Reactivity of clays and metal nanomaterials in waters and sediments from saline wetlands: the role of the bacterial communities

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Abstract

Saline fluids in eutrophic environments promote multiple mineral reactions coupled with biological activity in wetland sediments from river basins. Microbial redox reactions involving Fe and other metals control mineral authigenic sedimentary processes in these environments affecting the stability of clays, sulfides, oxides and phosphates in sediments. This contribution shows how the wetlands from the Chicamocha river Basin (Colombia) is an excellent natural laboratory to study factors controlling these reactions mediated by microorganisms. Most of the bacterial activity in wetland sediments is associated with organic matter degradation processes. These groups play the role of biogeochemical linkers that relate the reactions of C and S in sediments, favoring elemental mobility that affect the cycle of Fe and other metals of the sediments and the activity of iron- and sulfur-cycling bacteria, sulfur- and sulfate-reducing bacteria (SRB), sulfide-oxidizing bacteria (SOB), iron-reducing bacteria (IRB) and iron-oxidizing bacteria (IOB). Authigenesis and clay mineral reactivity is influenced by cation availability, frequently mediated by the microbial activity, and the presence of an appropriate mineral precursor. Fe-rich environment by hydrothermal and anthropic inputs in the Chicamocha Basin wetlands and the reducing conditions generated by the decay of abundant organic matter caused Fe mobilization mediated by the presence of SRB and SOB communities, which favored the processes of transformation of detrital clays. High concentration hydrothermal K in the waters of the lake and Fe uptake in the octahedral sheet promoted the illitization of the precursor clays (smectites or I-DV). Bacterial activity in organic matter rich sediments also favors the availability of sulfide (stimulated by SRB and their syntrophic partners that produce H_2) and Fe^{2+} (promoted by IRB and SRB) and other metals, such as Zn, that can be fixed as insoluble monosulfides encrusting microbial cells. IRB enrichment of the sediments stimulates a greater availability of Fe^{2+} and favors the reaction of Fe^{2+} with PO_4^{3-} to form vivianite. The stage of monosulfide and/or phosphate precipitation is followed by a dissolution step and a recrystallization process that produce pyrite framboids enhanced by the SOB activity, which also facilitate the oxidation of the reduced sulfides to S° and the release of toxic heavy metals again into the environment that can be increased by IOB oxidation reactions even in anoxic environments.

Resumen

Los fluidos salinos en ambientes eutróficos y la actividad biológica asociada promueven múltiples reacciones minerales en los sedimentos de los humedales de las cuencas fluviales. Las reacciones redox microbianas que implican al Fe y a otros metales controlan los procesos sedimentarios de formación de minerales en estos ambientes y afectan a la estabilidad de las arcillas, sulfuros, óxidos y fosfatos presentes en los mismos. Este trabajo muestra que los humedales de la cuenca del río Chicamocha (Colombia) son un excelente laboratorio natural para estudiar los factores que controlan estas reacciones mediadas por microorganismos. La mayor parte de la actividad bacteriana en los sedimentos de los humedales está asociada con los procesos de degradación de la materia orgánica. Estos grupos conectan biogeoquímicamente las reacciones del carbono y del azufre en los sedimentos, favoreciendo la movilidad elemental del hierro y de otros metales de los sedimentos, así como la actividad de las bacterias implicadas en los ciclos del hierro y el azufre: bacterias reductoras del azufre (SRB), bacterias oxidantes del azufre (SOB), bacterias reductoras del hierro (IRB) y bacterias oxidantes del hierro (IOB). La autigénesis y la reactividad de los minerales arcillosos están influidas por la disponibilidad de cationes, frecuentemente mediada por la actividad microbiana, y la presencia de un precursor mineral apropiado. El ambiente rico en hierro por aportes hidrotermales y antrópicos en los humedales de la Cuenca del Chicamocha y las condiciones reductoras generadas por la descomposición de abundante materia orgánica provocaron la movilización de hierro mediada por la presencia de

comunidades de SRB y SOB, que favorecieron los procesos de transformación de las arcillas detríticas. La alta concentración hidrotermal de K en las aguas del lago y la captación de hierro en la capa octaédrica promovieron la illitización de las arcillas precursoras (I-DV). La actividad bacteriana en sedimentos ricos en materia orgánica también favorece la disponibilidad de sulfuro (estimulada por SRB y sus socios sintróficos que producen H_2), Fe^{2+} (promovida por las IRB y SRB) y otros metales, como Zn^{2+}, que pueden fijarse como monosulfuros insolubles en incrustaciones de la pared de células microbianas. El enriquecimiento en IRB de los sedimentos estimula una mayor disponibilidad de Fe^{2+} y favorece la reacción de Fe^{2+} con PO_4^{3-} para formar vivianita. A la etapa de precipitación de monosulfuro y/o fosfato, le sigue una etapa de disolución y un proceso de recristalización que produce framboides de pirita potenciados por la actividad de las SOB, que también facilitan la oxidación de los sulfuros reducidos a S° y la liberación de metales pesados tóxicos que puede incrementarse por reacciones de oxidación de las IOB incluso en ambientes anóxicos.

Key-words: SRB, IRB, SOB, IOB, illite, mackinawite, pyrite.

1. Introduction

Water salinity of hydrologically-restricted environments such as continental wetlands can commonly increase due to natural inputs or pollutants affecting the chemical and composition of the sediments. Natural inputs are frequently associated to dissolution processes producing trace element-rich hydrothermal fluids, especially in geothermal or evaporitic areas (see e.g. references in Cifuentes et al., 2020, 2021a). Agricultural activities, smelting and urban wastewaters have been considered as some of the main types of anthropic activities promoting potential pollution in waters and sediments of wetlands (see e.g. references in Quevedo et al., 2020a). Moreover, fertilization techniques and organic matter from urban wastewaters contribute to environmental eutrophication.

Saline fluids in eutrophic environments can promote multiple mineral reactions coupled with biological activity in the sediments (Cuadros et al., 2017; Aghasian et al., 2019; Zhang et al., 2019). Microbial redox reactions involving Fe and other metals control mineral authigenic sedimentary processes in these environments affecting the stability of clays, sulfides, oxides and phosphates in sediments (Andrade et al., 2018).

The Chicamocha river Basin (Colombia) is an excellent natural laboratory to study the influence of natural and anthropic inputs on the composition of organic matter rich sediments deposited in saline wetlands (Cifuentes et al., 2020, 2001a, b and c; Quevedo et al. 2020a and b, 2021). Two main wetlands regulate the surface water outflow of the basin (Figure 1): the La Playa dam and the Sochagota Lake dam. These wetlands store water to meet various demands, such as ranching, agriculture, tourism and industry, and their impoundments receive anthropogenic input from farm activities and wastewater (La Playa reservoir) as well as input from natural hydrothermal waters (Sochagota Lake) that produce high salinity waters, intense eutrophication and organic-rich sediments.

This article reviews the sources of salinity and metal enrichment in wetlands from the Chicamocha Basin and the most important bacterial communities developed in the organic matter rich sediments deposited in these environments with the aim to show the influence of the microorganisms on the main reactions involving clays and other minerals associated to the metal nanoparticle fixation.

1. Sources of salinity and metal enrichment in wetlands

Wetlands are hydrologically-restricted environments where water salinity and metal concentrations can increase due to natural inputs or pollutants. Water wetlands salinity increase is frequently controlled by geological factors, such as the presence of regional evaporitic sediments or hydrothermal SO_4^{2-}-Na inputs. However, anthropogenic inputs from farm activities (using fertilizers and pesticides) and wastewaters (mainly urban sewage) can also produce high-salinity waters.

High heavy metals concentration is of particular concern for humans because of their detrimental health effects on people in excessive quantities. Polluted wetlands, can create potential risk of metal exposure to humans. The origin of heavy metal enrichment can also be associated to natural and anthropogenic processes.

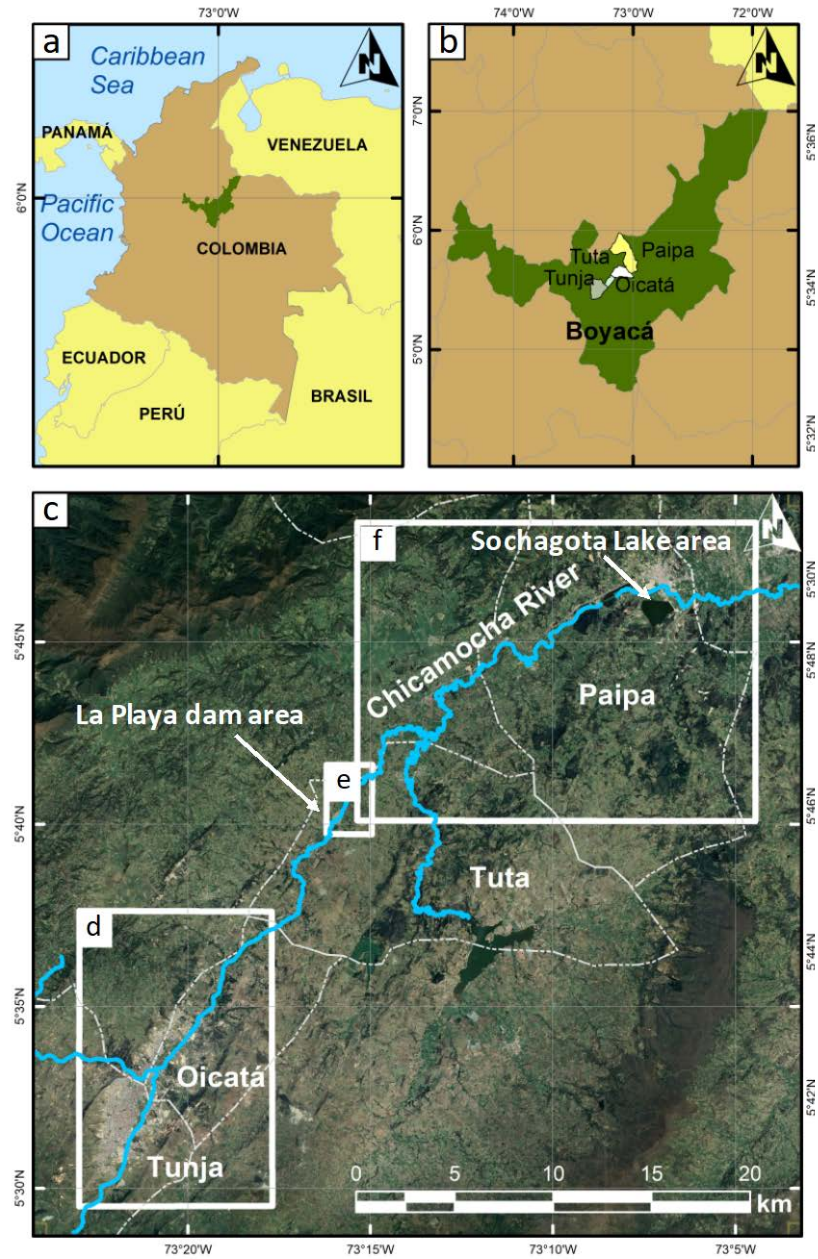

Fig.1. *Geographical setting of the Chicamocha river Basin (Colombia). (a) Global context of the area; (b) Regional map; (C) Sectors of the Chicamocha River between Tunja and Paipa, Boyacá Province indicating the location of the La Playa dam and the Sochagota Lake. Modified from Quevedo et al. (2020a).*

1.1. Natural hydrothermal inputs. The Sochagota Lake

The Sochagota Lake is an exceptional case study to show the influence of natural inputs on the composition of waters and sediments. An increase of water salinity and metal concentrations associated to natural inputs can be observed in this wetland located at the lowest segment of the Chicamocha Basin. This is an artificial lake constructed from a previous natural wetland (Figure 2). From a geological point of view, it is located in the main Andean geothermal system in Colombia with hydrothermal systems associated to the area's volcanoes (Alfaro et al., 2005). The rhyolitic Paipa volcano, which is characterized by a collapsed caldera (3 km wide) with several hydrothermal vents, is the nearest volcanic building to the lake. The hydrothermal waters flow through the El Salitre River (a tributary of the Chicamocha River) and are mixed with rain waters in Sochagota Lake (Cifuentes et al., 2021a).

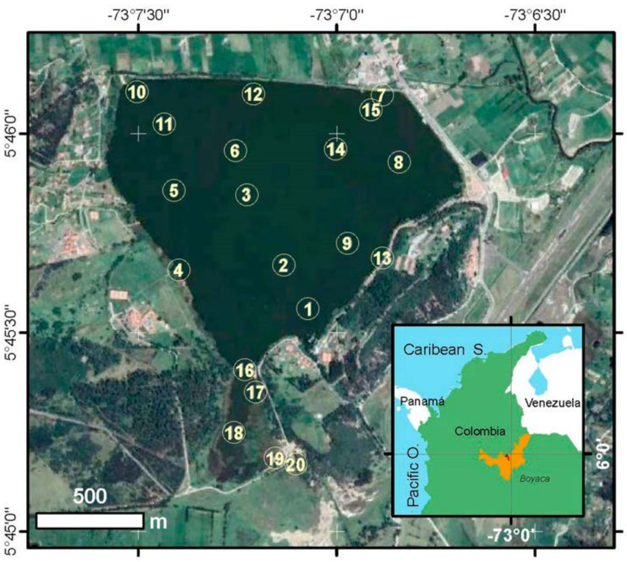

Fig.2. *Location of the Sochagota Lake. Numbers indicate sample positions. The small map represents the regional context of the global area, i.e., situation of the Paipa province (Boyaca region) in Colombia. Taken from Cifuentes et al. (2021a).*

Geothermal waters contribute to the chemical composition of the water of the El Salitre river as follows (see specific data in Cifuentes et al., 2021a): (i) SO_4^{2-}-(Cl^-) Na^+-K-rich hot waters; and (ii) Fe-rich, HCO_3^- (Cl^--SO_4^{2-}) cold waters. Hydrothermal fluids associated with geothermal systems contain potentially pollutant chemicals (e.g., S, Fe, As, Pb, Zn, Mn) in the liquid fraction that may be present in harmful concentrations and can cause environmental chemical pollution. The water isotopic composition of the Sochagota Lake waters (6.4‰ for $\delta^{34}S$ and 8.1 for $\delta^{18}O$, which is comparable to several hydrothermal liquids), and the lack of evaporitic rocks in the stratigraphic sequence indicated that the high mineralization of the lake water was a result of hydrothermal contributions of S-bearing fluids from springs feeding the Salitre River. The good correlations of SO_4^{2-} with metals in the lake waters also supported that its origin is associated with hydrothermal inputs to the Salitre River. The hydrochemistry of the cold waters can be related to the water–rock interaction of an alluvial shallow aquifer made of volcanic and sedimentary particles and recharged by rain. A mixing of thermal and saline waters with cooler groundwater is produced at the Salitre River bed, causing the SO_4^{2-}-Na^+-K^+-Fe-rich waters which are accumulated at the south entrance of the lake.

High electrical conductivity and sulfate-rich waters from the south lake entrance are characterized by high contents of Cl^-, Li, Be, Al, K, Fe, Co, Ni, Cu, Zn, As, Rb, Cs, and Pb. The concentrations of SO_4^{2-}, Cl^-, Fe and As exceeded the regulatory framework for contaminants in waters (250 mg/L for SO_4^{2-} and Cl^-, 0.3 and 0.01 mg/L, respectively) or electrical conductivity (1000 μS/cm). On the other hand, in the centre and north areas of the lake, conductivity, SO_4^{2-} and Cl^- were clearly lower than in the waters from the south entrance, although these contents slightly exceeded the Colombian regulations for pollutants in waters.

Two main types of sediments can be distinguished in the Sochagota Lake (see specific data in Cifuentes et al., 2020). Sediments from the southern part of the lake, deposited at the entrance of the hydrothermal inputs (El Salitre) under fast-flowing conditions, were found to contain negligible organic matter (TOC 0.7%). In this area, the deposition of organic matter is not favored by the hydrodynamic conditions, thereby promoting the oxygenation of the sediments (measured redox potential around 90 mV). By contrast, the central and northern parts of the lake, under slower-flowing conditions, are characterized by the deposition of the finest clay-rich sediments and organic matter (TOC up to 11.10%) with reduced conditions (redox potential around −150 mV).

The spatial distribution of trace elements in the sediments of Sochagota Lake seems to be associated with the distribution of organic matter content and mineral assemblages (see specific data in Cifuentes et al., 2021b). Organic matter-poor sediments from the southern part of the lake were found to be enriched in Zr (mean 567 mg/kg) and their mineral assemblages did not contain illite, I-DV or S-bearing minerals. The large contents of Zr, SiO_2 and TiO_2 in these sediments can be associated with the deposition of terrigenous zircon, quartz and rutile. On the other hand, organic matter-rich sediments with a fine-grain sized matrix rich in illite and I-DV located in the northern and central segments of the lake were found to be enriched in heavy metals (Cu, Zn, Cr, Ni, Co, Pb, Mo), Rb, Ba and

As. These sediments were characterized by the crystallization of S-bearing minerals (mackinawite, pyrite, and S°) (Cifuentes et al., 2020). The concentrations of heavy metals in these sediments exceeded the world standard averages, and the mean level of some of these elements was clearly higher than the value of unpolluted reference sediments from the Chicamocha River area (Quevedo et al., 2020a).

1.2. Anthropic pollution inputs. La Playa dam

La Playa dam, the most relevant anthropic change in the Chicamocha Basin, offers the opportunity of showing the influence of human activity inputs on several biogeochemical cycles. The reservoir of the La Playa dam receives wastewaters (urban sewage) from the towns of the region and waters of the agricultural activities, which generate a high nutrient load and intense eutrophication. Moreover, the La Playa dam is located less than 3 km east of an important smelter that produce smelting slags with high Zn contents.

Waters and sediments from La Playa reservoir reflect the effect of these anthropic inputs. Water composition is characterized by high heavy metals concentrations, especially for Zn (mean value 268 μg/L) as compared with waters from other segments of the Chicamocha River, and high P contents (mean value 6847 μg/L). Water salinity is very high (1478 μS/cm) and redox potential is low (-27 mV) (see specific data in Quevedo et al., 2020a).

The sediments from the La Playa dam are characterized by alternating bands of microlaminated organic-matter-rich layers and clay-rich layers, showing a high organic matter content (TOC of up to 11.1%), low redox potential (around −230 mV) and high electrical conductivity (2625 μS/cm) (see specific data in Quevedo et al., 2020a, b, 2021). Clay mineral assemblage in the sediments trapped in La Playa dam in the upper part of the basin is characterized by the presence of detrital kaolinite and I-DV and authigenic Fe-bearing smectite (up to 0.4 atoms per formula unit (a.p.f.u.). Fe and Zn-bearing minerals (pyrite, ZnS, vivianite, goethite) are exclusively found in sediments from the La Playa dam and are absent from the rest of the alluvial sediments from the Chicamocha river basin. Periodical water discharges in La Playa dam create areas with intermittently emerged sediments, whereas other areas contain permanently flooded sediments, producing important changes in the redox conditions of sediments (Figure 3). Pyrite is present in all of the sediments deposited in the reservoir. Permanently flooded sediments that are richer in organic matter and have a lower redox potential (around −230mV) from the northern part of the reservoir are characterized by the presence of vivianite and ZnS, and, by contrast, periodically emerged sediments from the southern part of the reservoir with lower organic matter contents (4.29%) and higher Eh values (−10mV) contain goethite.

Fig.3. *Location of the La Playa dam. Numbers indicate sample positions. Taken from Quevedo et al. (2020).*

From the geochemical point of view, clay-rich sediments from la Playa reservoir have lower SiO_2 contents (mean 61.24%) and higher Al_2O_3 contents (mean 17.17%) than quartz-rich sediments from the rest of segments of the Chicamocha Basin. The La Playa sediments are also characterized by the highest content in organic matter (TOC up to 13.84%), and LOI values (up to 15.43%). A significant enrichment in the P_2O_5 content (mean value of 0.58%) and heavy metals (Zn > Cu > Cr > Ni > Pb) of these sediments can also be observed.

2. Bacterial communities in organic matter rich saline environments

Several environmental variables, such as hydrodynamic conditions, organic matter content, salinity or cycles of wetting and drying, favor the presence of specific microorganism communities controlling some of the most important biogeochemical cycles in wetlands. Processes of organic matter degradation and mineral transformation in the C, Fe, P and S cycles are associated with the bacterial activity of the sediments of these environments. Thus, the presence of a diverse bacterial community composition made of the following groups can be identified (Cifuentes et al., 2021b; Quevedo et al., 2021).

2.1. Bacterial groups involved in the degradation of the organic matter

Most of the bacterial activity in wetland sediments is associated with organic matter degradation processes. In the Chicamocha Basin, the main bacterial communities belong to fermentative genera from anoxic zones from *Bacteroidetes*, *Chloroflexi* and *Firmicutes* phyla, which digest, grow on and degrade organic substrates (Rui et al., 2009; Zhou et al., 2016). *Sphingobacteriales* can play an important role during the initial degradation stages of organic matter whereas other groups like Bacteroidetes_vadinHA17 and *Dehalococcoidia* and *Anaerolineae* are more important during the final degradation stages of organosulfur compounds in sulfidic zones. Other groups, suchs as *Ignavibacteriales* order, have the function of CO_2 fixation. *Rikenellaceae* family (*Bacteroidetes*) in these sediments can be associated with being responsible for the decomposition of harmful algal bloom in ponds. Othes *Bacteroidetes* genera, such as WCHB1-32, BVS13 and *Macellibacteroides* (Ji et al., 2018), have been thought to be important in the formation of methanogenic precursors from organic matter degradation. Some members of the phylum *Firmicutes*, such as the *Christensenellaceae* family, are frequently reported in human feces and other animal feces, and show a fairly high capability for degrading carbohydrates and carboxylic acids. Finally, several communities, i.e. *Syntrophomonadaceae* members (*Firmicutes*) or *Anaerolineaceae* (*Chloroflexi*) can contribute to produce H_2 used by sulfate-reducing bacteria (SRB) acting as syntrophic partners (Timmers et al., 2018). Thus, these groups play the role of biogeochemical linkers that relate the reactions of C and S in sediments, favoring the mobility of these elements in the system, which can affect the cycle of Fe and other metals of the sediments and the activity of iron- and sulfur-cycling bacteria, sulfur- and sulfate-reducing bacteria (SRB), sulfide-oxidizing bacteria (SOB), iron-reducing bacteria (IRB) and iron-oxidizing bacteria (IOB).

2.2. SRB and IRB communities

SRB and IRB have direct effects on the availability of dissolved metals, which can be incorporated into the precipitated minerals (e.g., sulfides or phosphates).

An important SRB community was identified in the wetland sediments of the Chicamocha Basin (Cifuentes et al., 2021b; Quevedo et al., 2021). This community was dominated by *Desulfatiglans*, *Pseudomonas*, *Syntrophobacter*, and *Thermodesulfovibrionia* although other SRB microbial communities of *Desulfobacterales* (Fam. *Desulfobacteraceae*, G. *Sva0081 sediment group*), Sva0485, *Desulfomicrobium* and *Desulfobulbus* and *Desulfobacca* genera. were also identified. These bacterial groups are characterized by its elevated levels of metal resistance (*Pseudomonas*, Zampieri et al., 2020), its ability to colonize in sludge and sewage (*Desulfobacca*) in in sulfate-rich wetlands (*Syntrophobacter*) where play a crucial role in the cycles of nitrogen and sulfur (*Thermodesulfovibrionia*) and promoting P release at contaminated sediments (*Desulfomicrobium* and *Desulfobulbus*).

The presence of a significant proportion of iron-reducing *Latescibacteria, Geobacter*, *Dechloromonas*, *Paludibacter and Acidibacter* (Cifuentes et al., 2021b; Quevedo et al., 2021) suggests that these communities could have also contributed to the direct reduction of Fe^{3+}. *Geobacter* and *Paludibacter* was associated with organic-matter-rich sediments with humic acids, playing an essential function in the release of Fe^{2+} to the interstitials waters of sediments under anaerobic conditions. *Dechloromonas* has been found to be related to the reduction of Fe^{3+} to Fe^{2+} in sludges that contain P and Fe. *Paludibacter* has been described as a fermentative microorganism in high sulfate and metal concentration environments that is able to transfer electrons from anaerobic oxidations to promote the reduction of iron. *Acidibacter* has the capability of reducing dissolved Fe^{3+} in low pH and high Fe environments (Chen et al., 2020).

2.3. SOB communities

Some groups of *Gammaproteobacteria* and *Epsilonbacteraeota* are believed to be the functional SOB of the wetlands from the Chicamocha Basin (Cifuentes et al., 2021b; Quevedo et al., 2021), producing the transformation of Fe sulfides and contributing to the possible release of metals and producing the presence of sulfates and S° associated with areas with pyrite framboids.

Thioalkalimicrobium and *Thiobacillus* were the dominant SOB belonging to the *Gammaproteobacteria* group, whereas *Sulfurovum, Sulfuricurvum* , *Arcobacter* and *Sulfurimonas* are the main components of the *Epsilonbacteraeota* group. These two SOB communities use diverse strategies for the oxidation of sulfur. *Epsilonbacteraeota* need a continuous supply of reduced sulfur and oxygen, but *Gammaproteobacteria* are able to adapt their energy metabolisms to different reduced environmental conditions. *Thiobacillus*, *Sulfurimonas* and *Arcobacter* are commonly involved in the autotrophic denitrification of saline sewages and can be used as an indicator of sewer and human fecal pollution (especially *Arcobacter*). *Sulfuricurvum* is frequently the dominant SOB under elevated free sulfide concentrations.

2.4. IOB communities

Although IOB are commonly absent in reduced sediments of the Chicamocha Basin. The alternation of wetting and drying periods can favor an increase of the IOB amount. Thus, Gallionellaceae family and Sideroxydans genus are very well represented in the periodically emerged sediments of the La Playa dam (Quevedo et al., 2021). These groups can play an important role in the oxidation of Fe^{2+} in sediments with low oxygen levels.

3. Clay mineral reactions

Many mineral reactions at low temperature are not controlled by thermodynamics but kinetics. In organic matter rich sediments, authigenesis and clay mineral reactivity is influenced by cation availability, frequently mediated by the microbial activity, and the presence of an appropriate mineral precursor.

Regarding cation availability, continental saline environments are characterized by Fe-enrichment due to natural or anthropic input sources. The abundance of organic matter promotes reducing conditions generated by its decay and the proliferation of IRB and SRB. These bacterial communities cause Fe mobilization that can eventually be fixed as sulfide or phosphate minerals. However, the common coexistence of SOB in this type of sediments can favor sulfur oxidation and Fe-release. These processes can facilitate the presence of abundant dissolved and colloidal Fe^{2+} and Fe^{3+} in the interstitial water that promote formation of reactive Fe phases in constant transformation favoring silicate mineral neoformation and reactions (Andrade et al. 2018; Quevedo et al, 2020b). The authigenic formation of clay minerals, such as smectites, is frequently revealed the presence of small flakes forming rose-shaped aggregates that fill pores in the sediment, such those observed in the La Playa dam (Quevedo et al, 2020b). The existence of Fe easily mobilized by bacteria mediated oxidation–reduction reactions favored that, under the influence of the reducing environment produced by anthropic contamination, clay minerals uptake Fe and incorporate it into authigenic clays. The presence of up to 0.4 a.p.f.u. of Fe in the TEM-EDX analysis of smectite from La Playa sediments suggested that Fe was incorporated in the octahedral sheet (Quevedo et al, 2020b).

The crystallization of illite is a common feature of the end of the processes of authigenesis and clay mineral reactions in saline sediments rich in organic matter. The presence of an appropriate mineral precursor and cation availability (Fe and K) and are the two main factors controlling the illitization process in these environments (Cuadros et al., 2017).

Smectite or illite–smectite mixed layers are the most frequently proposed clay precursors for illite formation in sedimentary basins but the transformation to illite can also be produced through illite–dioctahedral vermiculite (I-

DV) interstratification, as in the Sochagota Lake (Cifuentes et al., 2021c). Climatic conditions in the Sochagota Lake area produced a partial transformation of primary minerals to kaolinite and vermiculitic minerals as the main clay minerals in the source materials draining the basin, favoring the deposit of small-sized metastable intermediates of I-DV minerals, which acted the mineral detrital precursor of the illitization process. TEM-EDS data revealed that well crystalized neoformed illite (Figure 4) has more Fe than I-DV, revealing that the uptaking of Fe played an important role during the illitization process. The chemistry of the lake water, which is enriched in Fe by hydrothermal input, and the reducing conditions generated by the decay of abundant organic matter caused Fe mobilization mediated by the presence of SRB and SOB communities. High concentration hydrothermal K in the waters of the lake and Fe uptake in the octahedral sheet can promote the illitization of the precursor clays (I-DV). The incorporation of Fe during illitization should be produced by the coupled substitutions of Al for Si in the tetrahedral sheet and of Mg and Fe for Al in the octahedral sheet, promoting the incorporation of K to the interlayer. This low-temperature illitization process highlights the importance of clays in the uptake of K from hydrothermal waters in geothermal areas.

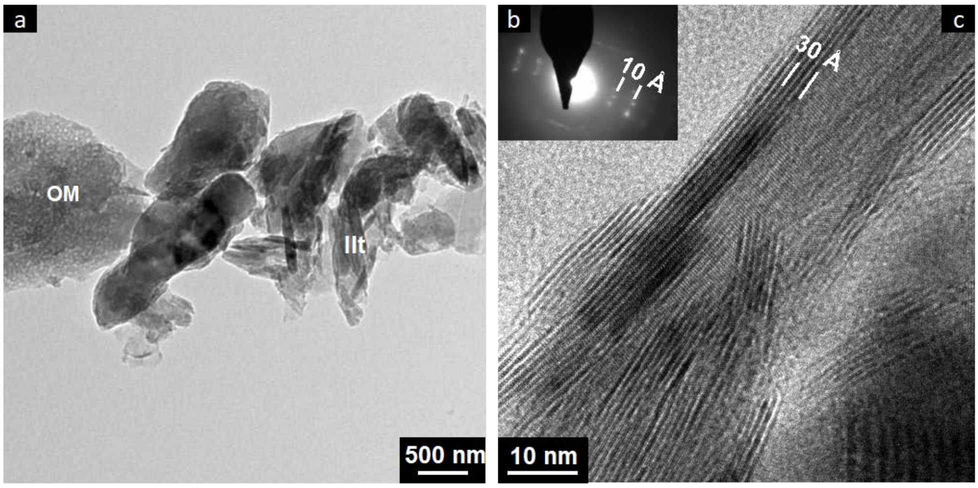

Fig.4. *TEM images of illite in samples from the Sochagota Lake. (a) Textural image of illite in clay aggregates. (b) SAED pattern of illite. (c) HRTEM image of illite showing wide areas of well-defined 10 Å lattice fringes. OM: organic matter, Ilt: illite. From Cifuentes et al. (2021c).*

4. Bacteria mediated reactions of metal-rich minerals

The redox reactions of metal-bearing minerals in organic matter-rich sediments have a strong effect on the speciation, mobility and bio-availability of pollutants. The precipitation of Fe and other metals in different minerals depends on the environmental conditions. Redox conditions are one of the main factors controlling the precipitation of Fe-bearing minerals, favoring the precipitation of Fe^{2+}-minerals (mainly phosphates and sulfides) under low redox potential conditions and Fe^{3+}-minerals (mainly oxides and oxyhydroxides) under high redox potential conditions. In anoxic environments rich in P and S, microbial processes can promote the formation of vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and iron and other metal sulfide minerals, such as mackinawite ((Fe,Ni)S), ZnS or pyrite (FeS_2). The crystallization of sulfide minerals can widely affect all of these reactions.

The importance of a decaying organic matter-rich environment for the crystallization of metal sulfides have been frequently described as important factor controlling the mineral assemblage of sediments (see e.g., Folk, 2005; Love, 1967; Love et al., 1984; MacLean et al., 2008). High metal concentrations in sediments is frequently related to the process of sulfide crystallization in these carbonaceous matter-rich environments.

Bacterial communities of this types of sediments in the Chicamocha Basin (Cifuentes et al., 2021b, Quevedo et al., 2021) are characterized by the presence of groups able to reduce sulfate (SRB, such as *Desulfatiglans, Desulfobacterales* and Sva0485 in the Sochagota Lake; *Pseudomonas, Desulfomicrobium* and *Desulfobulbus* in the La Playa dam) and Fe^{3+} (IRB, *Latescibacteria in the Sochagota Lake; Geobacter, Dechloromonas, Pseudomonas* and *Paludibacter* in the La Playa dam). The activity of these bacterial groups in the flooded sediments can be reinforced by syntrophic partners to produce H_2 used by SRB (such as *Syntrophomonadaceae*) and increase the sulfide availability. Therefore, bacterial activity in organic matter rich sediments favors the availability of sulfide (stimulated by SRB and their syntrophic partners that produce H_2) and Fe^{2+} (promoted by IRB and SRB) and other metals, such as Zn, that can be fixed as insoluble sulfides. SEM images showing cell-shaped aggregates with metal sulfide composition support the importance of the bacterial communities in the nucleation and transformation of sulfide minerals (Figure 5). HRTEM images of the nanoparticles encrusting bacterial cells frequently show (001) lattice fringes of ≈5 Å (Cifuentes et al., 2021b) suggesting mackinawite precipitation during the initial step of the sedimentary sulfide formation in the Sochagota Lake. Raman microspectrometry has confirmed the accumulation of these mackinawite particles at the inner part of plant fragments (Figure 5c).

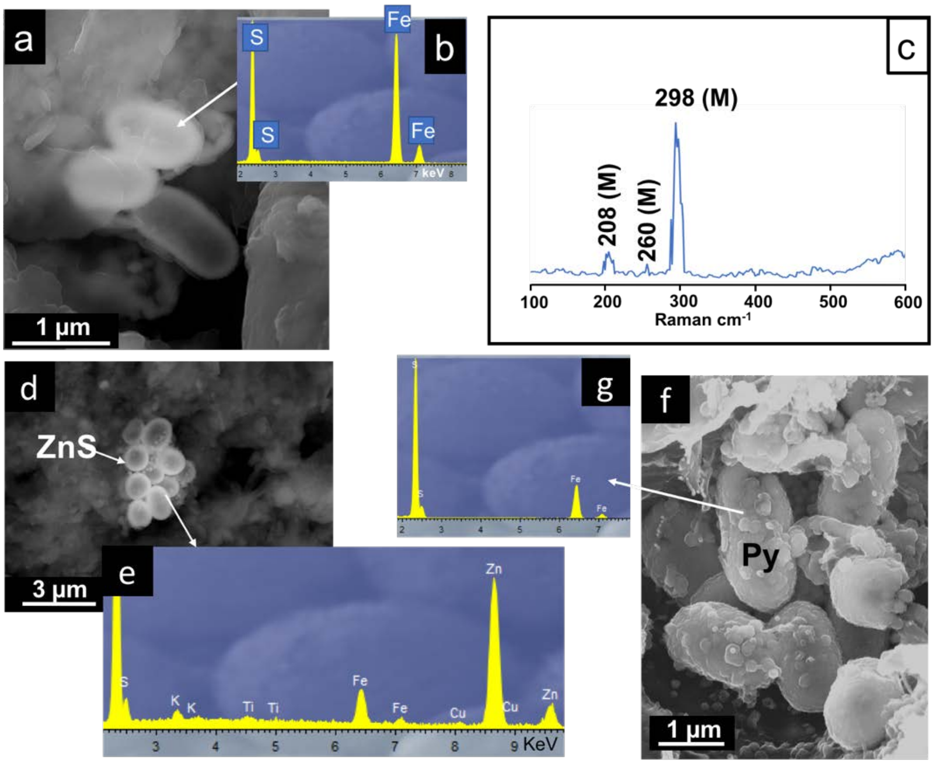

Fig.5. *Metal sulfide nanoparticles forming aggregates which oval and spherical shape and size closely resemble bacterial cell morphology. (a) FeS nanoparticles aggregates with bacterial cell morphology in the Sochagota Lake sediments. (b) EDX spectrum of the FeS minerals. (c) Raman spectrum of the FeS minerals confirming the presence of mackinawite. (d) ZnS cell-shaped aggregate in La Playa dam. (e) EDX spectrum of the ZnS minerals. (f) Pyrite cell-shape aggregates in La Playa dam. (g) EDX spectrum of pyrite M: mackinawite. Py: pyrite. Modified from Cifuentes et al. (2020) and Quevedo et al. (2020a, 2021).*

The monosulfide nucleation promoted by microbial cells can also enhance the accumulation of trace elements to the sediments. The Zn-enrichment of the sediments from the La Playa dam can be associated to the crystallization of ZnS nanoparticles encrusting SRB cells (Figure 5d), probably from the *Pseudomonas* group is a very good example of metal fixation by monosulfide precipitation.

Sulfide formation can compete with the precipitation of Fe^{2+}-bearing phosphate (vivianite) for the available reduced Fe of the environment. The formation of vivianite is frequently restricted to environments where an excess of Fe in dissolution is available after the crystallization of sulfides. However, microorganisms can play an important role in the availability of these substances and, therefore, in the concomitant crystallization of phosphates and sulfides.

IRB enrichment of the sediments (such as in the permanently flooded sediments of the La Playa dam which contain *Geobacter, Dechloromonas, Pseudomonas* and *Paludibacter*) can promote a greater availability of Fe^{2+}, which favors the precipitation of vivianite by the contribution of microbial iron- and sulfur-reducing processes, as in the La Playa dam (Figure 6). These bacterial communities play an essential function in the release of Fe^{2+} to the interstitials waters of sediments under anaerobic conditions and they have been found to be related to the reduction of Fe in sludges that contain P and Fe, promoting the reaction of Fe^{2+} with PO_4^{3-} to form vivianite (Wu et al., 2021).

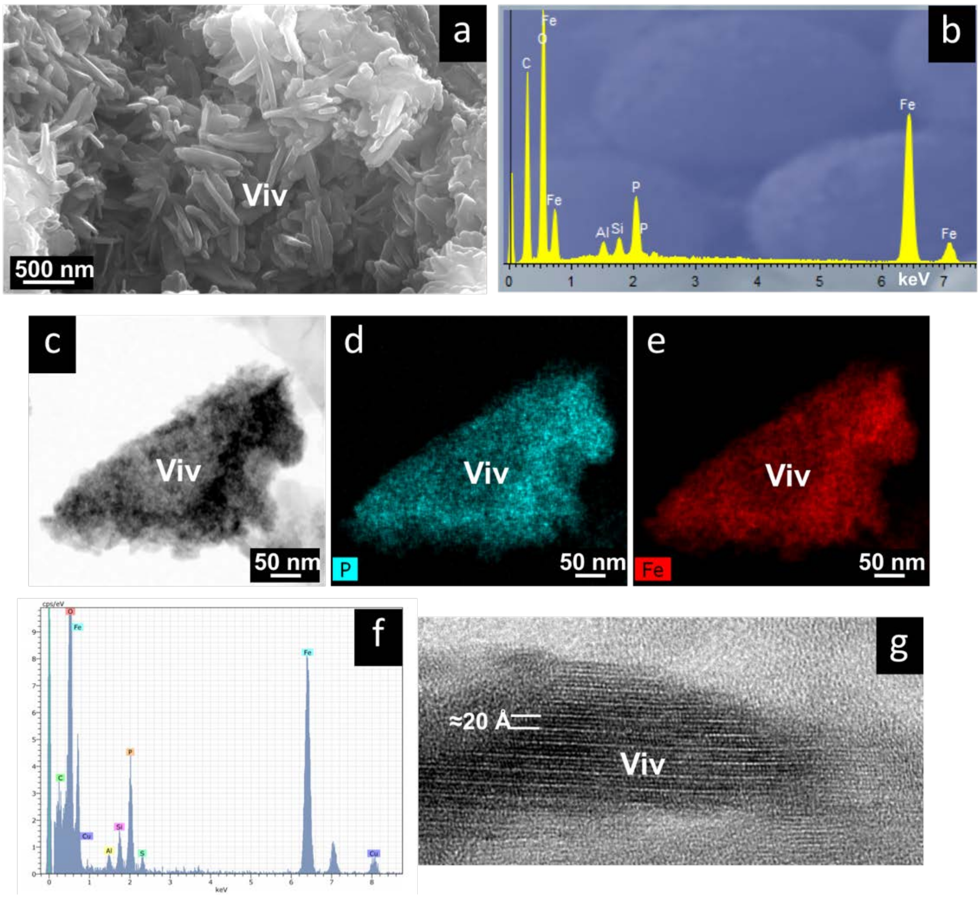

Fig.6. *Vivianite from sediments of La Playa dam: (a) prismatic to flat nanocrystals of vivianite frequently associated with the occurrence of plant fragments (SE image); (b) EDX spectrum; (c) HRTEM image (bright field) of a vivianite crystal; (d) EDX elemental map of P; (E) EDX elemental map of Fe; (f) EDX spectrum of vivianite from image c; (g) lattice fringe image of vivianite crystal from image c. Viv: vivianite. From Quevedo et al. (2021).*

The initial stage of monosulfide and/or phosphate precipitation is in many cases followed by a dissolution step under free sulfide excess conditions and a recrystallization process that produce pyrite framboids. This stage can be enhanced by the SOB activity. Several SOB communities, such as *Sulfuricurvum* or *Arcobacter* are the dominant SOB under elevated free sulfide concentrations increasing the pyrite crystallization rate. Morphology of the pyrite crystals in the framboids reveals physicochemical conditions controlled in some cases by the bacterial activity. In the La Playa dam, the formation of microframboids, including hopper pyrite crystals (Figure 7), suggests transformation processes under high supersaturation values of Fe and sulfide, which promote the fast accumulation of growth units at the crystal edges, causing the typical faces of hopper grains (García Ruiz et al., 2015).

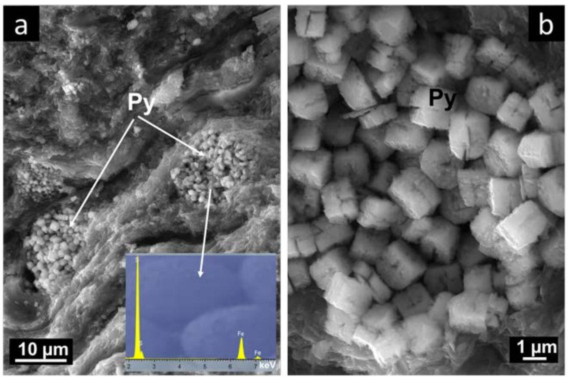

Fig.7. *SE images of pyrite from sediments of La Playa dam: (a) pyrite framboids; (b) pyrite hopper crystals forming framboids. Py: pyrite. Modified from Quevedo et al. (2021).*

During this stage, the presence of Cu-pyrite crystals (Sochagota Lake) and other Cu-bearing sulfides (Laguna Honda) in sediments from wetlands evidence the importance of the process of metal sulfidation on the metal take up into low-solubility minerals.

However, the persistent action of the SOB can facilitate the oxidation of the reduced sulfides to S° (Figure 8) and sulfates such as barite. In the Sochagota Lake, the SOB communities (*Thioalkalimicrobium*, *Sulfurovum, Arcobacter* and *Sulfurimonas*) might have played an important role during this oxidation stage. The oxidation processes of the reduced sulfide may promote the release of toxic heavy metals again into the environment.

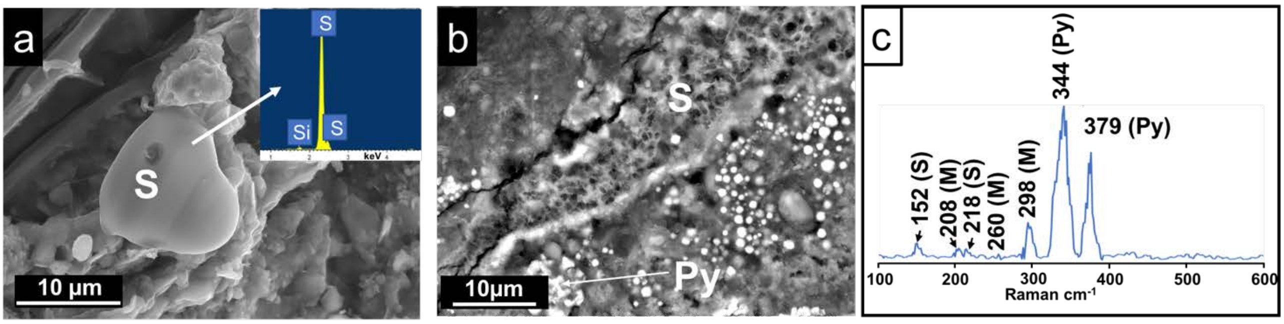

Fig.8. *Electron microscope image and spectroscopy data (EDS and Raman) of S° in sediments of the Sochagota Lake: (a) SE image of an individual grain of native sulfur near pyrite-rich zones; (b) BSE image of a S-aggregate formed by microfilaments that generate a vesicular texture; (b) Raman spectrum of pyrite-rich region. Py: pyrite, S: elemental sulfur. Modified from Cifuentes et al. (2020).*

The presence of IOB can promote this type of oxidation reactions even in anoxic environments. The high representation of Members of the Gallionellaceae family and the Sideroxydans genus in the periodically emerged of La Playa dam with Eh negative values reveal that these groups can be adapted to low oxygen levels, enhancing goethite precipitacion in these sediments (Figure 9). Watanabe et al. (2021) revealed the importance of bacteria that belong to the Gallionellaceae family and the Sideroxydans genus on the oxidation of Fe^{2+} in soils that alternate wetting and drying periods.

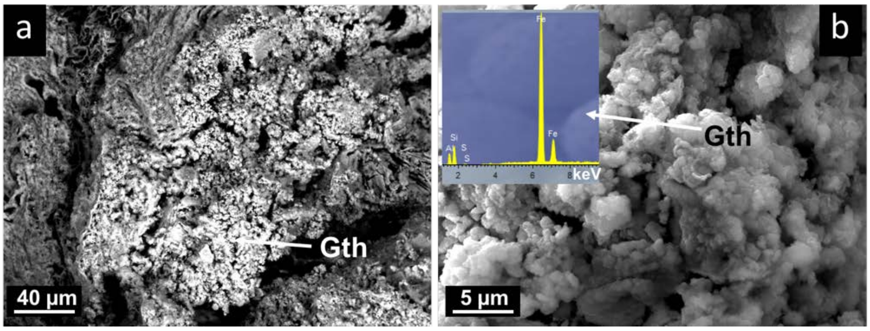

Fig.9. *SEM and EDX images of goethite sediments of La Playa dam. From Quevedo et al. (2021).*

Conclusions

Organic matter-rich sediments from wetlands of the Chicamocha Basin are characterized by the presence of bacterial communities producing biodegradation associated with eutrophication. These sediments show relevant SRB communities involved in the precipitation of Fe-sulfides. SEM images showing cell-shaped aggregates with metal sulfide composition support the importance of the bacterial communities in the nucleation and transformation of sulfide minerals (mackinawite, ZnS). The activity of these bacterial groups can be reinforced by syntrophic partners involved in the organic matter biodegradation, which produce H_2 used by SRB and increase the sulfide availability. IRB enrichment favors the precipitation of vivianite by the contribution of microbial iron- and sulfur-reducing processes producing the accumulation of metals into the sediments.

The presence SOB in the sediments can favor both pyrite crystallization under a high sulfide availability and the oxidation of microbially precipitated monosulfides releasing metals into the environment and promoting the precipitation of S° and sulfates. The Fe mobilization mediated by the presence of SRB and SOB communities favored the processes of transformation of detrital clays. High concentration hydrothermal K in the waters of the lake and Fe uptake in the octahedral sheet promoted the illitization of the precursor clays (smectites or I-DV).

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