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Organic matter and pyritization relationship in recent sediments from a tropical and eutrophic bay

Elisamara Sabadini-Santos [a,*], Thaise M. Senez [b], Tabatta S. Silva [b], Manuel R. Moreira [a], João Graciano Mendonça-Filho [c], Ricardo E. Santelli [d], Mirian A.C. Crapez [b]

[a] *Departamento de Geoquímica, Instituto de Química, Universidade Federal Fluminense, Niterói, RJ 24020-150, Brazil*
[b] *Departamento de Biologia Marinha, Instituto de Biologia, Universidade Federal Fluminense, Niterói, RJ 24020-150, Brazil*
[c] *Laboratório de Palinofácies and Fácies Orgânica (LAFO), Departamento de Geologia, Instituto de Geociências, Universidade Federal do Rio de Janeiro, RJ 21949-900, Brazil*
[d] *Departamento de Química Analítica, Instituto de Química, Universidade Federal do Rio de Janeiro, Rio de Janeiro, RJ 21941-909, Brazil*

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ABSTRACT

The degree of pyritization (DOP) and the extension of metals incorporation into pyrite was investigated at Guanabara Bay sediments. Maximum concentrations of total organic carbon (TOC), total sulfur, biopolymers and viable bacteria cells were observed in silted stations close to discharge points of sewage and minimum concentrations at sandy stations at the entrance of the bay. Pyrite iron concentrations (Fe_{py}) was always lower than the reactive iron and Fe_{py} were below the detection limit at sandy stations. The same trend was found to metals, which its degree of pyritization was $Mn = Cu > As = Co > Ni > Cd > Zn \gg Pb > Cr$. The bay gathers all required factors to sulfate reduction and pyrite formation, once the C:S ratio express the reduced tendency conditions, almost half of the TOC present in its sediments is labile and both reactive sulfur and iron are available. However the degree of trace metals pyritization did not exceed 20%, consistent with the median DOP (29%).

1. Introduction

Microbial processes exert a major control on the combined geochemical cycles of essential elements (e.g. carbon, nitrogen, sulfur and iron) because sediments are intensively colonized by microorganisms (about 10^{10} cells g^{-1} d.w.), most of them bacteria organized in biofilms consisting of extracellular polymeric substances secreted by the cells (Decho, 2000 and other; Flemming and Wingender, 2010; Fontana et al., 2010a). Besides oxygen, bacterial communities may use alternative electron acceptors (nitrate, manganese, iron, sulfate, and carbon dioxide) for the oxidation of organic material, configuring it a high metabolic potential (Demaison and Moore, 1980; Relexans et al., 1992). In environments of high organic matter supply, an overlying oxic water column may not be enough for the oxidation of sedimentary organic matter and sulfate reducing is utilized. Even if it may extend to several meters most of the reduction occurs within the top few to tens of centimeters of sediment (Berner, 1984; Dean and Arthur, 1989).

The H_2S produced during early diagenesis can upward and be reoxidized to sulfate in the oxic zone or can precipitate as authigenic sulfide minerals, which represents the main sink for sulfur in most anoxic sediments (Morse and Cornwell, 1987). Iron oxyhydroxides and iron-oxide coatings on grains are reduced to reactive ferric iron during organic matter oxidation under suboxic to anoxic diagenesis. These ion can react with the hydrogen sulfide and other sulfur compounds to form a variety of iron sulfide minerals or organosulfur compounds (Kohnen et al., 1989). Under near surface-sediment conditions, pyrite (FeS_2) is a thermodynamically stable phase relative to these iron sulfides (Berner, 1967; Sweeney and Kaplan, 1973; Berner et al., 1979; Morse et al., 1987).

Metal oxides and organic matter can liberate other trace metals during early diagenesis that can coprecipitate with iron sulfide minerals or form their own stable metal sulfides (Luther III et al., 1980; Jacobs et al., 1985, 1987; Huerta-Diaz and Morse, 1990), contributing for the enrichment of a number of trace elements in reducing marine environments (Jacobs et al., 1985, 1987; Huerta-Diaz and Morse, 1990). Different approaches have been applied to quantify sedimentary pyrite and the direct involvement in mobility and diagenetic pathways of metals under suboxic to anoxic environments, including sequential extraction methods. Assuming that only the reactive-Fe is available for the formation

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* Corresponding author. Tel.: +55 21 974682004; fax: +55 21 26292234.
E-mail addresses: esabadini@geoq.uff.br (E. Sabadini-Santos), senez.thaise@gmail.com (T.M. Senez), tabattass@yahoo.com.br (T.S. Silva), manuelmoreira@geoq.uff.br (M.R. Moreira), graciano@geologia.ufrj.br (J.G. Mendonça-Filho), santelli@iq.ufrj.br (R.E. Santelli), miriancrapez@id.uff.br (M.A.C. Crapez).

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of pyrite, Berner (1970) proposed a relation between the Fe concentrations in the pyrite and reactive fractions called the degree of pyritization (DOP), which later by analogy was extended to evaluate of trace metals incorporation into the pyrite (degree of trace metal pyritization – DTMP; Huerta-Diaz and Morse, 1990). These indexes have been applied in a wide variance of marine environments (e.g., Morse and Luther, 1999; Otero et al., 2003; Machado et al., 2014).

Guanabara Bay is urban and eutrophic coastal bay in the Southeast of Brazil, which receives domestic untreated sewage from at least 10 million people, which is equivalent to 453 t day^{-1} of biochemical oxygen demand (Bidone and Lacerda, 2004). This intense organic load is worsening the reduced tendency conditions of the bay and the anaerobic benthic microbial foodweb (Silva et al., 2008; Sabadini-Santos et al., 2014). Beside this there are also harbors, shipyards and marine terminals for oil in Guanabara Bay (Kjerfve et al., 2001). Those sources account for a total daily input of toxic metals estimated in 4.8 kg day^{-1} by the "Japan International Cooperation Agency"—JICA (2003) during researches for the Guanabara Bay Remediation Program. Its sediments are known as contaminated by Cu, Zn, Pb and Cr (Van Den Berg and De Luca Rebello, 1986; Perin et al., 1997; Baptista Neto et al., 2006; Fonseca et al., 2013), in which toxicity has been reported (Maranho et al., 2009; Sabadini-Santos et al., 2014). Regarding these characteristic and the reduction dominance that promotes the stability of metal-sulfide formed in this environment, organic/sulfide phases are as important regulators of metals in Guanabara Bay as amorphous and crystalline Fe/Mn (Perin et al., 1997; Fonseca et al., 2013). In this study, we try to estimate by chemical extractions the actual extent of sedimentary pyrite and incorporated trace elements (As, Cd, Co, Cr, Cu, Mn, Ni and Zn) at Guanabara Bay sediments, which can improve the prediction of metal behavior in this contaminated coastal environment.

2. Material and methods

Guanabara Bay has a mean water volume of 1.87 × 109 m^3 and a hydrographic basin extends over 4080 km^2 including 45 rivers, 6 of which are responsible for 85% of the runoff (Amador, 1980; Kjerfve et al., 1997). At the entrance of the bay, the water column is well mixed whereas by inwards it, where increasing width is observed, the system is moderately stratified, resulting in a renewal time of 50% of the bay water volume in 11.4 days (Kjerfve et al., 1997). The central channel (depths of 30–40 m) is delimited by the 10 m isobathymetric, resulting in a decrease of tidal current which spring velocity decline from 1.6 m s^{-1} at the main channel to 0.5 m s^{-1} inside the bay. Historically, the catchment areas around the bay have been seriously modified by anthropogenic activities, enhancing the bay's silting, contamination and eutrophication processes as the population grows without appropriate environmental management and sanitation structure (Bidone and Lacerda, 2004; Silveira et al., 2011and others).

The rivers and channels that discharge in Guanabara Bay cross greatly urbanized areas, receiving all kinds of effluents. According to Baptista Neto et al. (2006), Marques Júnior et al. (2006), Silva et al. (2008), Santos et al. (2008), Aguiar et al. (2011), Fonseca et al. (2013) and other authors, some hot spots of continental sources can be highlighted and were sampled: the Northwestern and Western area (St 15, 16, 19 and 20), where are the discharge point of the most polluted rivers and where the demography and the industrial activities (including oil refinery) are more concentrated; the Mangue Channel (St 6); the Rio de Janeiro Harbour (St 7); the embayments in the Southern portion of the bay, where is a sewage outfall (St 2 and 3); and the Easter area near by São Gonçalo city (St 8 and 9), the second biggest city in the State of Rio de Janeiro. Apart from St 18 (14 m of depth), a total of twenty surface sediment (0–10 cm) stations were sampled in shallow locations (less than 11 m depth) during the spring season of 2011 with an Ekman Type grab and their locations are represented in Fig. 1.

Sediments subsamples were grain size determined by using a Cilas 1064 particle size analyzer, which measures particles between 0.04 and 500 μm, after the organic matter destruction with H_2O_2 and sediment dispersion in a $Na_4P_2O_7$ solution and sonication. Fe, Mn, As, Pb, Cd, Zn, Cu, Cr, Ni and Mo associated with the operationally-defined reactive phase and the pyrite phase were determined according the sequential extraction of Huerta-Diaz and Morse (1990). The sum of iron concentrations determined in all phases from the sequential extraction of Huerta-Diaz and Morse (1990) was considered representative of total iron concentrations (TFe). The degree of pyritization (DOP) was calculated from the reactive iron and pyritic iron concentrations according to Huerta-Diaz and Morse (1990). The degree of trace metals pyritization (DTMP) were analogous calculated to that used for DOP. The reactive phase is fractions soluble in 1 M HCl and the pyrite phase is the fraction extracted in concentrated HNO_3 after removal of silicate and organic phases. Elemental analyses were carried out using a Jobin–Yvon Ultima 2 sequential ICP–OES (Longjumeau Cedex, France).

The total organic carbon (TOC) and total sulfur (TS) were determined after acidification in an elemental analyzer LECO SC 144 device. The adopted methods were ASTM D 4239 (ASTM, 2008) and NCEA-C-1282 (Schumacher, 2002). Concentrations of total biopolymers (carbohydrate, lipids and proteins) were determinate in triplicates. All determinations were done by spectrophotometric methods. Carbohydrates (CHO) were quantified using the same principle as Dubois et al. (1956), according to the modified method of Gerchakov and Hatcher (1972) for sediment analysis, using glucose as the standard. Lipids (LPD) were extracted with chloroform and methanol and analyzed according to Marsh and Weinstein (1966); tripalmitine was used as the standard. Proteins (PRT) were determined according to the method proposed by Hartree (1972), to compensate for phenol interference. Bovine albumin, fraction V (Sigma), was used as the standard. The concentrations of carbohydrates, proteins and lipids were expressed in carbon equivalent (mg C g^{-1}) using the conversion factors 0.40, 0.49 and 0.75 respectively (Fabiano et al., 1995). The sum of protein, carbohydrate and lipid carbon equivalents was referred to as biopolymeric carbon and can represent the bioavailable carbon amount present in the sediment, expressed in the percentage of TOC.

The total number of bacterial cells (CELL) was enumerated by epifluorescent microscopy (Axiosp 1, Zeiss, triple filter Texas Red – DAPI – fluorescein isothiocyanate, 1000 magnification) and using fluorochrome fluorescein diacetate and UV-radiation (Kepner and Pratt, 1994). Viable cells were determined in triplicates at 2 h after sampling.

Sample station locations were positioned by GPS (Garmin II) and plotted with the Surfer Version 8.00 software (Golden Software Inc., USA). Statistical procedures involved Spearman correlation with the software package STATISTICA® (StatSoft Inc., Tulsa, OK, USA). The relations of the grain-size (Sand and Fine – clay and silt), organic matter (TOC, TS, C:S, CHO, LPD and PRT), viable bacterial cells (CELL), degree of pyritization (DOP) and degree of trace metals pyritization (DTMP – trace metal) in the study area were analyzed using principal component analysis (PCA). Stations 1 and 3 were excluded from the PCA because its pyrite iron concentrations were undetectable and the DOP could not be calculated. Both DTMP of Pb and Cr were also excluded from the PCA because there values were almost null. The data were standardized using the "ranging for variables with arbitrary zero" procedure proposed by Milligan and Cooper (1985). The analyzed components were those that exhibited eigenvalues significantly higher than those