney et al., 2009). Aragonite is usually the most abundant form of $CaCO_3$ in shallow waters (Morse et al., 2007) and is about 50% more soluble than calcite at 25 °C (Mucci, 1983). Also aragonite is essential for many bivalve larvae (e.g., Waldbusser et al., 2014). As a result, the saturation state of aragonite (Ω_{arag}) has received more attention, particularly in the coastal ocean (Feely et al., 2010; Harris et al., 2013; Waldbusser and Salisbury, 2014; Wallace et al., 2014; Zhai et al., 2014). In addition, the controlling mechanisms of Ω_{arag} changes in the coastal ocean are more complex than in the open ocean due to the superposition of other processes such as eutrophication and upwelling (Cai et al., 2011; Duarte et al., 2013; Feely et al., 2008). Identifying the major controlling processes of Ω_{arag} in key coastal ecosystems is important for predicting Ω_{arag} changes in the future with increasing atmospheric CO_2 levels.

Upwelling systems are usually at a higher risk of acidification as they experience a natural decrease in carbonate ion concentration and Ω_{arag} (Feely et al., 2008; Gruber et al., 2012; Harris et al., 2013; Lachkar, 2014; Takahashi et al., 2014), in addition to the OA effects exerted by increasing atmospheric CO_2 levels. Upwelling brings cold and salty subsurface waters rich in CO_2 to or near the surface, lowering carbonate ion concentration and thus Ω_{arag} (Feely et al., 2008) (physical transport effect). At the same time, it brings waters enriched in nutrients to the surface, favoring the growth of phytoplankton (Hales et al., 2005); subsequently, biological production absorbs CO_2 and increases carbonate ion concentrations and thus Ω_{arag} (biological effect). Therefore, there are two

* Corresponding author. Tel.: +86 532 88960702.
E-mail address: xueliang@fio.org.cn (L. Xue).

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processes associated with upwelling that have opposite effects on the CO_2 system (Borges and Frankignoulle, 2002). The net effect of these two processes on CO_2 varies in different upwelling systems, depending on the extent of exhaustion of upwelled nutrients by biological production (Borges, 2005; Borges et al., 2005; Cao et al., 2014; Chen et al., 2004). Off the California coast (Feely et al., 2008), the transport effect of upwelling was predominant; in contrast off the Galician and Oregon coast (Borges and Frankignoulle, 2002; Hales et al., 2005), the biological effect of upwelling was found to be predominant.

Eastern boundary upwelling systems play an important role in marine ecosystems and commercial fisheries (Chavez and Messié, 2009). Covering less than 1% of the global ocean's surface area, they account for about 11% of the global new production (Chavez and Toggweiler, 1995) and up to 20% of the global fish catch (Pauly and Christensen, 1995). The marine ecosystems and related fisheries economics in these areas could be greatly influenced by OA (Cooley and Doney, 2009). Thus, examining carbonate mineral saturation state and its major controlling processes in eastern boundary upwelling systems is crucial for understanding the impacts of OA on marine biogeochemistry, organisms and ecosystems as well as the fisheries economics (Lachkar and Gruber, 2012).

The South Java upwelling system, an eastern boundary upwelling system in the tropics, is unique in that it is driven by typical Indian Ocean monsoon systems (monsoonal upwelling system). The upwelling is only present during the southeast monsoon from June to October (Susanto et al., 2001), unlike the relatively stable upwelling systems driven by trade winds in the Pacific and the Atlantic. It is also linked to climate phenomena such as El Niño–Southern Oscillation (ENSO) and the Indian Ocean Dipole (IOD) (Iskandar et al., 2009; Susanto et al., 2001). The South Java upwelling system hosts high levels of biological production, especially during the typical positive IOD (El Niño) years (Iskandar et al., 2009; Sachoemar and Yanagi, 2001; Susanto et al., 2006), and it acts as one of the most productive areas for oceanic migratory fish such as skipjack and tuna (Sartimbul et al., 2010). In addition, coral reefs, which are very sensitive to OA (Erez et al., 2011), are widely distributed along the Java coast (Allen and Adrim, 2003).

Influences of the South Java upwelling on nutrients, dissolved oxygen, chlorophyll *a* (Chl *a*), and fishery productivity have been explored before using satellite data such as sea surface temperature and Chl *a* (Iskandar et al., 2009; Ningsih et al., 2013; Sartimbul et al., 2010; Susanto et al., 2001, 2006), and sporadic field observations conducted during early periods (Sachoemar and Yanagi, 2001; Wyrtki, 1962). However, information on Ω_{arag} in the South Java upwelling region and the influence of upwelling processes on it is not available to date.

Based on field observations during September–October 2013, we report the Ω_{arag} distribution for the first time along the southern coast of Java, Indonesia during the decay of an upwelling event. We quantify how the two processes-physical transport vs. biological production-influence Ω_{arag} using a two end-member mixing model. In addition, we explore the influence on Ω_{arag} from interannual upwelling variability modulated by IOD events.

2. Study site and methods

2.1. Study site

The study site is located in the southeastern Indian Ocean, off the southern coast of Java Island, extending from 7°S to 10°S along 106°E and 114°E (Fig. 1). It is strongly influenced by seasonal monsoons, with southeast monsoons during June–October and northwest monsoons during December–February (Susanto et al., 2001). The southeasterly wind generates annual upwelling, which is eventually terminated because of the reversal of winds, associated with the onset of the northwest monsoon and impingement of the Indian Ocean equatorial Kelvin wave (Susanto et al., 2001; Wijffels et al., 1996; Wyrtki, 1962). The upwelling intensifies during positive IOD (El Niño) years

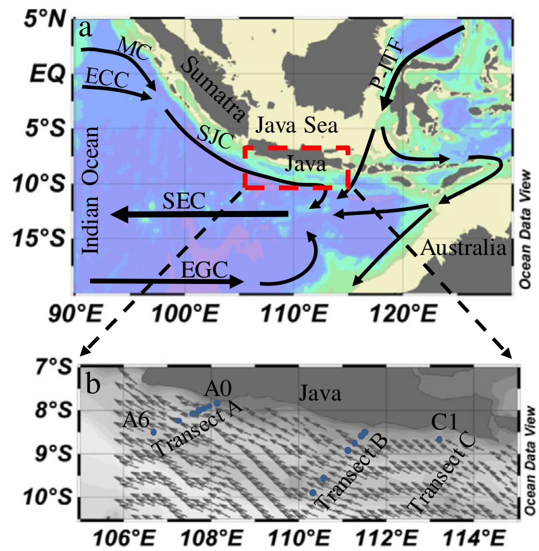

Fig. 1. Study site. (a) Shows the relative location of the study site (within the red dashed frame) in the southeastern Indian Ocean, and schematics of ocean currents during summer monsoon, redrawn from Wijffels et al. (1996). The currents shown in this map include Monsoon Current (MC), Equatorial Countercurrent (ECC), South Equatorial Current (SEC), Eastern Gyral Current (EGC), Pacific-Indonesian Throughflow (P-ITF), and South Java Current (SJC); and (b) shows the study site and sampling stations (blue dots) along Transects A, B, and C. Only one station along Transect C was completed due to malfunction of the CTD sampler. A wind field (gray arrows) in August 2006 is overlaid on Fig. 1b (QuikSCAT wind with a resolution of 0.125° × 0.125° http://coastwatch.pfeg.noaa.gov/erddap/griddap/erdQSwindmday.html). This figure and Figs. 2, 3, 5, and 6 were plotted with ODV software (Schlitzer, 2014).

and weakens during negative IOD (La Niña) years (Iskandar et al., 2009; Ningsih et al., 2013; Susanto et al., 2001). This study site is also affected by the South Java Current (SJC) and the Indonesian Throughflow (ITF) (Wijffels et al., 1996).

Our investigation was conducted from 22 September to 2 October 2013 onboard the R/V BJ-8 from the Indonesian Institute of Sciences (Indonesian: *Lembaga Ilmu Pengetahuan Indonesia* or LIPI), Indonesia. In total, there were 16 sampling stations (three transects included, Fig. 1). At each station, water samples with depths of 3 m, 10 m, 30 m, 50 m, 75 m, 100 m 150 m, 200 m, and 300 m were collected using a rosette sampler with 10-L Niskin bottles mounted on a SeaBird 911 Conductivity Temperature Depth (CTD) sensor (SeaBird Inc., Bellevue, WA, USA), which measured temperature and salinity in the water column.

2.2. Determination of dissolved inorganic carbon, total alkalinity, and Ω_{arag}

Water samples for dissolved inorganic carbon (DIC) and total alkalinity (TA) were collected from Niskin bottles and were stored in borosilicate glass flasks after adding saturated $HgCl_2$ solution (0.02% of the total volume) as a preservative. DIC was analyzed with an infrared CO_2 analyzer by acidifying seawater with phosphoric acid (H_3PO_4) and quantifying the release of CO_2; TA was measured by open cell Gran titration (Huang et al., 2012; Wang and Cai, 2004). DIC and TA measurements had a precision of 0.1% (Huang et al., 2012; Wang and Cai, 2004). During the analysis, Certified Reference Materials (CRMs) from Scripps Institution of Oceanography were used to check the accuracy of the system (~4 μmol kg^{-1} for DIC and TA). Ω_{arag} at in situ temperature ($\Omega_{arag@in\ situ}$) and a constant temperature of 25 °C ($\Omega_{arag@25}$) were calculated with DIC and TA data as well as phosphate and silicate data (see Fig. S1 in the Supplementary material) using the CO_2sys program (Lewis and Wallace, 1998) and the CO_2 system coefficients of Mehrbach et al. (1973) refit by Dickson and Millero (1987).

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