Pb-Isotopic tracing of metal-pollution sources in the Ribeira Valley, Southeastern Brazil

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ABSTRACT   *An attempt was made to trace the sources of metal pollution in the Ribeira de Iguape River, Southeastern Brazil, by using the lead isotopic compositions of stream sediments in comparison with the isotopic signatures of the Mesoproterozoic Pb-Zn-Ag ores in the region. The isotopic compositions of the stream sediments ($1.06 < {}^{206}Pb/{}^{207}Pb < 1.11$) are within the range of the lead compositions of Panelas-type deposits ($1.07 < {}^{206}Pb/{}^{207}Pb < 1.10$) but lower than those of sediments located upstream of mining areas (${}^{206}Pb/{}^{207}Pb = 1.16$). It is clearly indicated that the ore production in the filonar hydrothermal Panelas-type deposits was responsible for the elevated metal concentrations in the sediments found throughout the basin of the Ribeira de Iguape river, including its estuary. The environmental impact due to the mining of smaller stratiform Perau-type deposits and metallurgical processing of imported ore concentrates originated from younger ore deposits must have been very subordinated in the river.*

KEYWORDS   *Environmental geochemistry, isotope geochemistry, lead isotopes, Pb-Zn-Ag ore deposits, Ribeira Valley, Brazil*

Introduction

The Ribeira Valley is one of the most important metallogenic and geochemical provinces for Pb-Zn-Ag in Brazil. The main drainage system in the area is represented by the ca. 470 km long Ribeira de Iguape River which originates in the northeastern part of Paraná State and ends in the Iguape-Cananéia lagoonar-estuarine complex, in the proximity of town of Iguape, in the southeast of São Paulo State (Fig. 1). Since 1837, the final course of the river has partially been deviated from its natural estuary towards the Interior Sea due to the opening of the Valo Grande channel.

In the Iguape-Cananéia estuarine region, Tessler *et al.* (1987) indicated the occurrence of sediments with metal contents of 0.30-247 ppm Pb, 1.4-105 ppm Zn and 0.05-292 ppm Cu. The authors claimed that these fine-grained sediments were transported by the Ribeira de Iguape River and that the high metal contents were due to mining industry activities in the river headwaters.

Eysink *et al.* (1987, 1988), on the basis of geochemical results obtained by CETESB (Environmental Sanitation Agency of São Paulo State) in 25 sample stations, 11 of which were along the Ribeira de Iguape River, indicated that Pb, Zn and Cu contents in active stream sediments decreased exponentially from the mining areas (10^2-10^3 ppm) to the Ribeira de Iguape estuary (10-10^2 ppm). The sediments collected from the creeks downstream of the Rocha and Furnas mines yielded the highest lead concentrations.

In addition to the Pb-Zn mines of the upper Ribeira Valley, those authors also indicated the waste disposal of the Plumbum refinery situated in the same area as another possible source of heavy metal contamination of sediments along the river and in its estuary.

During the present investigation the lead isotopic compositions of stream sediments collected along the river and in the lagoonar-estuarine region were determined for the purpose of identifying the sources of heavy-metal pollution in the region. The main geological features of the Ribeira de Iguape Valley Province and of its Pb-Zn deposit types are summarized below.

The Ribeira Valley Metallogenic Province

The Ribeira Province is a folded belt mainly made up of Mesoproterozoic sedimentary and volcanic rocks which overlie a basement composed of gneisses and migmatites with some charnockitic cores and intercalations of quartzite, schists and mafic-ultramafic intrusive rocks. The supracrustal rocks are intruded by syn to post-tectonic granitoids of Neoproterozoic ages. Finally, the younger sedimentary cover unit includes the Phanerozoic formations of the Paraná Basin as well as the Cenozoic fluvial and coastal sediments.

According to previous studies (Chiodi Filho 1984, Campanha 1991, among others), the supracrustal rock consists of phyllites, schists, quartzite, calc-silicate rocks, marble, iron formation, metachert and basic volcanics, metamorphosed in the amphibolite facies as well as low-grade rocks such as metasiltite, phyllite, quartzite, conglomerate and basic and felsic volcanics, which are underlain by calcitic and dolomitic limestones with intercalated calc-schist and calc-phyllite.

The Ribeira Valley Metallogenic Province presents two main Pb-Zn deposit types (Fleischer 1976, Macedo 1986, Figueiredo 1992, Silva 1995, Daitx 1996) as follows:

(i) The Perau deposit type

These deposits are syngenetic, stratiform and sedimentary-exhalative in origin. They are hosted by calc-silicate rocks associated with iron and barite formations, quartzite and amphibolite. The Perau

Table 1 – Lead isotopic compositions of the Ribeira Valley Perau- and Panelas-ore types, ore deposits from Peru, modern pelagic sediments of Atlantic Ocean and actual mean crustal Pb values

	Perau-ore deposit type (1)	Panelas-ore deposit type (1)	Peruvian Pb-deposits (A)	Modern pelagic sediments (B)	Actual mean crustal Pb value (C)	Actual mean Pb for continental crust (D)
$^{206}Pb/^{204}Pb$	16.16 - 16.51	16.52 - 17.27	18.46 - 19.26	18.61 - 19.01	18.70	18.6 - 18.9
$^{207}Pb/^{204}Pb$	15.47 - 15.73	15.47 - 15.84	15.61 - 15.74	15.68 - 15.74	15.63	15.58 - 15.65
$^{208}Pb/^{204}Pb$	36.37 - 36.60	37.04 - 38.24	38.48 - 39.50	38.93 - 39.19	38.63	39.6 - 39.8
$^{206}Pb/^{207}Pb$	1.040 - 1.061	1.066 - 1.109	1.183 - 1.224	1.187 - 1.208	1.197	1.194 - 1.208

(1) Tassinari *et al.* (1990) and Daitx (1996); (A) Gunnesch *et al.* (1990) and Kontak *et al.* (1990); (B) Hoernle *et al.* (1991); (C) Stacey and Kramers (1975); (D) Rollinson (1993)

and Canoas ore deposits belong to this deposit type. Previous studies, including that by Tassinari *et al.* (1990) and Daitx (1996), attributed an age interval from 1.5 to 1.7 Ga to the Perau-type ore deposits based on Pb/Pb isotopic determinations in galena.

(ii) The Panelas deposit type

These deposits are epigenetic, discordant, filonar and are considered to have originated from hydrothermal metal remobilization from the basement and supracrustal rocks. They follow a NE-SW general strike and are hosted by dolomitic rocks. The Panelas, Rocha, Barrinha and Furnas ore deposits belong to this deposit type. Galena Pb/Pb isotopic dating yielded an age interval of 1.1 to 1.4 Ga for the ore deposits of this type (Tassinari *et al.* 1990).

For several decades, albeit discontinuously, this metallogenic province has been the host of significant metal production, which reached its maximum in the 1970s and 1980s. Until 1985, the estimated Pb production for the whole Ribeira Valley was 165,000 t, 56% of which was provided by the Panelas mine (Daitx 1985). The Rocha mine might have produced 25-30% and the other mines, such as Furnas, Barrinha, Perau and Canoas, 15-20% of the total lead production in the region.

Since 1945, the Plumbum refinery has been active in the region and accounted for an annual production of about 15-20 t of metallic lead (beside Ag, Au and other precious metals). In recent years, the mines have been closed one after the other. The Panelas mine was considered exhausted in 1990. The Perau and Furnas mines were closed in 1987 and 1992, respectively. The production in the Barrinha, Canoas and Rocha mines ended at the same time as the Plumbum refinery stopped its activities, in November 1995. For several years, the refinery sustained metal production by importing lead concentrates mainly from Peru and the USA.

The galena lead isotopic compositions, obtained and compiled by Tassinari *et al.* (1990) and Daitx (1996), clearly discriminate the two deposit-type ores in the Ribeira Valley (Table 1). It is worthwhile to point out that these Proterozoic ores yield isotopic ratios quite distinct from those obtained in Phanerozoic lead deposits (e.g. Peru, USA and other countries), and from those of present-day sources.

On the basis of the available isotopic data on lead ores and taking into account the elevated lead concentrations found in stream sediments along the Ribeira de Iguape River, an attempt was made to verify if the lead isotopic signature of these sediments could be used to trace the sources for heavy metal pollution in the region.

Materials and methods

The materials used in the present study mainly consisted of stream sediments sampled along the Ribeira de Iguape River and in its estuary (Fig. 1, Table 2). The sampling stations, procedures and dates are described as follows:

Station 1 is in the Ribeira de Iguape River about 100 m upstream of Rocha creek which drains through the Rocha mine and it is hence outside the area which has been affected by the mining activity. Sample 1 is a composite sample of sediments collected during four occasions in 1989 and 1990 (CETESB 1991) and may express a background value for Pb in the region.

Station 2 is in Canoas creek which is thought to be affected by Canoas mine (Perau-deposit type). Sample 2 was collected in May 1996, at 300 m downstream of Canoas mine.

Station 3 is situated in Laranjal creek, 2 km downstream of Barrinha mine (Panelas-deposit type).

Station 4 is downstream of Furnas mine (Panelas type) in Betari River. Sample 4 is a composite sample of sediments collected in 1989 and 1990, whereas Sample 4a was collected later, in February 1995, at the same locale.

Stations 5, 6 and 7 are along the Ribeira de Iguape River. The first ones (5 and 6) are situated near the town of Itapeuna and Registro city, respectively and, the latter is situated 500 m upstream of Valo Grande channel. These samples were collected in 1989 and 1990 (CETESB 1991).

Stations 8, 9 and 10 are in the Iguape-Cananéia lagoonar-estuarine region. The first one is situated in the estuary of the Ribeira de Iguape River. Station 9 is at the northern margin of Comprida Island outside the influence of the river waters. Station 10 is in the Interior Sea, between the coast and Comprida Island, where the fluvial waters flow through Valo Grande channel and meet the ocean waters leading to high precipitation of fine-grained sediments.

In addition to these sediment samples, Sample 11 was collected in 1991 from the tailings of Plumbum refinery where the waste of the Canoas (Perau-type) ore dressing was stored.

In laboratory the sediment samples were carefully homogenized and portions of them were dried at 60°C for a period of 7 days. Thereafter, 250 mesh (ASTM, 63 mm) grain size fractions were analyzed for lead content by AAS after solubilization in a HNO_3-$HClO_4$-HF mixture.
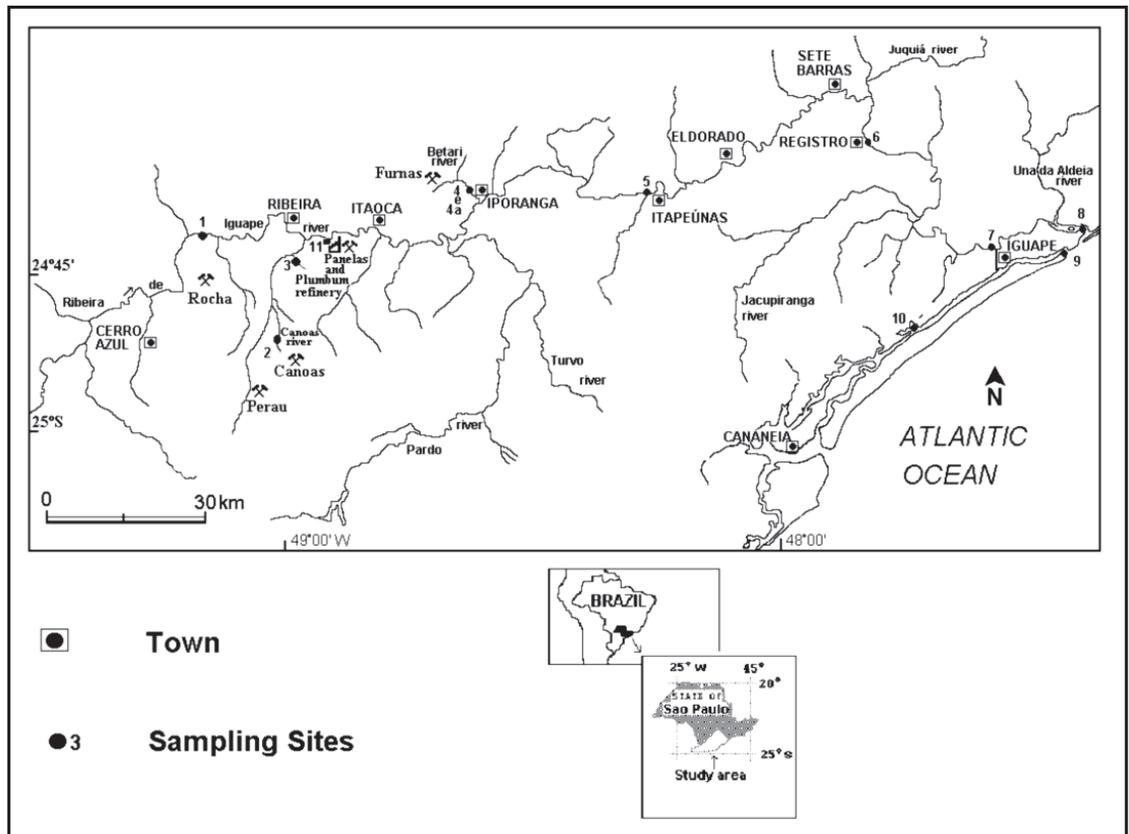
Figure 1 – Location map of the Ribeira Valley showing the Pb-Zn mines and sampling stations

Table 2 – Description of sediment and tailings samples and their lead contents

Sample	Sample location	Pb mg/kg
1	Ribeira River upstream of Rocha creek	6
2	Canoas creek 300 m downstream of mine	47
3	Laranjal creek downstream of Barrinha mine	845
4	Betari River, downstream of Furnas mine	560
4a	same as above	863
5	Ribeira River near the town of Itapeúnas	391
6	Ribeira River near the city of Registro	90
7	Ribeira River upstream of Valo Grande	110
8	Ribeira River estuary	26
9	Comprida Island northern margin	9
10	Coastland 15 km S of the town of Iguape	56
11	Tailings of Plumbum refinery	2800

Sample replicates (grain size less than 63 mm) were used as well for isotopic analysis in the Isotope Geology Laboratory of the Federal University of Pará, Northern Brazil. In the isotope laboratory, about 500 mg of the samples were solubilized by concentrated HNO_3 for 24 hours and by HNO_3+HCL over heat (80°C). The separation of lead was made by ion-exchange chromatography using DOWEX AG 1X8 200-400 mesh resin in HBr (0.5 N) media. An aliquot of each lead concentrate was deposited in Re filaments with purified H_3PO_4 (0.05 N) and silica gel. During the experimental procedures, the chemical blanks remained less than 5 ng Pb, which is not significant in comparison with the lead concentration in the samples of about 5 mg. Pb isotopic measurements were carried out in a VG Isomass 54E single-collector mass spectrometer.

The isotopic ratios were corrected for fractionating effect using a mass discrimination factor of 0.12% ± 0.03 per atomic mass unit. This factor was determined from repeated analyses of the NBS 982 "equal atoms" standard. Hence, the measurements of $^{206}Pb/^{204}Pb$, $^{207}Pb/^{204}Pb$ and $^{208}Pb/^{204}Pb$ were multiplied by factors equal to 1.0024, 1.0036 and 1.0048,

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Table 3 – Lead isotopic compositions of stream sediments from Ribeira de Iguape River Basin (Samples 1 to 10) and from tailings of Plumbum refinery (Sample 11)

Sample	Run	$^{206}Pb/^{204}Pb$	2s	$^{207}Pb/^{204}Pb$	2s	$^{208}Pb/^{204}Pb$	2s	$^{206}Pb/^{207}Pb$
1	1	18.028	0.023	15.571	0.029	38.916	0.097	1.158
2	1	16.891	0.020	15.580	0.028	37.329	0.090	1.084
3	1	17.057	0.024	15.546	0.031	37.476	0.098	1.097
4	1	16.975	0.022	15.549	0.030	37.628	0.092	1.091
	2	17.004	0.021	15.602	0.031	37.789	0.096	1.090
4a	1	16.937	0.022	15.516	0.028	37.230	0.092	1.092
5	1	16.873	0.020	15.510	0.029	37.507	0.092	1.088
	2	16.897	0.021	15.543	0.028	37.619	0.091	1.087
6	1	17.045	0.021	15.528	0.028	37.827	0.090	1.097
	2	17.068	0.021	15.537	0.028	37.918	0.090	1.096
	3	17.058	0.021	15.560	0.028	37.893	0.091	1.096
7	1	17.076	0.021	15.557	0.028	37.845	0.090	1.098
	2	17.085	0.021	15.568	0.029	37.886	0.092	1.097
8	1	17.109	0.022	15.537	0.032	37.515	0.102	1.101
9	1	17.277	0.020	15.548	0.028	37.842	0.090	1.111
10	1	17.043	0.020	15.533	0.028	37.421	0.090	1.097
11	1	16.477	0.021	15.538	0.031	37.163	0.100	1.060
	2	16.512	0.027	15.576	0.032	37.231	0.123	1.059

respectively. Duplicate analyses have been performed on some samples (4, 5, 6, 7 and 11). Although some differences in the isotopic compositions can be observed, the duplicate results for the same sample are always within the 2σ deviation on isotopic measurements. Therefore, the reproducibility can be considered as acceptable.

Results and discussions

The lead concentrations obtained after complete digestion of the samples are shown in Table 2. Background values for Pb in the region are estimated around 16 ppm for stream sediments from a database compiled from Morgenthal (1978). Sample 1 contains only 6 mg/kg Pb and it is considered free of contamination. Samples 3 to 5 showed the highest Pb contents and they are located in the Upper Ribeira Valley where the producing mines are concentrated. Sample 2 shows a lower Pb concentration (47 mg/kg) when compared with the other samples from the mining areas (391-863 mg/kg). This surprising result can be explained by the fact

that the Canoas lead ore was mostly processed at the Plumbum refinery and waste disposal into Canoas creek was minimum. Moreover, Sample 2 was collected in May, 1996, after the closure of the Canoas mine.

In general, lead content in stream sediments decreases exponentially towards the river estuary in accordance with previous studies, as mentioned before. The Pb concentrations found in the Ribeira de Iguape sediments are thus strongly suggestive of the influence of mining activities in the region.

The Pb isotopic compositions of the stream sediment samples are listed in Table 3, and plotted in the $^{206}Pb/^{207}Pb$ x $^{206}Pb/^{204}Pb$ diagram depicted in Figure 2. The galena isotopic composition ranges for the Perau- and Panelas-deposit types are also shown.

These data clearly indicated that most of the samples fall within the lead isotopic field of the Panelas-deposit type. Sample 1 was shown to be the most radiogenic and may represent a mixture of the uncontaminated sediments in the region. Its isotope composition is, however, lower than the expected value of the modern environmental lead. On the

other hand, Sample 11, from the Plumbum tailings (Canoas ore), was the least radiogenic among all analyzed samples and represents the older Pb-Zn ores of the Perau type.

Sample 2 was collected to demonstrate their similarity with the Perau type, i.e., the probable influence of the Canoas mine on the stream sediments. However, this sample yielded a Pb isotopic composition fairly more radiogenic than the Perau-ore type. That may indicate either that the Canoas ore deposits have experienced remobilization during its post-depositional history, as stated by Daitx and Venusso (1992), or that the sample represents a mixture of material from Canoas mine with other uncontaminated sediments. A post-depositional remobilization would have also affected the isotopic composition of Sample 11 which has the same origin.

Figure 2 – Isotopic compositions of sediments in the ^{206}Pb/^{207}Pb x ^{206}Pb/^{204}Pb diagram showing the fields for the Perau- and Panelas-ore types according to Tassinari *et al.* (1990) and Daitx (1996)

Thus, mixing processes are likely to have occurred at all sites along the river basin, moving the isotopic ratios of all sediment samples towards point 1. In the case of Sample 2, this mixture effect was more sensitive because of its lower Pb concentration which suggests a weak Pb ore contribution, as mentioned before.

Sample 3 from Laranjal creek downstream of Barrinha mine and Samples 4 and 4a from Betari River downstream of Furnas mine yielded Pb isotopic signatures similar to the Panelas-ore type, as expected. On the other hand, Sample 5 which was collected in the main course of the Ribeira de Iguape River showed a less radiogenic Pb isotopic composition, probably due to mixture of materials influenced by both ore types, although dominated by the Panelas type.

Looking at the isotopic ratios obtained for Samples 5, 6 and 7, it is clear that as the distance between the stations and the mining area increases, the lead contents in the sediments lower and their isotopic compositions become more radiogenic. Nevertheless, even Samples 8, 9 and 10 from the estuary showed isotopic compositions within the field of the Panelas-ore type. As the contamination decreases in the sediments (low Pb contents), their Pb isoto-
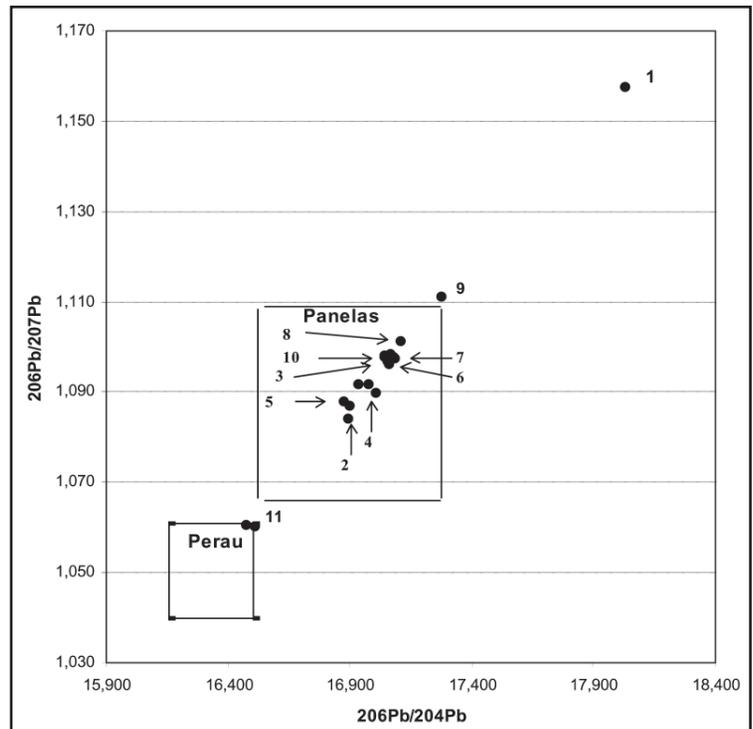
pic signatures approach to those of more modern lead, represented in the region by Sample 1 (uncontaminated sediment with the lowest Pb content).

For comparison, the Pb isotopic compositions of galena from 18 Phanerozoic ore deposits distributed in 9 ore districts in the Central Peruvian Andes (Gunnesch *et al.* 1990) and from seven other ore deposits located in the Eastern Cordillera in southeastern Peru (Kontak *et al.* 1990) are indicated in Figure 3. These deposits are younger than the Brazilian lead deposits and to a certain extent very similar to other sources of concentrates imported by the Plumbum refinery. As shown in Figure 3, the isotopic compositions of the Ribeira de Iguape River sediments not only differ from the lead isotopic signatures yielded by the Phanerozoic ores, but also depart from actual Pb crustal mean value of Rollinson (1993).

Thus, the lead found in the sediments along Ribeira de Iguape River clearly indicates that these sediments are affected by material addition from sources other than modern lead or imported lead concentrates commonly processed by the Plumbum refinery. As mentioned before, the mining activities in the Panelas-type ore deposits such as Rocha, Panelas, Barrinha and Furnas are likely to be

responsible for the present metal contamination in the Ribeira Valley. On the other hand, the similarity between ore and sediment isotopic signatures (grain size less than 63 mm) also supports the previously formulated hypothesis (Moraes 1997) that the lead may have been transported as fine solid particulate, such as suspended material in water, subsequently adsorbed in the mud portion of the sediments.

Decreasing lead contents in the sediments towards the estuary are coincidental with increasing Pb isotopic ratios in Samples 8, 9 and 10, which indicates dilution of material originated in the mines by mixture with other uncontaminated sediments derived from non-mineralized rocks and soils (Church *et al.* 1999).

As Sample 9 was collected outside the fluvial water plume and under influence of ocean waters, it is normal that this sample would yield the lowest Pb content and the highest Pb isotopic ratios among the analyzed sediments. However, the isotopic composition of this less-contaminated sample remains lower than the background value (Sample 1), indicating that the whole estuarine complex has been affected by lead contamination due to ore extraction.

The Pb isotopic compositions of stream sediments along Ribeira de Iguape River unequivocally proved the fact already suggested by previous geochemical studies that the mining industry in the upper Ribeira Valley is the source of heavy metal pollution in the drainage system, and furthermore, that some mines, such Panelas and Rocha (Panelas-type), which were responsible for the highest lead production in the region, dramatically contributed to metal pollution of the Ribeira de Iguape River.

Conclusions

The results obtained in the present study confirmed the hypothesis of previous geochemical studies which attributed to the mines in the upper Ribeira Valley the high concentrations of heavy metals in the Ribeira de Iguape River sediments,
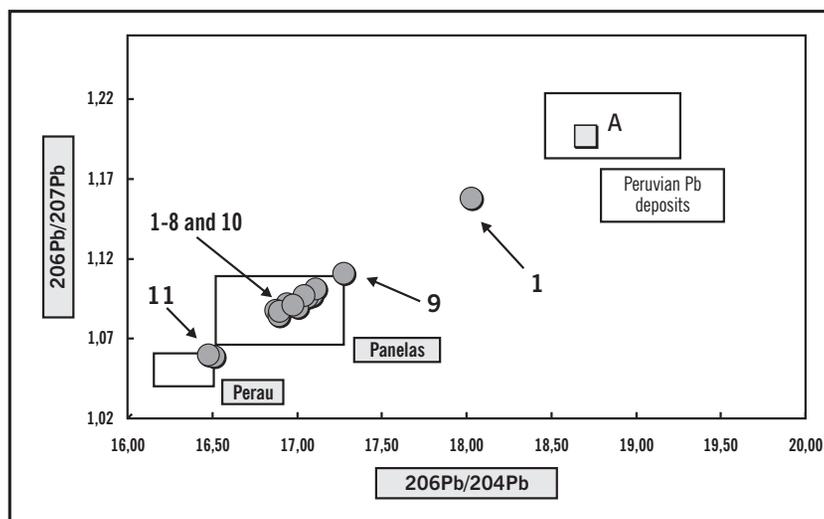
Figure 3 – Isotopic compositions of sediments in the ^{206}Pb/^{207}Pb x ^{206}Pb/^{204}Pb diagram showing the fields for the Phanerozoic Pb-ores from Peru after Gunnesh *et al.* (1990) and Kontak *et al.* (1990) and A) the actual mean Pb for continental crust after Rollinson (1993)

including those in the Iguape-Cananeia lagoonar-estuarine region.

Although the stream sediments might represent a mixture of various eroded lithologic types and soils which are being transported by the drainage in the Ribeira Valley, the coincidence between sediment and ore isotopic signatures strongly suggests that discharge of tailings have occurred during the period of intense mining in the region. It is also demonstrated that transport of lead and other associated heavy metals along the drainage is likely to have occurred as fine solid particulate, suspended material, subsequently adsorbed in minerals of the fine-grained fraction of the sediments.

Discrimination of the lead isotopic compositions found in stream sediments indicates that most heavy metal pollution in the Ribeira Valley originated from mining activities in the Panelas-type deposits, and that the environmental impact of mineral beneficiation of the Perau-type ores and of imported ore concentrates in the Plumbum refinery was of secondary importance.

The use of the lead isotope tracer method to fingerprint the sources for heavy metal pollution in mining regions was proved to work in the present study and may be applied to other Precambrian metallogenic areas. However, a more complete isotopic data set must be available both for metallic ores and for non-mineralized rocks and soils which are crosscut by the drainage system of the mineral province.

Acknowledgments

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