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Coralline Ba/Ca ratios and luminescent line records in Con Dao Island, offshore Vietnam, as indicators of Mekong river runoff between 1948 and 1999

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ABSTRACT

The Ba/Ca ratios and luminescent lines recorded in coral skeleton in near-shore corals are reflected by fresh river flows. This paper shows 52-year Ba/Ca ratios and bright luminescent lines recorded in coral Porites in the Con Dao Island area, offshore Vietnam, about 90 km from the mouth of the Mekong River. Bright luminescent lines and Ba/Ca ratios are cyclical and formed annually, where the bright luminescent lines and the highest Ba/Ca ratios are simultaneously formed. The measured Mekong River discharge (MRD) and salinity data recorded during the 1985-1999 period show that the annual maximum MRD and minimum salinity in Con Dao Island were synchronous, and that the annual maximum Ba/Ca ratio was formed during maximum MRD and minimum salinity. When the annual minimum MRD and salinity were stable, the annual minimum Ba/Ca ratio was variable. Overall, the mean annual MRD and Ba/Ca ratio slightly decreased during the 1985-1999 period, suggesting that the Ba/Ca ratio is mainly controlled by MRD. The decreasing trend in Ba/Ca ratios over the period between 1948 and 1999 is probably related to the MRD reduction due to human activities and/or climate change.

Keywords: Porites coral, Ba/Ca ratio, luminescent lines, Mekong River discharge.

1. Introduction

The luminescent lines in coral skeletons potentially offer an important proxy relating to the contribution of organic matters in river runoff from land (Isdale, 1984; Isdale et al., 1998). Further investigation suggested that the UV luminescent lines were resulted from association of the terrestrial humic acids (Boto and Isdale, 1985; Susic and Boto, 1989; Susic et al., 1991; Lough et al., 2002; Hendy et al., 2003). Meanwhile, poor relationships between UV luminescent lines and amounts of the river runoff were found in corals from Papua New Guinea and Indonesia (Scoffin et al., 1989; Smith et al., 1989). Fang and Chou (1992) found a weak relationship between local precipitation and amount of fulvic acids in the coral skeletons from Taiwan. Scoffin et al. (1992) found that the UV luminescent lines were formed during dry season in the coral from Phuket, Thailand. The UV luminescent lines had been also reported in the coral far from land or from any source of fresh water (Susic et al., 1991; Tudhope et al., 1996). The study in colonies from GBR provide the strong relationship between luminescence line and river runoff (Grove et al., 2010; Lough, 2011).

Marine humic materials are potential to form blue, background luminescent lines in coral skeletons (Boto and Isdale, 1985; Susic et al., 1991; Minle and Swart, 1994; Isdale, 1995). The organic compounds have been suggested as a

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possible source of the UV luminescent lines in the coral skeletons in the areas, which are far from fresh water inputs (Susic et al., 1991; Tudhope et al., 1996). Jones (1990) suggested that the UV luminescent lines of the inshore coral from Great Barrier Reef were resulted from humic materials created by breakdown of blue-green algae. Minle and Swart (1994) found the coral skeletons without the UV luminescent lines. They showed broad featureless emission signals at 450 nm in wave length characteristic to marine dissolved organic matters with emission signals between 440 and 490 nm in wave length (Boto and Isdale, 1985; Smith et al., 1989; Neil et al., 1995). Recently, Barnes and Taylor (2001) presented an alternative model in which luminescent lines and bands in coral skeletons are result of reduced calcification as coral responds to low salinity conditions incorporated with coastal runoff. Luminescent lines in massive coral skeletons, growing close to tropical coastline, can indicate tropical river runoff and rainfall in the catchments as well as river water supplied to the coral reef over the past several centuries.

Occasionally, other trace elements recorded in corals, such as U, Ba, Cd, Mn, Cu, B and F, have been used for investigating the environmental variations. The concentration of Ba and Mn in corals can potentially reflect elemental concentrations in seawater associating with an upwelling in the eastern equatorial Pacific (Linn et al., 1990; Shen et al., 1987, 1991, 1992a). The Ba/Ca ratio likely reflects fluvial Ba from freshwater discharge (Wan et al., 2005 Dunbar, 1995) and useful to estimate the past river discharge. In this research, records of UV luminescent lines and Ba/Ca ratios in coral skeletons collected in the Con Dao Island area, offshore Vietnam, are investigated with aim to highlight the relation between Ba/Ca ratios, luminescent lines and Mekong river discharge and the effect of human activities and/or climate change on the parameters.

2. Study area and sampling

In May 2000, a 68 cm long core (5.5 cm in diameter) was collected from the top of a living Porites sp (~0.8 m in height) in the western side of Con Dao Island, about 85 km from the coastal zone (8°39’36” N, 106°33’07”E) (Fig. 1).

The living coral colony has a round shape and smooth surface. The top of coral is ~ 4-5 m below the sea surface at the low tide (Fig. 2). The coral was taken using a pneumatic drill, which is driven by a SCUBA air tank. The seawater at sampling site was rich with suspended matters. The coral core was carefully taken out from coring sampler and put in the fresh water for several hours was then dried at room temperature and stored it in a plastic pipe.

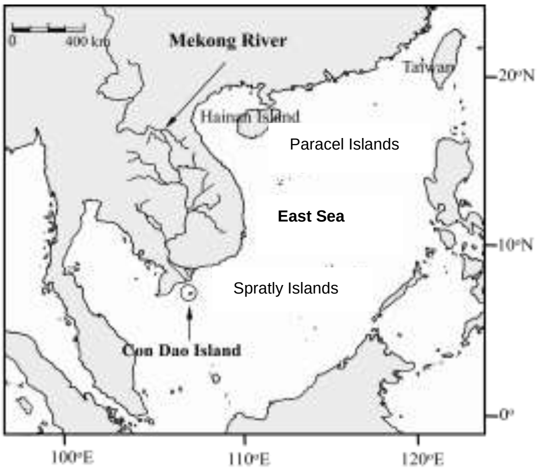

Figure 1. Location map of Con Dao Island, the south of Vietnam

Figure 2. Living Porites sp. coal colony on western side of Con Dao Island. The coral core was collected in May 2000

The southern continental shelf in the East Sea (South China Sea) is relatively shallow, covering partly the Sandra Shelf, an enormous submerged plain (water depth < 200 m) stretching from the Gulf of Thailand to the Java Sea. The tide is non-regular semi-diurnal, e.g., two high and low tides each day. The amplitude of the tidal fluctuation is about 1.0-1.5 m. Because of high rainfall, river and surface runoff, the seawater salinity in the East Sea is lower than global average. The broad shallow continental shelf of East Sea are strongly influenced by seasonally reversing winds of East Asian monsoon as well as the river discharge from nearby continental areas (Levitus et al., 1994). The winter monsoon drives a southwesterly flow along the northern and western coasts, fed by Pacific and East China Sea water bodies from the east and north, delivering water south to the Indonesia seaway and forming the western boundary of an anti-clockwise gyre circulating between Vietnam and Philippines . In summer, the ocean circulation is reversed and Indonesian waters from the south feed a broad northeasterly flow that covers most of the East Sea (Southon et al., 2002). The ocean current from north and east is derived from Kuroshio Current and its precursor when the Northeast (or winter) monsoon is active (Konishi et al., 1982; Southon et al., 2002). The complex circumstance is caused by mixing between North Pacific Equatorial (Fine et al.,1994; Gordon, 1986) and South Pacific Equatorial Current (Tchernia, 1980) when the Southwest monsoon is active.

During the hot and wet season between May and November, Con Dao Island is influenced by the Southwest monsoon and tropical cyclones that bring heavy precipitation. The meteorological observation records have been available since January 1980 in the Con Dao meteorological observation station (Institute of Hydrology and Meteorology of Vietnam), which is located in about 7 km away from the coral sampling site. The annual precipitation is about 2,100 mm and 95% of this occurs within six months, from May to November. In contrast, precipitation is minimal in the cool (dry) season, lasting from December till April, when the Northeast monsoon is active. Daily salinity and sea surface temperature have measured at the Con Dao station since 1980; unfortunately, suspended materials are not monitored.

The salinity varies from 30.0 ‰ in October when the discharge from Mekong River is maximal to 32.9 ‰ in February, coinciding with high and low precipitation, respectively.

Mekong River flows through six countries, including China, Myanmar, Laos, Thailand, Cambodia and Vietnam. This is the world's 12th longest river, with length of 4,800 km and a drainage area of 795,000 km^2. The river annually delivers approximately 160 million tons of sediment and 475 km^3 fresh water to the East Sea (Milliman and Meade, 1983). It changes dramatically from its upstream in the Tibetan mountains to its outlet in the East Sea. The Mekong River discharge (MRD) is subject to strong seasonal and inter-annual fluctuations having been effected by Indian monsoon, East Asian monsoon, West Northern Pacific monsoon, ENSO and their combined influence. There are a number of hydropower dams having been built along the Mekong river. For example, by 2009, 64 dams were completed, 33 were under construction and 200 others were under feasibility study ready to build (Xue et al., 2011). The construction of more dams and reservoirs along the Mekong River twill trap large amounts of sediments in reservoirs behind the dams, leading to significant decrease of sediment flux to downstream. As a result, the riverine sedimentation to the sea is decreased and coastal erosion as well as loss of coastal wetlands in lower part of Mekong river delta will be increased (Le at al., 2007). Records of the Mekong River discharge in the period of 1985-1999 were taken from the Kretia hydrological station which accounts of 90% of the total MRD (Mekong River Commission, 2005) as they are less affected by tidal and short time discharges as compared to those recorded at lower hydrological stations such as Tan Chau and Chau Doc, Vietnam.

3. Method

A 68-cm-long core (5.5 cm in diameter) was sliced into 6-mm- thick slabs along its longitudinal axis using a circular rock saw. The slabs were cleaned repeatedly with a large amount of distilled water in an ultrasonic bath and dried in a clean plastic box for a week. The slabs were then photographed under long-wavelength UV light (~ 352 nm) and X-rayed. The UV photo and X-ray photo revealed luminescent banding and density banding in the coral, respectively (Fig. 3). In each photo, there are 52 bands in total; and each band has a width of ~ 10-12 mm, which is a typical annual growth increment of Porites coral. Therefore, the 52 bands were assumed to be annual based on the UV-luminescence photo and X radiograph. 627 samples (2–3 mg each) were manually picked out at 1-mm interval using an etching/engraving needle. The sampling resolution of 1 mm corresponds to a temporal resolution of ~5 weeks. About 2 mg of sample was treated with 2 mL of 99.5% ethanol followed by 2 mL of 0.004 mol/L HNO3 at room temperature under ultrasonic agitation to remove possible contamination. The treated aliquot was then dissolved in 0.5 mol/L HNO3 for measurements of Sr/Ca, Mg/Ca and Ba/Ca ratios using a high-precision of charge coupled device (CCD) simultaneous ICP-OES (Varian Vista-PRO Simultaneous inductively coupled plasma – optical emission spectroscopy (ICP-OES)). Reproducibility (relative standard deviation: RSD) of the Sr/Ca, Mg/Ca and Ba/Ca measurements was estimated to be 0.20%, 0.41% and less than 1.0%, respectively, by repeated measurements of reference solutions. The standard solutions were routinely calibrated once in 10 samples. The sample treatment and analysis were performed at the Japan National Institute for Environmental Studies (Tsukuba, Ibaraki), using Varian ICP- OES.

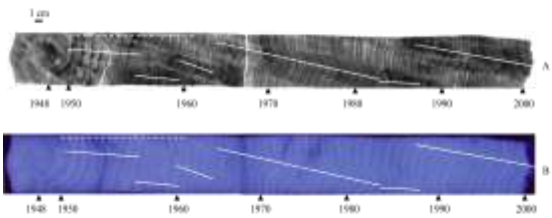

Figure 3. X-ray photograph (A); UV luminescence (B) of a 6mm-slab of Porites sp. from Con Dao Island, the south of Vietnam. The solid white lines show elemental sampling transects along the growth axis. The dotted white line shows ^{14}C sampling transects.

4. Result and discussion

A positive X-ray and luminescent lines were clearly recognized from the slabs of coral skeleton (Fig. 3). The total of 52 dark and light stripes seen in the X-ray image correspond to the high and low density bands, respectively, and represent 52 annual marks. The growth rate is in a range of 9-14 mm/year, yielding an average value of 12 mm/year. The high-density bands are formed during warm seasons (May and October) when the double peak of Sr/Ca ratio is also appeared (Dang et al., 2006).

The UV luminescent images also show 52 clear luminescent lines. The number of the luminescent lines is exactly the same as that of the density bands on X-ray image. Based on the growth rate (9-14mm/y) and annual bands, the formation of the bright luminescent lines occurs in the end of warm seasons. The age of growth bands of Con Dao Island coral was also confirmed by the ^{14}C anomaly included by the first nuclear bomb tests (Dang et al., 2004).

The Ba/Ca ratios recorded between 1948 and 1999 clearly show seasonal variations in a range of 2.5-8.57 μmol/mol. The annual Ba/Ca ratio peaks are recognized within bright UV luminescent lines, which are formed nearly each year. In addition, the decreasing trend in the Ba/Ca ratios at about 0.015 μmol/mol per year was also recognized during the period between 1948 and 1999 (Fig. 4). Correlation of the Ba/Ca variations with the luminescent lines shows Ba/Ca ratio peaks appear in the wet (warm) season, e.g. around October, when the salinity is lowest and the rainfall is highest. The peaks of the seasonal Ba/Ca ratio cycles appear within the span of bright luminescent lines (Fig. 5), suggesting that they may be formed simultaneously.

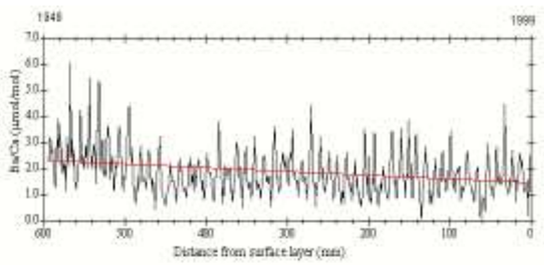

Figure 4. Ba/Ca variations during 1948-1999 in Porites sp. coral skeleton from Con Dao Island, southern continental shelf of Vietnam. The red straight line shows the dataset's linear regression

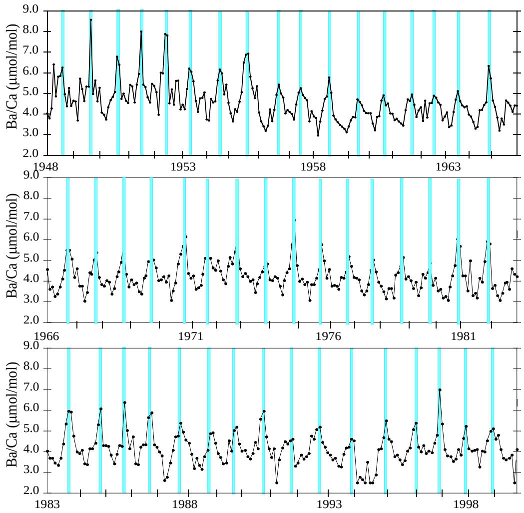

Figure 5. Ba/Ca variation in *Porites* sp. coral skeletons from Con Dao Island during 1948-1999. The blue colors show the bright luminescent lines.

The Mekong river annual maximum discharge recorded at the Kretia hydrological station is variable while the annual minimum discharge is stable around 2000 m^3/s (Fig. 6a). The MRD depends on Indian monsoon, East Asian monsoon, West Northern Pacific monsoon, ENSO and their combined effect (Xue et al., 2011). Each of the above natural factors affects a certain part of Mekong River watershed, for example, lower Mekong River basin is dominated by Asian monsoon. The annual minimum seawater salinity at Con Dao island station shows the same fluctuation with annual maximum MRD (Fig. 6b). The annual maximum salinity is stable around 33‰ except for abnormal year of 1998, suggesting certainly that salinity in Con Dao Island is controlled by MRD. The annual Ba/Ca ratio peaks are formed during maximum MRD and minimum salinity (Fig. 6c), however the variation is not similar to those observed for the MRD and salinity. The annual minimum Ba/Ca ratio is not as stable as annual minimum MRD and annual maximum salinity, meaning that not only MRD but also seawater chemistry are affected by ocean currents at times when East Asian monsoon is active.

Since Con Dao Island is close to the mouth of the Mekong River, the maximum Ba/Ca variation in the coral skeletons also is mainly influenced by fluvial Ba input from Mekong River (Shen et al., 1992a; Lea et al., 1989; Linn et al., 1990; Alibert et al., 2003). Furthermore, the ^{14}C value of shell in the Ho Chi Minh city area is in excellent agreement with that of Con Dao island (Dang et al.,2004). The trend lines of mean annual MRD and Ba/Ca ratios recorded between 1985 and 1999 slightly decrease while the salinity increases (Fig 7). This observation again suggests that MRD is the main factor that controls the salinity and Ba/Ca ratios in around the Con Dao Island area. The mean annual MRD at Kretia station recorded a decrease in discharge in 1993 due to post- Manwan hydropower dam effect (Lu and Siew, 2006; Kammu and Vais, 2006; Xue et al., 2011), leading to decrease in the mean annual Ba/Ca ratio.

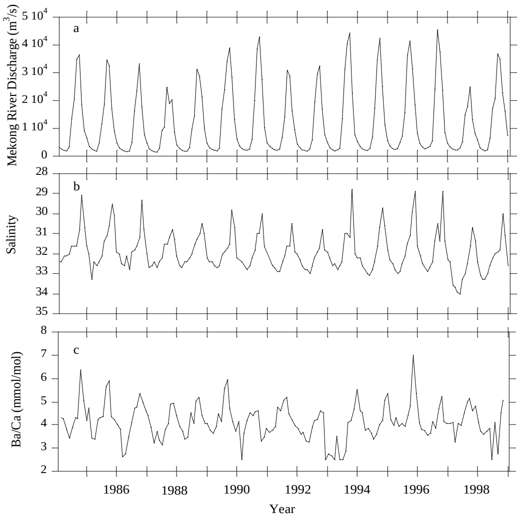

Figure 6. Correlation between Mekong River Discharge (a), Salinity (b) and Ba/Ca (c) ratios recorded from 1985-1999

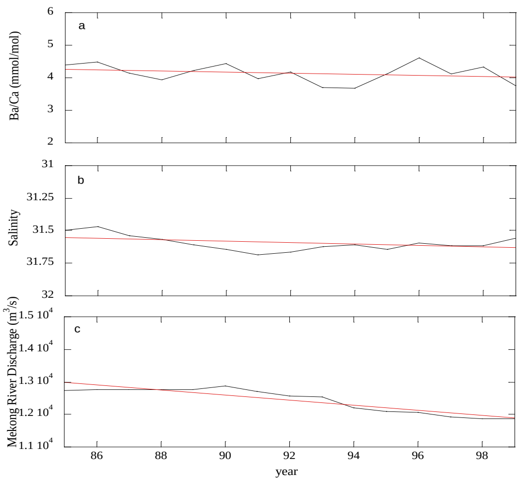

Figure 7. Correlation of mean annual Mekong River Discharge (a), Salinity (b) and Ba/Ca (c) ratios recorded in the period between 1985 and 1999

The Ba/Ca ratio of the coral skeletons from Con Dao Island is predominately controlled by terrestrial inputs from MRD. Over a half century the Ba/Ca ratio gradually decreases to the present of 0.015µmol/mol y-1. The decrease may be induced by the change in the terrestrial inputs due to human activities or/and climate change.

5. Conclusions

The Ba/Ca ratios recorded in Porites coral in Con Dao Island, southern continental shelf of Vietnam from 1948 to 1999 show annually cyclical change with peak being formed along with bright luminescent lines in October when the MRD is maximal and the salinity is minimal. The annual maximum MRD and minimum salinity are synchronous, while the highest Ba/Ca ratios are formed during the maximum MRD. The annual minimum MRD and maximum salinity are stable, but annual minimum Ba/Ca ratio is variable. It is possible that the Ba concentrations and organic matters in seawater around the Con Dao Island area are controlled mainly by the MRD. The annual trend of MRD and Ba/Ca ratios slightly decreased during the period between 1985 and 1999. Although the long-term variation of the MRD may be estimated by inferring the mean annual Ba/Ca cycle; however, a quantitative relation between bright luminescent lines, Ba/Ca ratios and MRD may be identified in further studies using oxygen isotope and monitoring suspended sediment flux in Con Dao Island.

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