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Black coral as a new environmental recorder: The lead profiles in coral skeletons over the past century

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ABSTRACT

Lead (Pb) is a typical heavy metal pollutant in the environment, and most Pb contamination comes from human activities. In the present work, the Pb contents of two black coral specimens (*Cirrhipathes* spp.) collected from the northern South China Sea were measured by synchrotron radiation micro X-ray fluorescence (SR μ-XRF) analysis with 2.5 μm resolution. The results showed that sample SY-1 from the Sanya Bay (near the continent) exhibited higher Pb levels and greater fluctuations than sample XS-1 from the Xisha Islands (off the continent), reflecting the influence of terrestrial input and atmospheric deposition in coastal surface seawater. The present work also demonstrated that the Pb profile in black coral nearshore was highly influenced by human activities, mainly by war and economic development. Thus, black coral may serve as a new potential environmental Pb recorder with SR μ-XRF analytical technology.

1. Introduction

Extensive records of lead (Pb) pollution to the environment have been found in many types of environmental archives, such as sediments (Pekey, 2006; Zhu et al., 2010), peats (Weiss et al., 1999; Shotyk et al., 2001), ice cores (Hong et al., 1994; Vallelonga et al., 2010) and scleractinian corals (Shen and Boyle, 1987; Bastidas and García, 1999). Among them, scleractinian corals, such as *Porites*, have been regarded as a promising species for reconstructing temporal records of Pb in marine environments because they are easily dated and have a high resolution, and they also contain high accumulations of metals (Shen and Boyle, 1987; Inoue and Tanimizu, 2008; Song et al., 2014). However, scleractinian coral has a few shortcomings: 1) Analysis of Pb in scleractinian coral skeleton requires strict avoidance of surface Pb contamination during handling and measurement (Shen and Boyle, 1987; Inoue et al., 2006); 2) the dependence on photosynthetic algae restricts scleractinian coral to generally existing in the shallow sunlit oceans of the tropics and subtropics (Cohen and McConnaughey, 2003); and 3) the rapid growth rate of scleractinian corals (~0.2 to 5 cm yr^{-1}) results in sampling and handling difficulties because several meters of a coral core only provides a chronology of a few hundred years (Dunbar et al., 1994).

To date, black corals have gained widespread attention for paleoceanographic reconstruction because of their unique advantages. They are non-scleractinian corals, of which the semi-rigid skeletons are mainly composed of proteins and chitin (Goldberg et al., 1994; Nowak et al., 2005). They are widely distributed throughout the world's oceans and across large ranges of depths, from the near-sea surface to thousands of meters deep (Grigg, 1965). Their long lifespan (the oldest living organism reported is approximately 4265 years old) and low radial growth rate (~4 to 35 μm yr^{-1}) lead to the shorter radius of coral transects offering a longer continuous time series (Williams et al., 2006; Roark et al., 2009). Recently, stable isotopes in the organic skeletons of black coral have been successfully used as a proxy for nutrient sources (Williams et al., 2007; Risk et al., 2009). Williams and Grottoli (2011) used LA ICP-MS with 50 μm resolution and measured the trace elements in organic skeletons of black corals from the central Pacific Ocean, which suggested that some trace metals in black coral may be useful for paleoceanographic reconstructions. However, elemental proxies in black corals have not been fully developed due to the difficulties of detecting trace elements in low-growth organic skeletons at high resolution. Thus, a high resolution technique is essential for developing elemental proxies in black corals.

Synchrotron radiation micro X-ray fluorescence (SR μ-XRF) has the unique property of having a synchrotron source, which makes SR μ-XRF well suited for in situ speciation and elemental mapping studies (Lombi and Susini, 2009). Compared with other micro-analytical techniques, SR μ-XRF is characterized by non-destructive and less sample preparation, multi-elemental distribution, high spatial resolution (submicron scales),

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and high sensitivity (attogram level) (Lombi et al., 2011; Majumdar et al., 2012). Furthermore, SR μ-XRF has been successfully applied to the study of the elemental distribution in red corals (Nguyen et al., 2014). Hence, the micrometer-scale spatial resolution of SR μ-XRF allowed for obtaining in situ elemental information in this kind of corals.

Using the radionuclide ^{210}Pb dating method, it was proved that black corals in the northern South China Sea have grown continuously for more than one hundred years (Williams et al., 2006; Zhang et al., 2015). Here, we measured the time-series variations of Pb in two black coral samples using SR μ-XRF with 2.5 μm resolution. Our purpose is to explore the potential of black coral as an environmental recorder of Pb.

2. Materials and methods

2.1. Sample collection

Two black coral samples were collected from Jinyin Island of the Xisha Islands (XS-1) in January 2011 and Luhuitou Reef in Sanya Bay (SY-1) in April 2012, respectively (Fig. 1). Historically, local people lived along the coast of Luhuitou Reef. Now Sanya Bay developed to be the largest open tropical estuary on Hainan Island (Yang et al., 2004; Mao et al., 2006). Jinyin Island of the Xisha Islands is a coral island located in the northern South China Sea and far from the mainland. There are no permanent human residents and very few anthropogenic activities.

Both of the coral specimens were alive and growing when they were collected. The basal section was removed directly above the holdfast and transported frozen to the laboratory. The radius (semi-major axis) of the skeletal basal slices was 2.37 mm for sample SY-1, and 2.52 mm for sample XS-1, respectively. The coral samples were identified as *Cirrhipathes* spp. And the cross sections with 200 μm thickness were prepared and imaged using the digital camera (Olympus, E-M10) (Fig. 2).

2.2. Skeletal ^{210}Pb dating

The detail methodology of each coral chronology in this study was previously described elsewhere (Zhang et al., 2015). Briefly, using the radioactive decay of ^{210}Pb in black coral skeletons, the age of specimen SY-1 and XS-1 was calculated as follows:

$$A_{ex} = A_0 e^{(-\lambda S/V)} \quad (1)$$

where A_{ex} is ^{210}Pb activity measured in each slice (layer) at specific time, A_0 is the initial activity at edge of coral, S is the distance from the outermost edge of the black coral, V is the radial growth rate, and λ is the decay constant of ^{210}Pb (0.0311 yr^{-1}) (Baskaran, 2012). Implicit assumptions in this calculation are the initial activity and radial growth rate remained constant throughout their growth periods.

The activity of ^{210}Pb (dpm/g) for SY-1 and XS-1 decreased from 3.96 (S = 0.39 mm) to 0.22 (S = 2.04 mm) and from 9.63 (S = 0.20 mm) to 0.34 (S = 2.11 mm), respectively. Based on the growth chronology for each slice of coral (Eq. (1)), the results of the ^{210}Pb dating revealed that the sample SY-1 was of 134 years with a radial growth rate of 0.0177 mm yr^{-1}, and sample XS-1 was of 140 years with a radial growth rate of 0.0180 mm yr^{-1}, respectively.

2.3. SR μ-XRF analysis

Basal sectional slices approximately 0.5 mm thick were cut for analysis. A piece of sandpaper was used to polish the basal slice surface smooth. To ensure that all particles were removed and not incorporated onto the skeleton, each cross-sectional skeletal slice was cleaned three times (each time for 10 min) in the ultrasonic bath using 18 MΩ Milli-Q water, and then dried over night at 60 °C (Williams and Grottoli, 2011). The SR μ-XRF analysis was conducted at Beamline 15U1, Shanghai Synchrotron Radiation Facility (SSRF). When tested, the sample was mounted in a sample holder that could be moved in the X and Y directions by computer-controlled step motors. Ten parallel SR μ-XRF scans on the black coral samples were conducted at a resolution of 2.5 μm × 2.5 μm from edge to center and covered an area of approximately 25 × 2500 μm^2 along the radial direction (Fig. 2). The radiation power was 16.5 keV. The scanning was performed at a typical acquisition time of 0.5 s per step.

2.4. Data analysis

Python Multichannel Analyzer (PyMCA) software (version 4.3.0) was used to fit the spectra with constraints on the fitting parameters and to calculate Pb mapping with correction of the various fluorescence contributions. Fluorescence intensities were normalized to Compton effect and measurement time (lifetime). ArcGIS 10.0 and origin 8.5 were used for map-making.

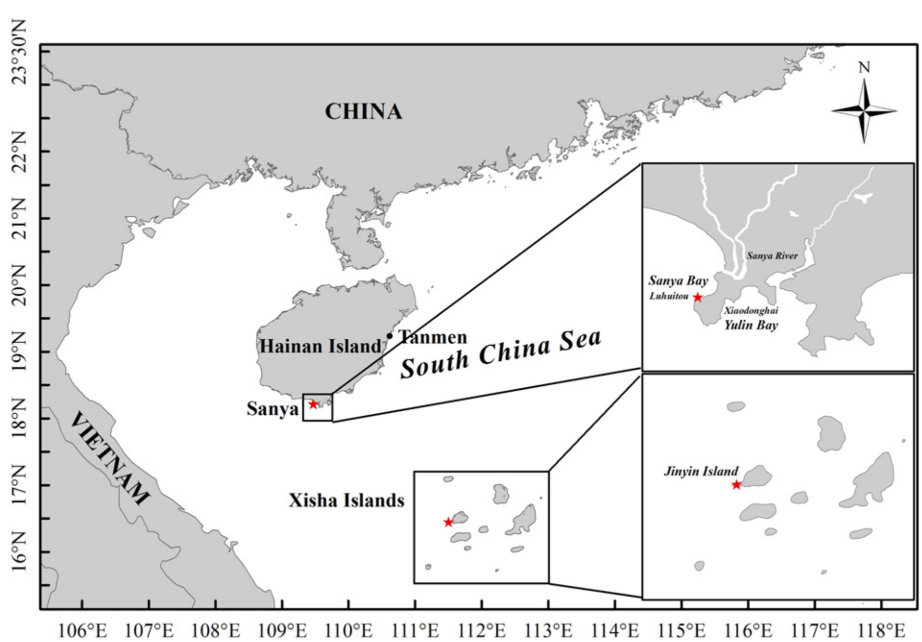

Fig. 1. Sampling sites in northern South China Sea near Sanya Bay and the Xisha Islands.