Patterns of rare earth elements in sediments as tracers in a fluvial system influenced by a gold mine, El Triunfo, BCS, Mexico

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Abstract

Concentrations of rare earth elements (REE) were analyzed to determine their variations in various samples, such as sediments, tailings, and ash at the mining district El Triunfo (MDET) and its adjacent coastal zone. The REE concentrations were measured in tailings and ash, showing a clear variation in their contents, distribution, and the Eu anomalies among the MDET. These were compared with the surface sediments along the Hondo–Las Gallinas–El Carrizal (H – G – C) arroyo, a test pit, sediment core, and dunes at the end of the arroyo discharge adjacent to the Pacific Ocean. The results show a clear anthropogenic influence because of the depleted contents in the tailings, ash, and the test pit. Although larger REE concentrations were found in the arroyo basin, its contents remain depleted as compared to the National American Shale Composition (NASC). Therefore, the perturbation caused by the mining is masked by the natural contents and the high weathering degree of the rocks. The artisanal mining has altered the El Triunfo fluvial system, and its associated sediments, in its discharge to the Pacific Ocean.

Keywords: Rare earth elements, gold mine, sediments, tailings, Mexico.

1. Introduction

The normalized rare earth element patterns have been widely used in the understanding of water-rock interaction processes [1]. Their geochemical and coherent behavior [2] can help explain environmental processes [3] and the identifying of anthropogenic impacts in sediments [4]. The REE can be fixed or adsorbed by minerals during hydrothermal processes and weathering [5]. Studies dedicated to the REE in systems influenced by ore mines [6-8] had anomalies and processes in the sediments. One type of

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anomaly is the Eu anomaly that indicates hydrothermal environments [9] and in some cases is associated with volcanism and/or tectonic influence [10]. These previously studied systems were in temperate climates, such as a river-estuary system Tinto and Odiel (Spain) where the REE can be dissolved in acid drainage and precipitated after reaching the slightly alkaline estuarine waters [7], or in the tropics [8] where weather produces the transport of the sediments by water.

In contrast, the El Triunfo mining district is in a semiarid zone (Fig. 1). This area has regional and national importance because gold and silver have been extracted since the 18th century. This generated great tailings along the drainage basin. It is located in an arid zone with little rain during the year; from < 200 mm to 430 mm per year. This zone is affected sporadically by tropical storms and hurricanes. The strong winds of the storms in summer can transport soil and tailing particles, which can travel great distances. These tailings are enriched in potential toxic elements accumulated in the past by the artisanal mining, [8]. This caused geochemical variations in the arroyo sediments from the source to their destination, their discharge into an evaporitic basin adjacent and a few meters from the Pacific Ocean. To show the geochemical variations occurring in this anthropogenically impacted system, and their environmental influence, tracers such as the REE were analyzed to identify (i) their concentrations, (ii) their distribution (REE patterns) compared to one another and normalized to the North American Shale Composite (NASC), (iii) their anomalies, and (iv) the characteristic fingerprint of natural and anthropogenic sediments in this semiarid environment.

![Fig. 1. Study area: the El Triunfo mining district (MEDT) in Baja California Sur, Mexico. The number 1 corresponds to the MDET, and it is the source of the tailings and ashes. The line between the two points (number 1 and 2) indicate the test pit and surface sediments (it is the main arroyo of the basin (H – G – C), which is 48.8-km long. The point 2 shows the core and dune sampling sites.](image)

2. Material and Methods

Surface sediments in the arroyo were sampled along 48.8 km (n = 26) and the overbank tailings of 2-m height (n = 19), and clastic material from the test pit 1-m deep (n = 9) close to the alteration zone. In the same hydrographical basin we sampled in La Noria, which is a pristine area 3-km from the mining district (n = 6). The arroyo (H-G-C) discharge into the evaporitic basin adjacent to the Pacific Ocean was sampled with core 1 (C1) 34-cm deep (n = 17) and core 2 (C2) 28-cm deep (n = 14).

Sediments were nearly fully digested using four acids. A 0.25 g sample is digested beginning with hydrofluoric acid, followed by a mixture of nitric and perchloric acids and heated using precise programed controlled heating in several ramping and holding cycles that takes the samples to dryness. After dryness is attained, the samples were dissolved in hydrochloric and nitric acids. The REE
concentrations were measured by ICP-MS analysis Perkin Elmer Sciex ELAN 6000, 6100, or 9000 ICP-MS. The methods were validated with the reference materials GXR-1, GXR-4, and GXR-6. The analyses were made at the Actlabs in Ontario, Canada.

3. Results and Discussion

The concentrations of rare earth elements in the overbank tailings, ash (in the burning and sublimation chambers), test pit, and surface sediment along the 48.8 km from the source to its destination, in the sediment cores, and dunes are shown in Table 1.

Table 1. Rare earth element concentration ranges of the MDET samples, surface sediments, and in the discharge of the main arroyo at the evaporitic basin adjacent to the Pacific Ocean. Units are in mg kg\(^{-1}\).

| REE | Surface Sediment | Tailings | Ashes | Test Pit | Core | Dune | NASC |
|-----|------------------|----------|-------|----------|------|------|------|
|     | \(n = 26\)       | \(n = 7\) | \(n = 2\) | \(n = 10\) | \(n = 17\) | \(n = 3\) | [11] |
| Mean ± SD | 98.4 ± 67 | 29.1±1.2 | 3.41±1.8 | 82.6 ± 13 | 78.1±12.3 | 80.2 ±28.9 | 173.21 |

The surface sediments have a lower concentration of the REE compared to shale (NASC - North American Shale Composite; Table 1), though their contents were the most concentrated of the system. In contrast in samples of the mining district, such as tailings and ash, the concentrations were even lower. In the evaporitic basin, where discharges from the arroyo H-G-C end up, the contents of the cores and dunes (Table 1) were also less concentrated than the surface sediments.

Despite the low contents of the lanthanides, the Eu anomaly was detected in the surface sediment, test pit, cores, and dunes. It can be caused by the volcanic and sedimentary rocks occurring in this study area. The anthropogenic effect was identified with the different signature in the ash and tailings (Fig. 2), with a significant decrease in the ash (Table 1). The behavior of the system did not reflect the influence of the acid drainage nor the accumulation and enrichment of the REE in zones altered by ore mines as previously reported by Borrego et al. [7]. The sediments are probably influenced by an impoverished magma with a low content of rare earth elements.
4. Conclusion

The REE are less concentrated than shale and there is no evidence of their accumulation caused by an anthropogenic influence. The distribution of the lanthanides along the system had differences in the microenvironnments with the ash the evidence of an anthropogenic influence. The Eu anomaly was detected and it was more pronounced in the surface and the test pit sediments. The Eu anomaly was determined in the sedimentary core, tailings, and dunes. The REE determination is useful to characterize an anthropogenic impact through the rare earth concentrations and their different signatures for each microenvironment of the system.

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