CONTAMINATION RELATED TO ANTHROPIC ACTIVITIES. CHARACTERIZATION AND REMEDIATION

Enrichment of trace elements in the clay size fraction of mining soils

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Abstract Reactive waste dumps with sulfide minerals promote acid mine drainage (AMD), which results in water and soil contamination by metals and metalloids. In these systems, contamination is regulated by many factors, such as mineralogical composition of soil and the presence of sorption sites on specific mineral phases. So, the present study dedicates itself to understanding the distribution of trace elements in different size fractions (<2-mm and <2-μm fractions) of mining soils and to evaluate the relationship between chemical and mineralogical composition. Cerdeirinha and Penedono, located in Portugal, were the waste dumps under study. The results revealed that the two waste dumps have high degree of contamination by metals and arsenic and that these elements are concentrated in the clay size fraction. Hence, the higher degree of contamination by toxic elements, especially arsenic in Penedono as well as the role of clay minerals, jarosite, and goethite in retaining trace elements has management implications. Such information must be carefully thought in the rehabilitation projects to be planned for both waste dumps.

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Introduction

Mining activity produces a large amount of not availed material that must be stored in appropriate conditions of stability, security, and integration with the surrounding landscape (Gomes 2011). These sterile materials, or mining wastes, are generated at various stages of the production process. If they are reactive, they will pose more environmental concern, due to their participation in contaminant mineral-water interactions processes. So, abandoned mining lands represent one of the most outstanding environmental risks, such as soil pollution by potentially toxic metals and metalloids. These problems affect many countries with historic mining activity (Thornton 1996; Fernández-Caliani et al. 2008), including Portugal. Across the country, about 200 abandoned mines were identified (Santos Oliveira et al. 2002), which constitute the national mining liability, whose abandonment occurred in an uncontrolled manner. In some of these mines, especially those which represented a great mobilization of sulfides, there is still a depreciation of environmental quality motivated by the reactive waste dumps (Valente 2004; Valente et al. 2011, 2012). In the weathering process of sulfides, oxidation generates acid mine drainage (AMD) mobilizing high amounts of acidity, sulfates, metals, and metalloids (Valente et al. 2009; Gomes 2011; Sarmiento et al. 2012; Valente et al. 2012), from which results water and soil contamination. Also, the pollutants may be transferred from these sites to nearby soils and water by wind-blown dispersion of fine particles. These events are responsible for the impact of mining and ore treatment on the ecosystem, even at long distances.

The behavior of trace elements in AMD-affected systems is regulated by many factors. First, element distribution into different particle sizes depends of the presence of sorption sites and of the mineralogical composition of soil (e.g., Acosta et al.

67 2011). Fine particles, which include clay fraction, have high
68 specific area that retains high amounts of metals. In addition,
69 small particles are often soluble (Martínez-Martínez et al.
70 2010). Moreover, mobilization or fixation of elements in the
71 soil can be regulated by the interactions between several bio-
72 geochemical processes, such as formation of secondary min-
73 erals (Kabata-Pendias and Pendias 1984; Cox et al. 1995;
74 Malpas et al. 2001). Besides, the Fe-rich materials that com-
75 pose the typical ochre-precipitates may adsorb or co-
76 precipitate the toxic elements carried by AMD solutions
Q3 77 (Valente et al. 2014). Therefore, to know the trace ele-
78 ment distribution in fine soil particles is an important
79 step for risk assessments of mining soils (Hardy and
80 Cornu 2006; Acosta et al. 2009; Luo et al. 2011).

81 So, the main purpose of the present study comes in line
82 with this environmental concern. It deals with the subject
83 of trace elements distribution in two distinctive sulfide
84 waste dumps, abandoned after decades of W and Au ex-
85 ploitation, respectively, Cerdeirinha and Penedono (Portu-
86 gal). These two sites (Fig. 1) were not yet the subject of
87 technical intervention for their environmental rehabilita-
88 tion. The specific objectives of the present study are to
89 evaluate the degree of contamination by trace elements
90 and to analyze the role of the clay size fraction in the
91 retention of contaminants.

Material and methods

92

Sites description

93

94 The two selected sites are located in regions with strong min-
95 ing tradition for metals and so with a long historic in water and
96 soil contamination by AMD (Valente and Leal Gomes 2009;
97 Valente et al. 2012).

98 Cerdeirinha (Fig. 1) was exploited for W, in a skarn deposit
99 with sulfides, mainly iron sulfides. The waste dumps have
100 been formed by successive accumulation of sterile material
101 from the treatment of tungsten ores. Penedono (Fig. 1), in a
102 granitic context, was exploited, mainly for Au, in quartz veins
103 with sulfides. It was an important mining center for gold and
104 other elements, such as arsenic, and the waste dumps are com-
105 posed by sterile materials resulted from milling, hydrogravitic,
106 and flotation operations.

107 Cerdeirinha has a more diverse mineral association, due to
108 the skarn nature of the ore deposit. Here, phyrrhotite and py-
109 rite are the most abundant sulfides, while at Penedono, there is
110 arsenopyrite with minor pyrite. A main difference between the
111 two ore deposits relies on the absence of carbonates and cal-
112 cium silicates in Penedono, which act as neutralizing minerals
113 in Cerdeirinha. A more complete paragenetic description of
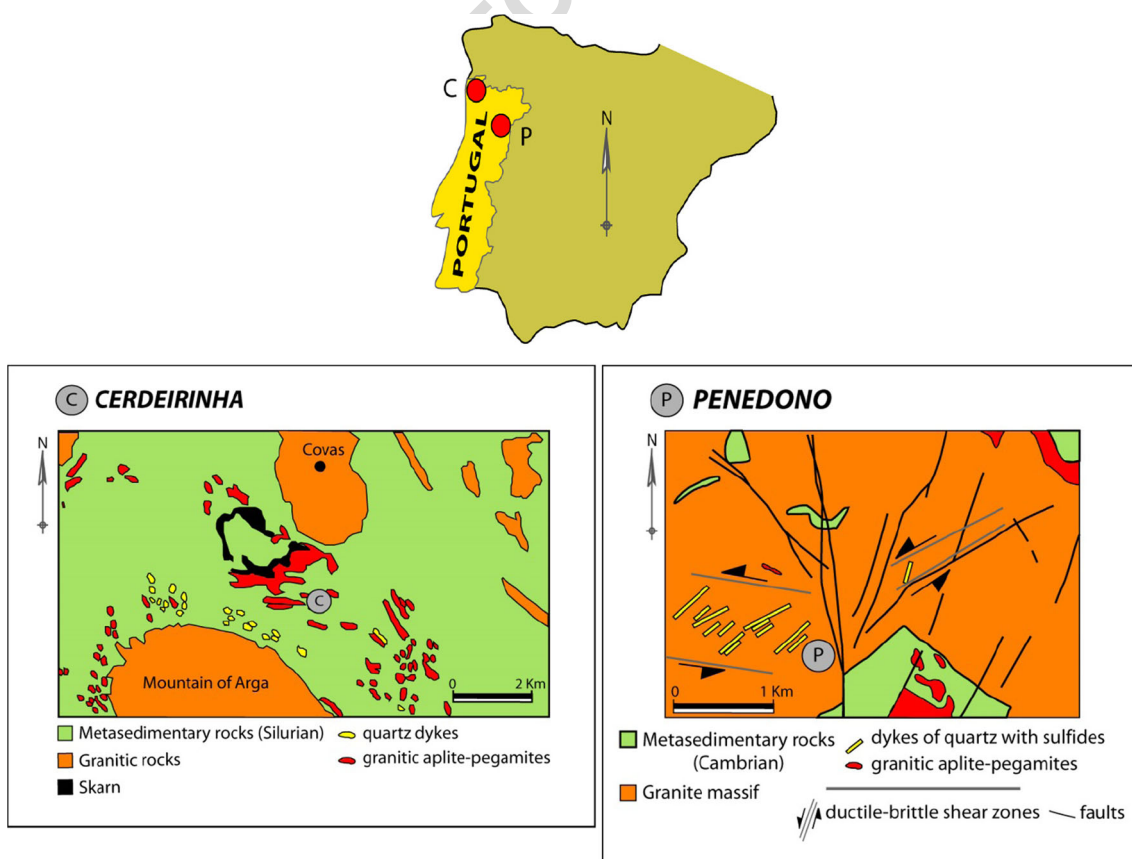114 the two ore deposits can be found in Valente et al. (2012).

Fig. 1 Localization of two study sites

Sampling and analytical methods

The methodology includes sampling and preparation procedures followed by a general characterization of the mining soils, regarding texture, general properties, mineralogy, and chemistry in two grain size fractions: <2 mm (named bulk sample) and the clay size fraction (<2 μm).

In the field, the samples represent the first 20 cm of substrate on which plants grow on the waste dumps. At each mine, the sampling sites represent the spatial variability, controlled by different aspects, including by the differences in the vegetation cover.

Analytical procedures followed classical methodological approaches for texture and general soil properties (Gomes 2011).

Mineralogy was analyzed by X-ray diffraction (XRD) applied to both fractions. XRD was performed with a Philips X'pert Pro-MPD diffractometer, using Cu-Kα radiation, operated with a 2 theta step size of 0.02° and a counting time of 1.25 s. For the identification of clay minerals, the <2-μm fraction was separated by sedimentation and analyzed in oriented aggregates of air-dried, ethylene gycol-treated, and thermal-treated samples. The relative abundance of the mineral phases in both fractions was estimated by measuring the intensity of diagnostic diffraction peaks (Valente et al. 2012). For the study of compositional and morphological aspects, scanning electron microscopy (on gold coated samples) was used, with a LEICA S360 microscope combined with an energy dispersive system (SEM-EDS). Also, transmission electron microscopy was applied to provide compositional spectra, mineral identification by microdiffraction and morphology properties.

The chemical composition (Fe, Al, Mn, Cu, Ni, Pb, Zn, As, Ba, Bi, Cr, Sr, and W) of both size fractions was analyzed by inductively coupled plasma/mass spectrometry (ICP/MS) at Activation Laboratory, Ltd. (Actlabs, Canada). For that, samples were pulverized in an Agata mortar and submitted to *aqua regia* digestion. Duplicate samples and check precision blanks as well as certified standards (GXR series) for accuracy were used.

Results and discussion

The two studied sites have acidic soils (pH<4), with low contents of nutrients. They differ in the contents of organic matter, presenting Cerdeirinha higher concentration (5 %) compared with Penedono, whose samples do not surpass the 1 %. Both soils can be considered as coarse soils, being classified as sandy loam, in accordance with the USDA texture classification system. So, the general properties are relatively similar in the two waste dumps. A detailed characterization of the mining soils can be found in Valente et al. (2012).

Mineralogy

The mineralogy of the mining soils is presented in Table 1. According to XRD study, the most common minerals in bulk soil (<2-mm fraction) are quartz, k-feldspar, plagioclase, and mica. In a general way, marcasite, pyrrhotite, pyrite, and jarosite are prominent minerals at Cerdeirinha. In contrast, Penedono shows clearly lower variability in this fraction, with quartz and feldspar as dominant phases. This result reflects the differences in the two ore paragenesis. In fact, at Cerdeirinha, the skarn nature of the ore deposit in association with massive sulfides contributes to higher mineralogical diversity (Gomes 2011), with minerals such as wollastonite and apatite. Table 2 reveals the differences in <2-μm fraction in the two waste dumps. The clay size fraction is also more diverse at Cerdeirinha. Here, the iron-rich minerals jarosite and goethite are the most abundant phases, followed by a set of clay minerals, including kaolinite and 2:1 clay minerals. On the other hand, at Penedono, kaolinite dominates, followed by jarosite and clay minerals, while goethite is vestigial.

Geochemistry

Metal concentrations in different size fraction

Chemical composition of the soil is shown in Fig. 2, where concentrations are compared in the two size fractions: <2 mm and <2 μm. It is possible to assess that elements such as Fe, Al, and As are present in high quantities in the two waste dumps (i.e., in a range between 1537.5 mg/kg for Al in the <2-mm fraction at Penedono and 1,765,000 mg/kg for Fe in the <2-μm fraction at Cerdeirinha). Despite this fact, Fe was the most abundant element in soil of the two waste dumps and As has higher values at Penedono (with 25,875 mg/kg in the <2-μm fraction). Results suggest that the ore deposits have influence in the concentrations of trace elements in the soil. Cerdeirinha is dominated by iron sulfides, thus increasing the concentration of Fe. The element As is present at Penedono in higher amount, due to dissolution of arsenopyrite, which is the main sulfide phase present in the ore deposit.

Furthermore, Ni, Ba, Cr, and Sr appear in low concentrations at both sites. As opposed to Cerdeirinha, Penedono has lower concentrations of Mn, Cu, Zn, and Bi, showing a less mineralogical and metal diversity (Table 1), also because soils enriched in quartz tend to have lower levels of trace elements (Silva et al. 2013). On the other hand, Penedono has higher concentration of Pb. Moreover, in this site, all elements are concentrated in <2-μm fraction, without exception. In contrast, some elements such Mn and W are in larger amount in the bulk soil fraction of Cerdeirinha. These exceptions can be explained by the presence of wolframite crystals as a consequence of low recuperation rates in the ore treatment.

t1.1 **Table 1** Mineralogical assemblage of the two size fractions: <2-μm fraction (clay minerals and associated minerals) and <2-mm fraction (bulk soil)

t1.2 Size fraction		Cerdeirinha (n=6)	Penedono (n=8)
t1.3 <2 μm		Jt >>Il>Go>S>Gb>M-V>Cl > K	K>Jt>Il>S>Go
t1.4 <2 mm		Q >>P>F>Mi>Mar>Pry=Mgs> Py=Go=Jt=Ap>Cm=Am=Wo>To	Q >>>F>Mi>P>Cm=Jt

Jt jarosite, *Il* illite, *Go* goethite, *Gb* gibbsite, *ML* mixed-layered mica-vermiculite, *S* smectite, *Cl* chlorite, *K* kaolinite, *Q* quartz, *F* k-feldspar, *P* plagioclase, *Mi* mica, *Cm* clay minerals, *Py* pyrite, *Mar* marcasite, *Pyr* pyrrhotite, *Mgs* magnesite, *Ap* apatite, *Am* amphibole, *Wo* wollastonite, *To* Tourmaline

212 Although not detected in XRD study, such a presence was
213 confirmed by SEM study.
214   Therefore, the results obtained for soil chemistry reflect the
215 original differences in the ore paragenesis as already noted in
216 the mineralogy. Cerdeirinha has the highest concentrations of
217 Fe, reaching 15 %, which is in accordance with the abundance
218 of iron sulfides. On the other hand, the highest contamination
219 by As occurs at Penedono, with contents up to 3 %.
220   These results also show that both sites have a similar trend
221 in what concerns the relation between the two size fractions.
222 In fact, the highest concentrations are observed in the clay size
223 fraction for most of the elements, with the exception of man-
224 ganese and tungsten in the Cerdeirinha samples.

225 *Correlation between trace elements*

226 Correlation analysis provides an effective way to reveal the
227 relationships between trace elements in soil. Tables 3 and 4
228 show the correlation matrixes for Cerdeirinha and Penedono,
229 respectively, considering the concentrations obtained in the
230 <2-μm fraction.
231   Strong correlations occur between concentrations of some
232 trace elements in this fine fraction. However, the elements
233 behave somewhat differently at both sites. At Cerdeirinha
234 (Table 3), Fe is significant and positively correlated with Bi
235 (0.890). Al is correlated with Ba (0.819); Mn had close rela-
236 tionships with Zn (0.815) and As (0.823). Cu and Ni are re-
237 lated with Cr. These high correlations indicate that these ele-
238 ments associate in the parent materials and suggest similar
239 geochemical behavior during weathering process, as observed

240 for Bi. Bismuth occurs at the ore deposit of Cerdeirinha as
241 native bismuth and bismuthinite (Valente et al 2012). Howev-
242 er, in this Fe-rich paragenesis, dissolution of bismuth followed
243 by precipitation of iron-rich minerals may take place. Convo-
244 lute bands of iron oxyhydroxides (probably goethite) with Bi
245 inside iron-rich crusts were observed by SEM. In fact, previ-
246 ous studies revealed the tendency of Bi to co-precipitate with
247 hydrous Fe oxides (Augustithis 1995), hence justifying the
248 observed correlation between Fe and Bi.
249   Close correlation between Cu, Cr, and Ni indicates the
250 sulfides, such as pyrite, chalcopyrite, sphalerite, gersdorfite,
251 and other complex sulfides from the ore paragenesis (Valente
252 et al. 2012) as the main common source of these elements. The
253 same happens for Mn with As and Zn, reflecting the associa-
254 tion between ore minerals and sulfides. Identically, in geo-
255 chemical processes, Ba is commonly associated with K, in
256 alkaline feldspars and biotite. So, the high correlation
257 (0.819) of the pair Ba-Al is reflecting this lithophilic affinity.
258   At Penedono, the correlation matrix (Table 4) indicates that
259 Al is effectively correlated with Mn (0.939) and Sr (0.782)
260 while Mn appears correlated with Ba (0.765) and Pb is related

t2.1 **Table 2** Mineralogical composition of the mining waste dump soils estimated by XRD in the <2-μm fraction (clay minerals and associated minerals)

t2.2 Waste dumps		<2-μm fraction (%)							
t2.3		C	Il	M-V	Sm	K	Go	Jt	Gi
t2.4 Cerdeirinha	Average	5	10	6		8	4	9	51	7
t2.5 Penedono		–	19	–		13	40	1	27	–

C chlorite, *Il* illite, *M-V* mixed-layer mica-vermiculite, *Sm* smectite, *K* kaolin mineral, *Go* goethite, *Jt* jarosite, *Gi* gibbsite
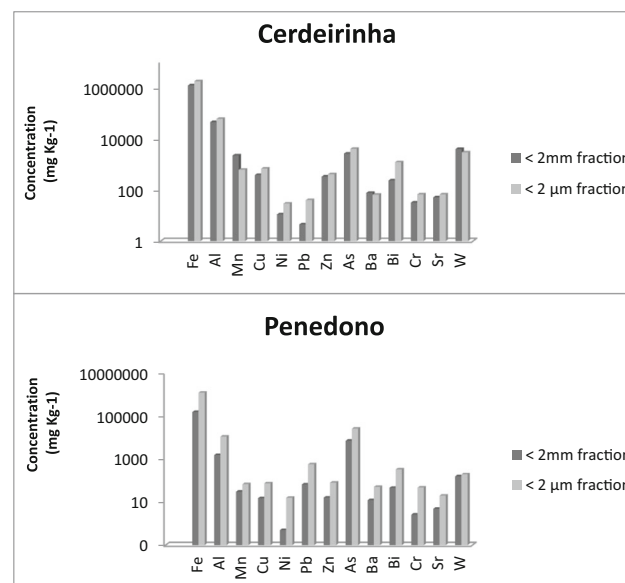

Fig. 2 Concentration and distribution of metals in different particle size fractions

Q4 t3.1   **Table 3**   Correlation matrix of trace elements concentration in Cerdeirinha (<2-µm fraction)

		Fe	Al	Mn	Cu	Ni	Pb	Zn	As	Ba	Bi	Cr	Sr
t3.3	Fe	1.000											
t3.4	Al	−0.722	1.000										
t3.5	Mn	0.306	0.112	1.000									
t3.6	Cu	−0.785	0.253	−0.359	1.000								
t3.7	Ni	−0.176	−0.377	−0.283	0.512	1.000							
t3.8	Pb	0.131	−0.672	0.014	0.439	0.721	1.000						
t3.9	Zn	0.146	0.120	0.815	−0.378	−0.037	−0.029	1.000					
t3.10	As	0.452	−0.206	0.823	−0.300	−0.391	0.240	0.507	1.000				
t3.11	Ba	−0.375	0.819	0.341	−0.039	−0.195	−0.621	0.355	−0.180	1.000			
t3.12	Bi	0.890	−0.826	0.208	−0.464	−0.100	0.422	−0.089	0.560	−0.646	1.000		
t3.13	Cr	−0.548	−0.098	−0.495	0.921	0.745	0.653	−0.472	−0.386	−0.268	−0.232	1.000	
t3.14	Sr	0.767	−0.820	−0.310	−0.472	0.254	0.249	−0.290	−0.164	−0.503	0.687	−0.103	1.000

261 with Bi (0.783). In turn, the clear association between Ni and
262 Zn (0.809) and Ni and Cr (0.976) stands out, which reveals a
263 common origin for all, possibly represented by the sulfides. At
264 this site, Bi correlates more strongly with Pb, which may also
265 be reflecting its chalcophile affinity, which results in its
266 partitioning into sulfides, especially galena. In fact, Bi is com-
267 mon in late Pb-Zn veins or perigranitic hydrothermal vein
268 deposits as that of Penedono. The strong correlations among
269 Mn, Al, Sr, and Ba may reveal the lithophilic affinity of these
270 elements and their link with plagioclase and micas, highly
271 abundant in the clay size fraction as demonstrated by the
272 XRD study.

273 *Accumulation factor*

274 The enrichment in the clay size fraction with respect to the
275 bulk soil can be expressed through the determination of an
276 accumulation factor, which reflects the ratio between contents
277 in both fractions.

278 Figure 3 represents the accumulation factor (AF_x) for a set
279 of elements that pose greater environmental concern, calculat-
280 ed by using Eq. (1) (Acosta et al. 2009).

$$AF_x = X_{\text{fraction}}/X_{\text{bulk}} \tag{1}$$

281
282
283

284 As can be seen in Fig. 3, the accumulation factor (AF) for
285 Cerdeirinha showed consistent values ~1.0 for Cu, Zn, and
286 As. Here, Ni and Bi and specially Pb showed higher enrich-
287 ment trends (AF=14). At Penedono, the AF is generally
288 higher than at Cerdeirinha. Ni stands out with an AF around
289 28.
290 In a general way, the concentrations (Fig. 2) and AFs
291 (Fig. 3) of trace elements in the two fractions demonstrated
292 an enrichment of the finer fraction. Preliminary works report-
293 ed that the preferential partitioning of trace metals is in the
294 clay fraction (Moore et al. 1989; Fernández-Caliani et al.

t4.1   **Table 4**   Correlation matrix (Person coefficients) of trace elements concentration in Penedono (<2-µm fraction)

|		Fe	Al	Mn	Cu	Ni	Pb	Zn	As	Ba	Bi	Cr	Sr
t4.3	Fe	1.000											
t4.4	Al	−0.457	1.000										
t4.5	Mn	−0.240	0.939	1.000									
t4.6	Cu	−0.375	0.308	0.325	1.000								
t4.7	Ni	0.552	−0.170	−0.024	−0.187	1.000							
t4.8	Pb	−0.417	−0.238	−0.433	0.453	−0.392	1.000						
t4.9	Zn	0.418	0.264	0.360	−0.333	0.809	−0.709	1.000					
t4.10	As	0.102	0.583	0.556	−0.490	−0.084	−0.591	0.397	1.000				
t4.11	Ba	0.349	0.584	0.765	0.129	0.508	−0.547	0.682	0.435	1.000			
t4.12	Bi	−0.376	−0.423	−0.533	0.123	−0.334	0.783	−0.673	−0.624	−0.578	1.000		
t4.13	Cr	0.598	−0.307	−0.122	−0.116	0.976	−0.360	0.713	−0.245	0.431	−0.271	1.000	
t4.14	Sr	−0.579	0.782	0.649	0.335	−0.460	−0.139	−0.006	0.442	0.098	−0.461	−0.540	1.000
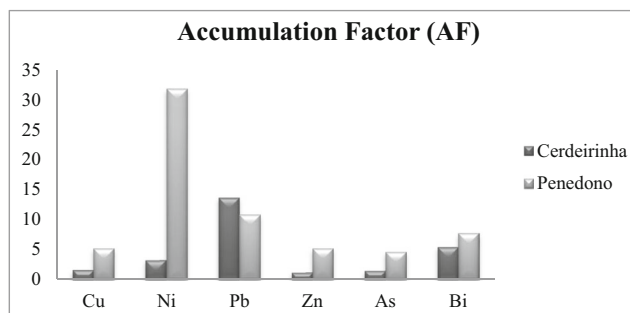
Fig. 3 Average values for accumulation factor in two waste dumps

2008; Luo et al. 2011). These might be attributed to greater surface area per unit of mass of the fine particles, which increase the adsorption capacity of this fraction (Wong et al 2006). Furthermore, finer soil particles have greater content of secondary minerals (clay minerals, Fe, Mn, and Al oxides and hydroxides and hydroxysulfates). In addition, metal enrichment in clay fraction was especially noticeable for Ni, Bi, and Pb at both waste dumps. Sposito (1989) suggested that duo to isomorphous substitution of Ni for Fe or Mg in the octahedral sheet of illite, Ni tends to accumulate in the finest fractions. This may be an explanation for having a higher amount of these elements in the <2-μm fraction, especially in Penedono, where there is a significant quantity of illite. Also, Kohut and Warren (2002) indicated that Ni may occur in Mg-bearing minerals such as smectite. Moreover, chlorite is normally composed by Mg, Al, and Fe and can also contain elements, such as Cr, Ni, and Cu, according to the same author. This can justify the higher contents of these elements because they can be related to chlorite which was found in soils of the study area in Cerdeirinha (Table 2). Although, the accumulation of these elements are not limited to clay minerals but also appear in Fe oxides (Kataeva et al. 2004). As well known (e.g., Bigham et al. 2002), oxide-hydroxides have high sorption capacity of trace elements, such as Ni, Pb, Cu, and Zn. In accordance with Ni et al. (2009), it is thought that the main adsorbent for Pb are oxides phases, under conditions of weathering, which can occur in both waste dumps. However, it is known that quartz and feldspars are very weak adsorbent for trace metals, and in turn, the bulk soil fraction is largely composed by these primary minerals. So, trace elements are not concentrated in this fraction, as seen in Figs. 2 and 3.

In addition, clay fraction showed the highest levels of Fe for both soils (Fig. 2), which mean that clay-sized minerals such as jarosite and goethite (Table 2) are significant sources of Fe. Also, according with Arocena et al. (1995), these two phases can retain metals such as Pb and so play a significant role in metal enrichment in fine fraction.

The obtained results suggest a higher capacity of retention by the clay size fraction present at Penedono. Although oxyhydroxides, such as goethite, are known by their high

sorption capacity of trace elements, in Penedono, goethite is vestigial. Nevertheless, the mineralogical assemblage composed by kaolinite, illite, smectite, and jarosite seems more effective than the one present at Cerdeirinha. In addition to smectite, illite may also play a significant role in the retention of trace elements, such as Ni, by means of isomorphous substitution of Fe in the octahedral sheet of illite. This may be an explanation for having a higher amount of this element in the <2-μm fraction, especially in Penedono, where there is more quantity of illite.

Conclusion

Metal and metalloid concentrations in soil reveal that elements, such as Fe, Al, and As were present in high quantities in the two waste dumps, being Fe the most abundant element. The XRD study of Penedono shows lower mineralogical variability in the two analyzed fractions, in contrast with Cerdeirinha. These results suggest that the ore deposits have strong influence on the mineralogy of the soil.

The accumulation factor in Penedono presents values higher than 1 for all studied elements. In Cerdeirinha, this accumulation occurs for almost all analyzed elements, with exception of Mn and W. This study indicated that the two waste dumps are heavily polluted with metals and arsenic and that these elements are concentrated in the finer fraction. Thus, it is believed that clay minerals and associated minerals, especially jarosite, may play an important role in sorption of toxic elements at both soils. On the other hand, this enrichment may enhance the environmental risk for pollutant dispersion by wind, water, and animal activity. Hence, the higher degree of contamination by toxic elements, especially arsenic in Penedono, as well as the role of clay minerals, jarosite, and goethite in retaining trace elements has management implications. Such information must be carefully thought in the rehabilitation projects to be planned for both waste dumps.

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