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Geochemical partitioning of lead in biogenic carbonate sediments in a coral reef depositional environment

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ABSTRACT

The fate of trace elements in reef depositional environments has not been extensively investigated. The aim of this study was to determine the partitioning of Pb in sediments of the Veracruz Reef System, and its relation to local environmental sources. Lead was determined in four geochemical fractions: exchangeable (3.8 ± 0.4 μg g^{-1}), carbonate (57.0 ± 13.6 μg g^{-1}), organic matter (2.0 ± 0.9 μg g^{-1}), and mineral (17.5 ± 5.4 μg g^{-1}). For the mineral fraction, lead concentrations were higher in those reefs influenced by river discharge or by long-distance transport of terrigenous sediments. The bioavailable concentration of lead (range: 21.9–85.6 μg g^{-1}) indicates that the Veracruz Reef System is a moderately polluted area. As expected, the carbonate fraction contained the highest proportion of Pb (70%), and because the reef framework is largely made up of by biogenic carbonate sediments, hence, it is therefore the most important repository of Pb in coral reef depositional environments.

1. Introduction

Since the industrial revolution in the 18th century, the main sources of lead (Pb) into the environment have been the aerosols generated by the smelting and processing of ores in the metallurgical industry and the combustion of alkyl-lead gasoline by automotive vehicles (Nriagu, 1989; Nriagu and Pacyna, 1988; Weiss et al., 1999). On a global scale, these two processes have contributed to the increase in the concentration of Pb in almost all environmental compartments, as has been extensively documented by various geochemical archives such as ice cores (Murozumi et al., 1969; Vallelonga et al., 2002), sediments (Graney et al., 1995; Soto-Jiménez et al., 2006), soils (Renberg et al., 2000), peat bogs (Leroux et al., 2004), tree rings (Bellis et al., 2002), sclerosponges (Lazareth et al., 2000), and reef corals (Shen and Boyle, 1987; Horta-Puga and Carriquiry, 2014). In the late 20th century the use of improved methods for the recovery of dust and fumes during the metallurgical processes (Murozumi et al., 1969; USEPA, 1998) and the phase-out of alkyl-lead gasoline (Wu and Boyle, 1997) has substantially diminished its release into the environment (Weiss et al., 1999). However, previously released Pb-aerosols that have been stored in topsoils and sediments of continental water reservoirs (Soto-Jiménez et al., 2006; Tanaka et al., 2013) can be redistributed by resuspension into the atmosphere caused by winds (Shotyk et al., 1998) or transported out by river flow into the ocean (Horta-Puga et al., 2013; Horta-Puga and Carriquiry, 2014). This process has been recorded in the southern Gulf of Mexico (SGM) (Ruiz-Fernández et al., 2003, 2007) and has contributed to the maintenance of high environmental levels of Pb in nearshore areas long after the main sources of Pb have ceased in the 1990s (Rosales-Hoz et al., 2007; Horta-Puga et al., 2013; Horta-Puga and Carriquiry, 2014), hence becoming the main source of Pb in coastal areas at the present time.

In coral reef depositional environments, biogenic carbonate coarse sands, which are the highly eroded and fragmented remains of scleractinian corals, coralline algae, mollusks, and foraminifers (among others) are the main component of sediments (>90% dry weight), along with a lower proportion of fine terrigenous siliciclastic particles (<63 μm) derived from continental runoff (Kornicker et al., 1959; Emery, 1963; Boss and Lidell, 1987; Gischler and Lomando, 1999; James and Ginsburg, 2009). Carbonate skeletal structures at the precise moment of their deposition by living organisms incorporate Pb, as well as several other trace elements, by direct substitution of calcium in the carbonate molecule, or they may be included in other skeletal phases (Shen and Boyle, 1987; Reuer et al., 2003). Thus, the Pb content varies concomitantly with its environmental availability in the seawater column as has been recorded in sclerosponges (Lazareth et al., 2000; Swart et al., 2002; Rosenheim et al., 2005), foraminifers (Frontalini et al., 2009), hermatypic corals (Shen and Boyle, 1987; Dodge and Gilbert, 1984; Desenfant et al., 2006; Inoue and Tanimizu, 2008; Kelly et al., 2009; Horta-Puga and Carriquiry, 2014) and bivalve mollusks (Richardson et al., 2001; Gillikin et al., 2005). Once calcareous shells and skeletons of organisms become part of reef sediments they constitute the final repository of Pb, unless they are recycled into the water column and/or redistributed into the different sedimentological

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geochemical fractions: Some of these are then available for the incorporation of Pb by reef organisms (Santschi et al., 1990). The biological and physicochemical processes that determine the spatial, temporal and compartmental variation of Pb in sediments are: (1) the sources of sediments (biogenic or terrigenous) and sedimentation rates; (2) the degree of mechanical disturbance (e.g. water turbulence, tidal currents), which causes sediment resuspension; (3) bioturbation due to feeding, moving and burrowing by benthic organisms; (4) the desorption and adsorption onto particle surfaces caused by changes in the sediment-water interface chemistry, such as the redox potential, dissolved oxygen concentration, pH, temperature, and salinity; and (5) the biological activity of microbial communities (Santschi et al., 1990; Calmano et al., 1993; Simpson et al., 1998; Eggleton and Thomas, 2004; Atkinson et al., 2007). Hence, high concentrations of Pb are expected in bulk reef sediments. Its partitioning in the exchangeable, carbonate, organic and mineral (siliciclastic) geochemical fractions is likely to be highly variable due to differences in the local sources of Pb, the proximity to human settlements and the influence of river discharge.

The Veracruz Reef System (VRS), constituted by several single coral reefs (Fig. 1), is the most extensive reef system in the southern Gulf of Mexico (SGM). It lies in front of Veracruz, the largest city and port in the SGM, wherein human activities release into the surrounding environment several contaminants including Pb, from sewage effluents, industrial discharges, urban runoff and atmospheric fallout (Horta-Puga, 2007; Rosales-Hoz et al., 2007). The Jamapa River also influences the VRS, which is a major source of freshwater, terrigenous sediments and Pb into the coastal zone (Carriquiry and Horta-Puga, 2010; Horta-Puga et al., 2013; Horta-Puga and Carriquiry, 2014). Hence, the aim of this study was to determine the partitioning of Pb in the geochemical fractions of recent biogenic sediments, and its spatial distribution, in the VRS, a coral reef setting that is heavily influenced by terrigenous sediments from fluvial discharge, and to contribute to the knowledge of the fate of trace elements in coral reef depositional environments.

2. Materials and methods

The geochemical partitioning of lead and its spatial distribution was determined in samples of recent biogenic carbonate sediments that were collected from open sandy areas in the SW reef flat zone (<1.5 m depth), in fifteen representative reefs of the VRS (Fig. 2); nine of the Northern Group (NG): Anegada de Adentro, Blanquilla, Gallega, Galleguilla, Hornos, Isla de Sacrificios, Isla Verde, Pajaros, and Punta Gorda; and six from the Southern Group (SG): Anegada de Afuera, La Blanca, Cabezo, Chopas, Isla de Enmedio, and Rizo. The sediments were collected during two field surveys in July, the early rainy season (ERS), and September, the late rainy season (LRS) in 2008. Considering the low sedimentations rates on reefs, the results from the two field surveys were averaged. Each recent sediment sample (top 10 cm, ~250 g) was collected with a plastic scoop, transferred into an acid-washed polythene bag and frozen in a cooler box with dry ice (solid CO_2). Samples were transported to the lab and preserved at −4 °C. The sample bags with sediments from Gallega and Hornos reefs during the July survey accidentally broke and mixed during transportation, therefore the results from these two sites are not presented.

In the laboratory, the sediments were oven-dried (60 °C, 48 h), and homogenized in an agate mortar. Sediment aliquots (~20 g) were

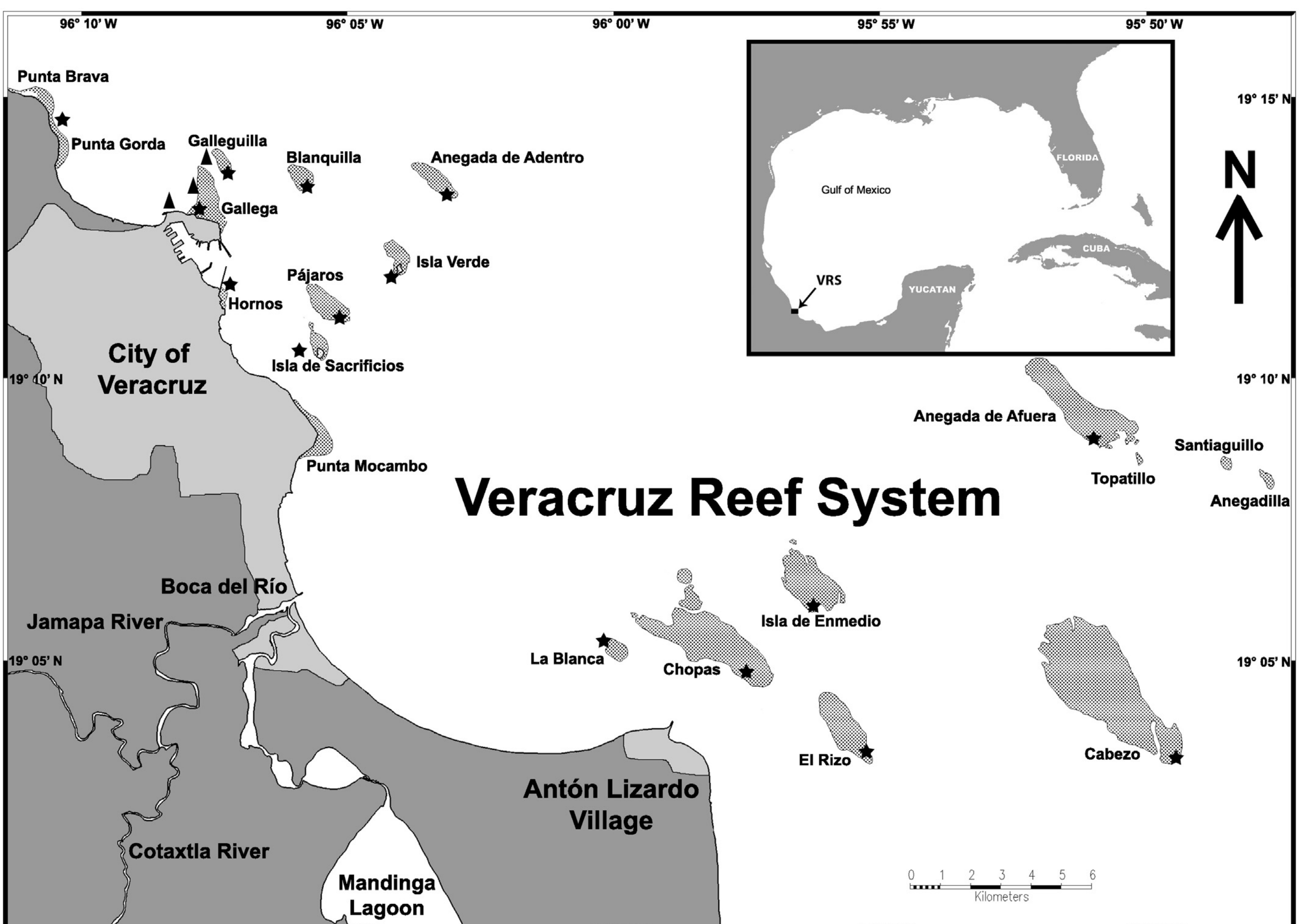

Fig. 1. Study area, Veracruz Reef System, Gulf of Mexico. The marks (stars) indicate the coral reefs wherein sediment samples were collected.