The mineralized veins and the impact of old mine workings on the environment at Segura, central Portugal

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Abstract

At Segura, granitic pegmatite veins with cassiterite and lepidolite, hydrothermal Sn–W quartz veins and Ba–Pb–Zn quartz veins intruded the Cambrian schist–metagraywacke complex and Hercynian granites. Cassiterite from Sn–W quartz veins is richer in Ti and poorer in Nb and Nb + Ta than cassiterite from granitic pegmatite. Wolframite from Sn–W quartz veins is enriched in ferberite component. The Sn–W quartz veins contain pyrrhotite, arsenopyrite, sphalerite, chalcopyrite, stannite, matildite and schapbachite and the Ba–Pb–Zn quartz veins have cobaltite, pyrite, sphalerite, chalcopyrite, galena and barite, which were analyzed by electron microprobe. The presently abandoned mining area was exploited for Sn, W, Ba and Pb until 1953. Stream sediments and soils have higher concentrations of metals than parent granites and schists. Sn, W, B, As and Cu anomalies found in stream sediments and soils are associated with Sn–W quartz veins, while Ba, Pb and Zn anomalies in stream sediments and soils are related to Ba–Pb–Zn quartz veins. Sn, W, B, As, Cu, Ba, Pb and Zn anomalies in stream sediments and soils are also related to the respective old mining activities, which increased the mobility of trace metals from mineralized veins to soils, stream sediments and waters. Stream sediments and soils are sinks of trace elements, which depend on their contents in mineralized veins and weathering processes, but Sn, W and B depend mainly on a mechanic process. Soils must not be used for agriculture and human residence due to their Sn, B, As and Ba contents. Waters associated with mineralized veins were analyzed by flame atomic absorption spectroscopy (FAAS) and ICP-AES have high As, Fe and Mn and should not be used for human consumption and agriculture activities. The highest As values in waters were all related to Sn–W quartz veins and the highest Fe and Mn values were associated with the Ba–Pb–Zn quartz veins. No significant acid drainage was found associated with the old mine workings.
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1. Introduction

Mining and mineral-processing activities can modify the environment in a variety of ways. These activities affect relatively small areas, but they can have a large local impact on the environment. Mining activities extract and process valuable pit materials, which are crushed and milled. These materials have large surfaces and are very susceptible to both erosion and chemical weathering, causing a potential danger to the environment.

Sulphide mineralization is notorious for producing acid waters bearing high concentrations of heavy metals from mining, which is a great environmental concern (Rahn et al., 1996). A major source of acid mine drainage may result from the closure of a mine

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and if it is not controlled, it can cause a serious threat to the environment.

Large amounts of metals found in soils, stream sediments and waters are related to the occurrence of polymetallic mineralization in mining areas (Marszalek and Wasik, 2000). Large heavy-metal concentrations are the most important indicators of a possible environmental hazard emanating from abandoned mines (Rösner, 1998). However, the element concentrations in the environment depend on their dissolution from rocks and subsequent mobility in stream sediments and waters. The abandoned mining sites are frequently located close to populated rural areas. Consequently, surface water contamination by acid mine drainage has the potential to contaminate subsurface waters, wells and irrigation water supplies (Allen et al., 1996).

In the past, the mining industry frequently showed a lack of concern for the environment. In particular, the disposal of waste has led to unsightly spoil heaps being left to disfigure the landscape and to pollute surface streams and groundwater. Today, however, the greater awareness of the importance of the environment has led to tighter regulations being imposed by many countries to lessen the impact of mining (Bell, 1998).

At Segura, central Portugal, there are Sn−W and Ba−Pb−Zn mineralized deposits, which were exploited in the past for Sn, W, Ba and Pb. The extractions ceased in 1953 and there has not been any significant development work in the area. The tailings and rejected materials were deposited on the ground and are not covered by vegetation. They are exposed to the air and water that can change the environmental geochemistry of the area.

This paper evaluates the geochemical impact of Sn−W and Ba−Pb−Zn mineralized deposits and of the respective abandoned old mine workings on stream sediments, soils and waters at Segura.

2. Geological setting

The studied area, Segura, is located at central Portugal near the Portuguese−Spanish border (Fig. 1). At Segura, Hercynian granitic rocks intruded the
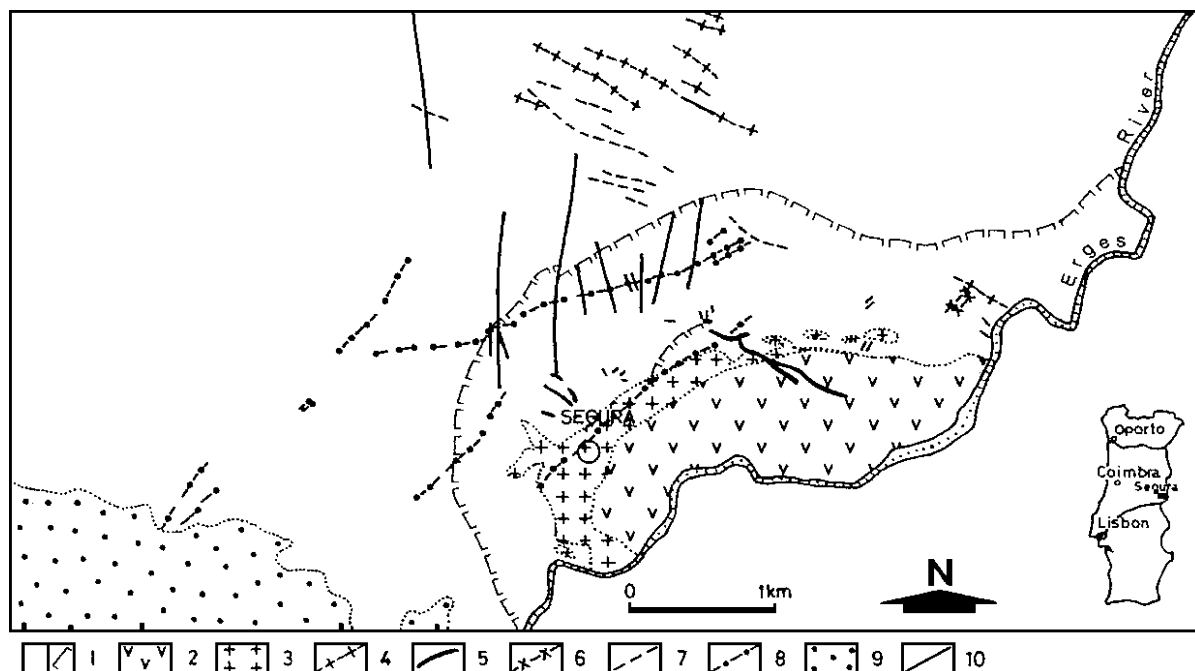

Fig. 1. Geological map of Segura, central Portugal. 1—Schist–metagraywacke complex, contact metamorphic aureole; 2—medium-to coarse-grained two-mica granite; 3—medium-to fine-grained muscovite granite; 4—granodiorite porphyry veins; 5—granitic aplite veins; 6—Li-bearing granitic pegmatite veins with cassiterite; 7—Sn–W quartz veins; 8—Ba–Pb–Zn quartz veins; 9—arkoses; 10—faults.

Cambrian schist–metagraywacke complex, which consists of alternating metapelites and metagraywackes with metaconglomerate and marble intercalations. The Segura pluton consists mainly of medium- to coarse-grained two-mica granite, but there is also a medium- to fine-grained muscovite granite. Both granites produced a contact metamorphic aureole up to 500 m thick (Fig. 1).

NW–SE to NNW–SSE granitic aplite veins intruded the schist–metagraywacke complex and granites, whereas subhorizontal NE–SW granitic pegmatite veins containing cassiterite and lepidolite and NW–SE to WNW–ESE quartz veins with cassiterite and wolframite intersect this complex. Later, ENE–WSW to NNE–SSW quartz veins with barite, galena and sphalerite cut the schist–metagraywacke complex, while a few of them intruded the muscovite granite.

The mineralized veins fill late- to post-tectonic Hercynian faults. The granitic pegmatite veins with cassiterite and lepidolite are up to 15 cm thick and 300 m long. The lenticular quartz veins with cassiterite and wolframite are up to 10 cm thick and 1300 m long, but one of them has a thickness of 50 cm. The lenticular quartz veins with barite, galena and sphaler-

ite are up to 3 m thick, but at their contact with the muscovite granite, they appear many thin quartz veins of 2–15 cm thick. The longest one is 2500 m. Commonly, barite represents 20–30% of the mineralogical composition of the veins (Instituto Geológico e Mineiro, 1988).

Nowadays, it is difficult to look for the mineralized veins. They are generally found through the old mine workings, which were carried out from 1942 to 1953. In this region, 100 tons of cassiterite, 12 tons of wolframite, 525 tons of barite and 211 tons of galena were exploited.

3. Methods

Detailed studies of samples collected from the mineralized veins and tailings included transmitted and reflected-light microscopy and electron microprobe analyses.

The ore minerals were analyzed for major and minor elements on a Cameca Camebax electron microprobe at Instituto Geológico e Mineiro, S. Mamede de Infesta, Portugal, and a Jeol JXA 8600
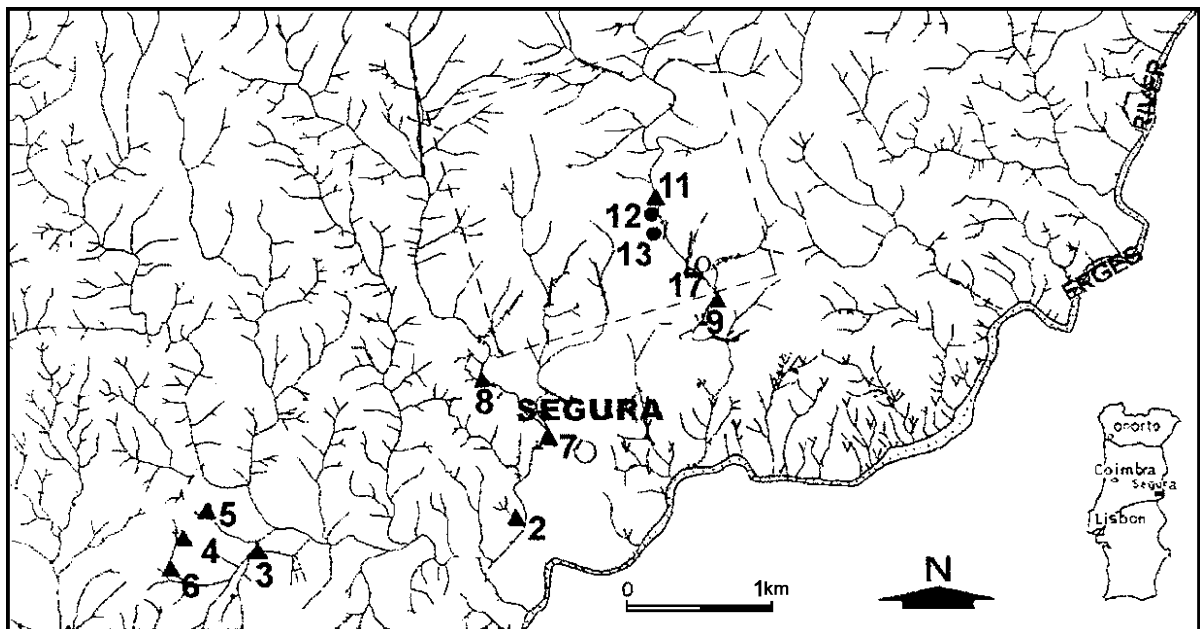

Fig. 2. Map of streams from Segura, central Portugal with the selected soil area and sample locations. ▢—selected area for soil prospection (Instituto Geológico e Mineiro, 1988). Location of water points: ●—springs; ○—well; ▲—streams and small retentions.

electron microprobe at Bristol University, UK. Standards used include cassiterite (Sn Lα), Ta (Lα), Nb (Lα), W (Lα), $MnTiO_3$ (Mn Kα and Ti Kα), Fe_2O_3 (Fe Kα), Mo (Lα) and apatite (Ca Kα) for oxides, sphalerite (Zn Kα and S Kα), pyrite (Fe Kα), galena (Pb Mα), $MnTiO_3$ (Mn Kα), SnO_2 (Sn Lα), Ni (Kα), Cu (Kα), As (Lα), Ag (Lα), Cd (Lα), Sb (Lα), Bi (Mα) and Mo (Lα) for sulphides and barite (Ba Lα and S Kα), wollastonite (Ca Kα), orthoclase (Si Kα), galena (Pb Mα), MgO (Mg Kα) and Fe_2O_3 (Fe Kα) for sulphosalts.

In the Segura area (Fig. 2), a total of 717 samples of stream sediments were collected for mineral and geochemical prospections (Instituto Geológico e Mineiro, 1988). Of those, 671 samples of stream sediments were collected on schists and 46 samples on granites from selected locations between 50 m upstream and 100 m downstream the confluence of streams. Sn and W were determined by X-ray fluorescence, while B, As, Cu, Ba, Pb and Zn were analyzed by ICP-AES at Instituto Geológico e Mineiro, S. Mamede de Infesta with a precision of 10%.

Based on the stream sediments data, an area of 3.8 km^2 at north of Segura (Figs. 1 and 2) was chosen to improve geochemical prospecting and 1008 samples of soils derived from schist were collected up to a depth of 30 cm. They were analyzed for As, B, Cu, Ba, Pb and Zn using the same analytical techniques applied for stream sediments and with the same precision of 10% (Instituto Geológico e Mineiro, 1988).

Tin, W, Cu, Ba, Pb and Zn of parent chlorite phyllite and granites were analyzed by X-ray fluorescence, while As was determined by neutron activation. The measurements on phyllite samples were carried out at Manchester University (Neiva et al., 1990), while the granite samples were analyzed at Bristol University. The overall precision was 5%.

The Segura region has a dry climate and during summer only, a few streams, springs and wells contain water. Twelve sampling points located close to the abandoned old mine workings (Fig. 2) were selected to collect water four times, at each sampling point, during a year and making a total of 48 water samples. Waters were collected at the end of summer (October 1996), at the middle of winter (December 1996), at the

Table 1

Electron-microprobe data on cassiterite, columbite and wolframite from Li-bearing granitic pegmatite veins and Sn–W quartz veins at Segura

	Cassiterite			Manganocolumbite	Wolframite		
	1		2			Rim	Core
	a	b					
					FeO	16.94	15.79
Nb_2O_5	0.45	2.54	0.05	56.79	MnO	6.14	7.16
Ta_2O_5	0.59	1.46	0.37	23.12	CaO	0.01	0.02
TiO_2	–	0.04	0.39	0.20	TiO_2	0.01	0.03
SnO_2	98.76	95.17	99.15	0.23	Nb_2O_5	0.03	0.04
WO_3	–	0.34	0.03	4.87	WO_3	75.95	75.85
MnO	0.11	0.28	0.03	13.68	MoO_3	–	0.03
FeO	–	0.03	0.04	1.07	SnO_2	0.02	0.02
Total	99.91	99.86	100.06	99.96	Total	99.10	98.94
					Fe	0.722	0.674
Nb	0.005	0.029	–	1.594	Mn	0.265	0.300
Ta	0.004	0.010	0.003	0.390	Ca	–	0.001
Ti	–	0.001	0.007	0.009	Ti	0.001	0.001
Sn	0.987	0.945	0.988	0.006	Nb	0.001	0.001
W	–	0.002	–	0.078	W	1.003	1.003
Mn	0.002	0.006	0.001	0.719	Mo	–	0.001
Fe	–	0.001	0.001	0.056	Sn	0.001	–
Total	0.998	0.994	1.000	2.852	Total	1.993	1.981

1—Li-bearing pegmatite vein, 2—Sn–W quartz veins; (a) lighter zone, (b) darker zone of the same crystal. Oxides in wt.%. (–): Not detected. Cation formula based on 2, 6 and 4 atoms of oxygen for cassiterite, columbite and wolframite, respectively. Analyst: I. Antunes.

middle of spring (March 1997) and at the beginning of the summer (July 1997).

Temperature, pH, Eh, specific conductance and dissolved oxygen were determined in situ. The waters were acidified and kept at 4 °C. Na, K, Ca, Mg, As, Fe, Mn, Cu, Pb and Zn were determined by Spectrometer Perkin Elmer 303 flame atomic absorption at the Department of Earth Sciences, University of Coimbra, while Sn, B and Ba were determined by ICP-AES with a Spectrometer PU7000 ICP at Instituto Geológico e Mineiro, S. Mamede de Infesta. Alkalinity and Cl^- were determined by titrations. Sulphate was analyzed by gravimetry, while NO_3^- was determined by molecular absorption spectrometry, at the Department of Earth Sciences, University of Coimbra. The precision of all analyses was within ± 5%. Sn, B, Cu and Pb were not detected in waters from Segura (Antunes, 1999).

4. Results and discussion

4.1. Geochemistry of ore minerals

Cassiterite from Li-bearing granitic pegmatites is zoned and the darker zones are richer in Nb and Ta than the lighter zones (Table 1), which are nearly pure SnO_2. The darker zones are oscillatory and have Nb>Ta and Mn>Fe. Manganocolumbite exsolutions (Table 1) were found particularly in darker zones of cassiterite. Cassiterite from Sn−W quartz veins is unzoned, does not show any exsolutions and is poorer in Nb and Nb + Ta and richer in Ti than cassiterite from Li-bearing granitic pegmatite veins (Table 1 and Fig. 3).

Wolframite occurs in the Sn−W quartz veins and is richer in ferberite component than in heubnerite component (Table 1).

Sulphides and sulphosalts occur in quartz veins. Their average chemical compositions are given in Table 2. In Sn−W quartz veins, the later sphalerite associated with wolframite is richer in Zn and poorer in Fe than the earlier sphalerite. Generally, sphalerite from Ba−Pb−Zn quartz veins is richer in Zn and poorer in Fe than sphalerites from Sn−W quartz veins (Table 2). Chalcopyrite from Ba−Pb−Zn quartz veins is richer in Cu and Fe than chalcopyrite from Sn−W quartz veins (Table 2).

In the Sn−W quartz veins, matildite is richer in Ag and Bi and poorer in Pb than schapbachite (Table 2). Stannite with the composition $Cu_{1.93}(Fe_{0.79}Zn_{0.21})SnS_4$ also occurs in these veins and is the last sulphide.
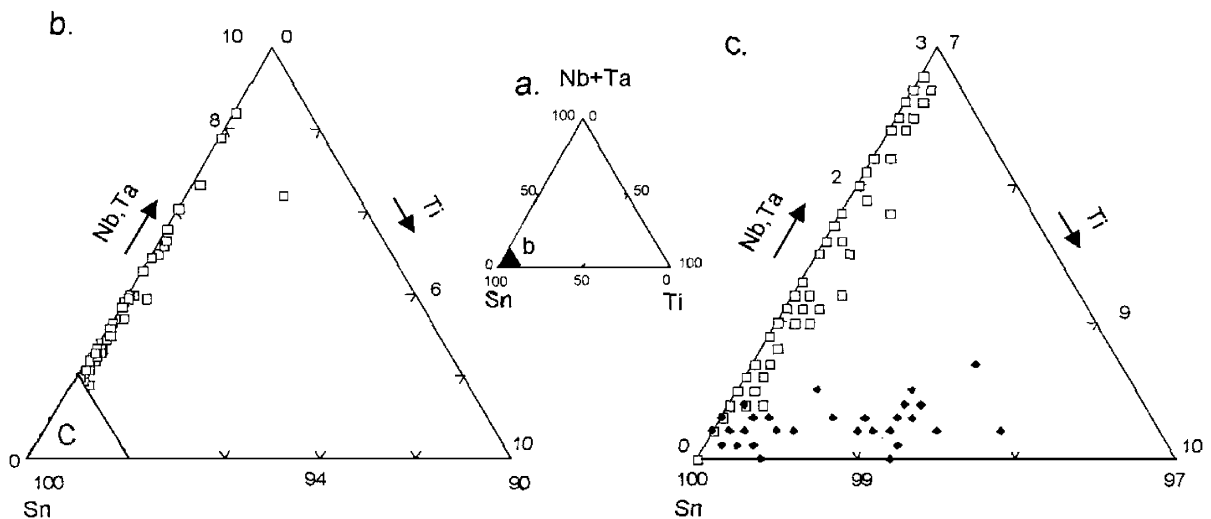
Fig. 3. (a) (Nb,Ta)−Ti−Sn diagram showing the location of diagram (b); (b) composition of the cassiterite richest in Nb + Ta from Li-bearing granitic pegmatite veins from Segura and showing the location of cassiterite in diagram (c), which is expanded in the following figure to avoid data superposition; (c) cassiterites from Li-bearing granitic pegmatite veins and Sn−W quartz veins from Segura. Symbols: □—granitic pegmatite; ◆—Sn−W quartz veins.

Table 2
Electron-microprobe analyses (wt.%) of some sulphides and sulphosalts from Sn–W quartz veins and Ba–Pb–Zn quartz veins from Segura

		Cu	Ag	Zn	Fe	Mn	Cd	Sb	As	Bi	Pb	Sn	Ni	Co	Mo	Se	Te	S	Total
a	pyrrhotite	–	0.03	0.51	56.31	0.02	0.02	0.04	0.02	–	–	–	–	0.03	–	–	–	42.69	99.67
a	arsenopyrite	–	–	–	35.26	–	–	0.01	44.71	–	–	–	0.02	0.03	–	–	–	19.52	99.55
a	pyrite	–	–	–	47.54	–	–	–	0.05	–	–	–	0.02	0.05	–	–	–	51.87	99.53
b	pyrite	–	–	–	48.21	–	–	–	0.16	–	–	–	0.03	0.07	–	–	–	51.21	99.68
a[1]	sphalerite	0.03	–	54.89	9.15	0.16	1.44	–	–	–	–	–	–	0.01	–	–	–	34.10	99.78
a[2]	sphalerite	0.09	–	60.37	4.07	0.11	0.96	–	–	–	–	–	–	0.01	–	–	–	34.37	99.98
b	sphalerite	0.11	–	61.79	2.56	0.02	0.75	–	–	–	0.16	–	–	0.01	0.09	–	–	34.53	100.02
a	chalcopyrite	34.10	0.27	–	29.24	–	–	–	–	–	–	–	–	–	–	–	–	36.03	99.64
b	chalcopyrite	34.62	0.08	–	29.51	–	–	–	–	–	–	–	–	–	–	–	–	35.41	99.62
a	matildite	0.40	27.81	0.34	0.12	–	0.13	0.04	–	52.87	1.22	–	–	–	–	0.36	0.14	16.49	99.92
a	schapbachite	0.73	18.12	0.35	0.40	–	0.11	0.06	–	34.22	30.49	–	–	–	–	0.26	0.03	15.42	100.19
a	stannite	28.59	–	3.18	10.30	–	–	–	–	–	–	27.59	–	–	–	–	–	29.91	99.57
b	galena	0.04	0.01	0.08	0.04	0.01	0.14	0.01	–	0.01	85.95	–	–	–	–	–	–	13.78	100.07

(a) Sn–W quartz veins, (b) Ba–Pb–Zn quartz veins; (–): not detected. Analyst: I. Antunes.
[1] Earlier sphalerites.
[2] Later sphalerites.

Galena and barite were only found in the Ba–Pb–Zn quartz veins. Commonly, both have homogeneous compositions (Tables 2 and 3), but barite has up to 1.82 wt.% SrO.

Some secondary phases were also found, like scorodite (Table 3) as the alteration product of arsenopyrite in the Sn–W quartz veins and anglesite, mimetite and kintoreite (Table 3) associated with the galena alter-

ation. Mimetite with As/P ratio of 1.02–1.04 and kintoreite are presented in Neiva et al. (2001).

4.2. Geochemistry of stream sediments and soils

At Segura, stream sediments and soils are enriched in metal composition with respect to parent schist and granites, except for Sn in stream sediments on granites

Table 3
Electron microprobe analyses of barite and some secondary minerals of mineralized quartz veins from Segura

	Barite		Scorodite		Anglesite	Mimetite		Kintoreite
SiO_2	0.03	Fe_2O_3	32.28	P_2O5	0.09	6.97		19.52
FeO	0.02	As_2O_5	46.55	CaO	–	0.38		–
MgO	–	Total	78.83	As_2O5	–	11.51		–
CaO	0.04			SO_3	27.07	–		1.62
SrO	0.79			PbO	72.30	78.29		31.00
BaO	64.65			Fe_2O_3	–	–		32.39
SO_3	34.58			CuO	–	–		0.12
Total	100.11			Cl	–	3.05		–
					99.46	100.20		84.65
				$O \equiv Cl$		0.67		
				Total		99.53		
Ca	0.002	Fe^{3+}	1.000	Pb	0.966	5.086	Pb	1.027
Sr	0.017	As	1.002	Ca	–	0.099	Cu	0.022
Ba	0.975			P	0.004	1.424	Fe^{3+}	3.000
S	1.002			As	–	1.453	P	2.034
				Cl	–	1.247	S	0.149
				S	1.008			

Barite, anglesite, mimetite and kintoreite from Ba–Pb–Zn quartz veins; scorodite from Sn–W quartz veins. Atomic contents calculated on the basis of 4(O) for barite and anglesite, 1 Fe for scorodite, 13 anions for mimetite and 3 Fe for kintoreite. Analyst: I. Antunes.

Table 4
Trace element contents in ppm of parent rocks, stream sediments and soils from Segura compared with recommended maximum concentrations

	Segura									Soils		
	Parent rocks			Stream sediments on				Soils on schists		1	2	3
	Chlorite phyllite	Two-mica granite	Muscovite granite	Schists		Granites		Minimum	Maximum			
				Minimum	Maximum	Minimum	Maximum					
	Average	Average	Average									
Sn	*	20	49	<2.5	>20	<2	>12.5	<4	>75	5	50	300
W	*	6	13	<10	>50	<18	>70	<10	>45	–	–	–
B	–	–	–	<46	>175	<40	>60	<55	>300	2	–	–
As	*	10	4	<20	>175	<20	>45	<20	>375	20	30	50
Cu	28	2	1	<39	>60	<24	>50	<40	>100	150	100	500
Ba	588	163	19	<625	>1100	<500	>840	<675	>1500	750	500	2000
Pb	19	22	8	<27	>75	<40	>75	<20	>120	375	500	1000
Zn	92	48	57	<125	>225	<125	>165	<125	>290	600	500	1500

Contents of trace elements from Cambrian phyllite (Neiva et al., 1990). (*): Below limit of detection; (−): not determined or not defined. Recommended maximum values for: (1) agricultural soil; (2) human residence soil; (3) commerce and industry soil (Canadian Council of Ministers of the Environment, 1991). (−): Not defined.

(Table 4). In parent rocks, Sn, W, Cu and Zn are retained in micas and Ba and Pb are concentrated in K-feldspar and micas. Arsenopyrite is the main concentrator of As, but is rare. The maximum concentrations for trace elements of soils are generally higher than those of stream sediments (Table 4).

In general, the highest content of Sn, W, B, As, Cu, Ba, Pb and Zn in stream sediments was found in those collected on schist (Table 4) and are from a restricted area at north of Segura (Fig. 2). The highest Sn, W and B concentrations on stream sediments are associated with exploited Sn–W mineralizations. The highest concentrations on As and Cu are also associated with these mineralizations, but some of them, as well as the highest contents of Ba, Pb and Zn are related to Ba–Pb–Zn quartz veins, which were exploited in the past.

The class distribution of analyzed elements in soils is presented in Fig. 4. Sn, W, B, As and Cu anomalies of soils are mainly related to exploited Sn–W quartz veins, which also contain arsenopyrite and chalcopyrite, while the anomalies on Ba, Pb and Zn of soils are associated with quartz veins containing barite, galena and sphalerite (Figs. 1 and 2), which were also exploited. These mineralized veins mainly control the chemistry of stream sediments and soils.

The abandoned mine workings increase the mobility of trace elements from mineralized veins to soils and stream sediments because ore minerals have large exposed surfaces, which become weathered and, con-sequently, metals are released. Mechanical transport of metals, ore minerals and other materials also becomes important.

The mechanical process is the most responsible for Sn and W contents in stream sediments and soils. They are retained in micas derived from parent rocks and Sn–W quartz veins, but are mainly concentrated in cassiterite and wolframite, respectively derived from these veins and their old mine workings (mine tailings and waste heaps). However, a small amount of Sn concentration is released by weathering of stannite, which is much less abundant than cassiterite in Sn–W quartz veins. Tungstite can be formed by chemical alteration of wolframite. The mechanical process is also responsible for B content of stream sediments and soils and is retained in tourmaline derived from parent rocks, mineralized veins and waste heaps. However, B can be released by alteration of tourmaline into muscovite, which will take place mainly in soils.

Mechanical transport of sediment downstream is an important mechanism for the mobility of heavy metals from mineralized veins and tailings (Boulet and Lar-ocque, 1998), particularly because at Segura, the separation of ore minerals from gangue minerals was carried out at the top of streams with the help of water. However downstream, the effect of chemical process increases progressively.

Arsenopyrite concentrates As, chalcopyrite retains Cu and Zn, but sphalerite is the main concentrator of
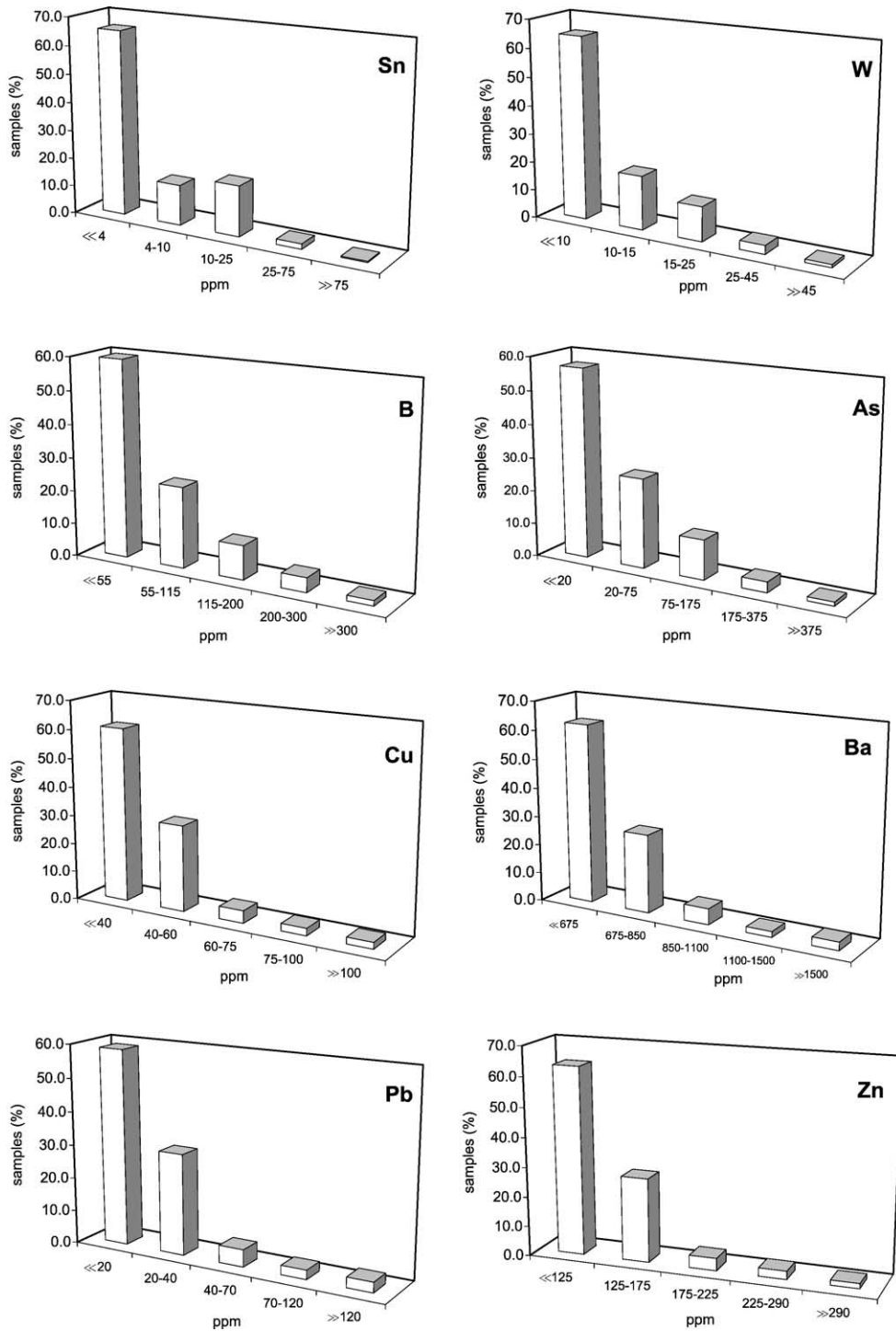
Fig. 4. The class distribution for trace element contents of soils from an area at north of Segura marked in Fig. 2. The lower limits of the classes are the average, σ, 2σ and 3σ.

Zn, while galena is responsible for Pb and barite concentrates Ba in the mineralized veins, mine tailings and in very small amount in waste heaps. The exploitation of these veins favored the exposition of sulphides and barite to weathering. Scorodite, anglesite, mimetite and kintoreite (Table 3) were found in the quartz veins and certainly also occur in mine tailings and waste heaps. Although some of the sulphide minerals and barite were carried by mechanical transport and occur in stream sediments, their alteration products are more important downstream.

The chemical processes involve selective dissolution of sulphides and barite from mineralized veins, mine tailings and waste heaps, transport of metals and their precipitations in soils and stream sediments. Small particles incorporated by mechanical process in soils will be weathered and metallic elements will be released. In soils, metals will be absorbed in clay minerals, Fe-oxides, Fe-hydroxides and organic matter. Soil pH and this absorption of metals controls metallic element contents (Boulet and Larocque, 1998) and explains the higher metal concentrations found in soils than in stream sediments (Table 4).

At Segura, metals in stream sediments and soils depend mainly on contents of these elements in mineralized veins and weathering processes, but mechanical process was the most important for Sn,

W and B. Both stream sediments and soils are sinks of trace metals.

The soils have a large content in Sn, B, As and Ba and must not be used for agriculture and human residence because they are above the recommended maximum values-VMR (Table 4 and Fig. 5). The As levels are the most problematic due to the high toxicity of this element. Soils from Segura should not be used even for industrial settings (Fig. 5). It is significant that 28% of soil samples have As content higher than 50 ppm (the recommended maximum value-VMR for industrial soil).

There are no recommended maximum values for W contents in soil. However, at Segura, W contents in soils are higher than those commonly found in soils (Brooks, 1972), confirming the mobility of W between Sn−W quartz veins and soils.

4.3. Geochemistry of waters

The results of the chemical composition at water samples from Segura are given in Table 5. Most of the water samples contain arsenic above the detection limit and those were plotted in the Eh−pH diagram (Fig. 6). The waters associated with Sn−W quartz veins fall in the $Fe_2O_3 + H_2AsO_4^-$ stability field, while those associated with Ba−Pb−Zn quartz veins
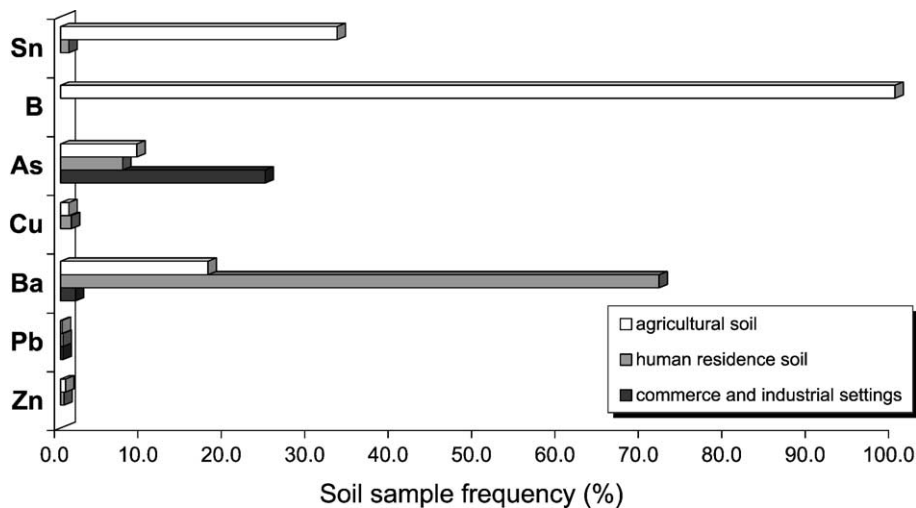

Fig. 5. Soil samples frequency (%) from Segura above recommended maximum values (Canadian Council of Ministers of the Environment, 1991).

Table 5
Concentration of constituents in waters from Segura

Quartz veins	Sample	Dates	Temp. (°C)	pH	Eh (mV)	Sp. Cond. (μS/cm)	Na (mg/l)	K (mg/l)	Ca (mg/l)
Sn–W	12s	July 97	20.7	6.95	*	237	20.7	1.4	6.4
		October 96	14.0	6.40	189	180	19.0	1.6	7.0
		March 97	20.0	6.80	192	210	19.3	1.2	6.3
		December 96	12.5	6.80	284	165	19.8	1.2	6.4
	13s	July 97	20.6	7.39	*	318	24.4	2.8	10.8
		October 96	13.0	6.80	284	230	25.4	2.1	9.7
		March 97	19.0	7.20	181	245	23.8	1.2	8.4
		December 96	11.0	7.00	281	195	21.3	1.3	8.1
	17w	July 97	26.2	7.13	*	177	14.8	1.1	5.0
		October 96	12.0	6.60	340	130	13.9	1.0	6.4
		March 97	19.5	6.70	189	118	12.1	0.9	3.3
		December 96	12.0	6.70	294	80	9.9	0.6	3.1
	9st	July 97	32.2	7.14	*	194	15.0	2.7	7.1
		October 96	14.2	7.50	*	162	15.1	3.4	9.1
		March 97	19.0	7.10	165	132	13.0	0.3	5.1
		December 96	10.0	6.72	263	72	9.8	0.9	3.0
	11st	July 97	28.3	7.07	*	244	21.4	1.6	7.0
		October 96	13.0	6.50	355	58	7.4	0.6	2.3
		March 97	24.0	7.30	171	130	12.9	0.3	4.0
		December 96	12.0	6.80	259	75	10.4	0.9	3.2
Ba–Pb–Zn	2st	July 97	29.2	7.12	*	764	57.1	16.4	34.4
		October 96	16.7	7.50	*	620	75.3	20.1	39.7
		March 97	12.8	7.50	173	294	30.3	8.7	18.9
		December 96	11.5	7.40	281	800	77.2	35.0	90.4
	3st	July 97	30.7	8.00	*	196	18.2	9.6	5.4
		October 96	18.4	7.55	*	175	13.9	8.1	15.5
		March 97	18.0	7.20	177	70	6.9	0.8	4.4
		December 96	6.0	6.60	271	22	6.8	0.9	1.8
	4st	July 97	22.5	7.55	*	47	5.7	1.3	0.5
		October 96	16.7	5.95	*	51	6.5	1.8	0.9
		March 97	17.0	5.60	210	35	5.1	1.4	0.5
		December 96	10.5	5.20	296	30	5.1	3.5	0.6
	5st	July 97	28.6	7.88	*	111	5.5	2.3	5.0
		October 96	16.5	8.25	*	181	8.3	6.4	12.5
		March 97	20.0	7.20	178	61	3.6	1.3	3.7
		December 96	11.0	6.80	283	32	3.8	1.6	2.4
	6st	July 97	*	*	*	*	13.8	22.3	10.8
		October 96	16.1	5.90	*	279	22.0	25.3	7.8
		March 97	20.0	6.80	180	55	3.8	2.7	3.4
		December 96	10.0	6.50	308	40	3.1	1.7	1.9
	7st	July 97	26.6	6.85	*	345	28.6	1.8	11.1
		October 96	14.6	7.35	*	280	29.0	1.7	7.8
		March 97	20.0	7.40	168	165	16.5	0.4	6.6
		December 96	7.5	7.10	284	180	19.2	1.8	12.5
	8st	July 97	25.6	7.08	*	328	24.2	3.8	1.3
		October 96	15.8	7.40	*	236	23.6	2.9	11.0
		March 97	24.0	7.80	128	121	12.5	0.3	3.5
		December 96	9.0	6.90	286	62	9.5	0.5	2.4
	VMAh		25.0	9.5		400	150	12	100
	VMRr		**	**		**	**	**	**

| Mg (mg/l)	As (mg/l)	Fe (mg/l)	Mn (mg/l)	Ba (mg/l)	HCO_3^- (mg/l)	Cl^- (mg/l)	SO_4^{2-} (mg/l)	NO_3^- (mg/l)	Dry residue (mg/l)
11.6	0.081	3.69	0.57	*	73.1	11.4	34.9	0.48	181.0
12.1	0.409	5.76	0.52	0.12	77.6	12.6	34.5	0.30	190.9
12.1	0.130	5.35	0.62	*	73.2	10.0	39.7	0.21	175.2
11.9	0.490	5.60	0.68	*	74.8	12.7	39.8	0.11	167.1
17.5	1.111	0.62	0.33	*	115.8	17.1	40.8	0.77	218.3
17.8	0.636	4.80	0.45	0.09	101.6	13.5	57.4	1.30	236.1
15.0	0.326	4.38	0.15	*	90.0	10.5	50.2	0.33	208.7
14.2	1.190	5.94	0.63	*	88.8	11.7	43.2	0.10	192.4
7.5	0.122	4.20	0.22	*	58.3	17.1	10.9	0.95	117.4
8.8	0.082	2.10	0.37	–	41.6	14.5	34.9	6.00	132.7
5.3	0.007	0.44	0.18	*	30.8	10.4	17.8	0.36	89.1
4.7	0.015	0.12	0.02	*	22.4	10.5	14.3	4.95	100.4
8.8	0.011	0.54	0.12	*	58.3	17.1	20.9	0.61	125.9
10.0	0.039	0.43	0.06	0.11	52.4	19.7	25.9	3.10	155.7
7.0	0.002	0.13	–	*	40.4	8.3	24.8	0.68	90.2
3.8	0.001	0.21	–	*	19.2	8.7	16.2	4.32	89.8
4.1	0.047	3.41	0.41	*	50.3	28.5	18.4	0.67	173.8
3.2	0.002	0.43	–	–	15.2	9.1	10.5	4.00	69.0
5.4	0.003	–	–	*	32.0	7.8	22.6	0.11	80.1
4.2	0.001	0.33	0.05	*	26.4	9.2	16.3	2.12	77.1
29.4	0.040	1.84	1.03	*	155.7	102.4	54.7	0.70	460.7
34.0	0.006	0.21	0.06	0.10	87.2	163.0	116.9	7.00	560.2
15.0	0.003	–	0.03	*	78.0	57.7	43.6	47.65	253.5
28.9	0.056	–	–	*	171.2	160.1	85.4	173.00	772.5
7.8	0.045	2.12	0.27	*	79.9	18.6	4.1	0.61	157.3
8.8	0.012	1.26	0.50	0.22	107.2	16.0	9.9	1.30	149.7
3.1	0.002	0.35	0.05	*	38.2	3.0	9.0	0.19	83.9
1.2	–	0.17	–	*	14.0	3.9	9.0	0.38	62.2
0.7	–	0.14	0.17	*	5.6	5.3	5.7	0.26	38.5
1.3	0.004	1.22	1.27	0.41	7.2	9.9	11.0	1.10	59.0
0.8	–	0.26	0.05	*	4.8	3.2	8.6	0.79	83.9
1.1	0.002	0.37	0.16	*	2.6	3.9	9.2	5.23	163.0
6.5	0.005	0.33	0.20	*	58.3	5.7	2.4	0.18	83.9
13.8	0.005	0.38	0.37	1.60	130.8	8.7	5.9	0.60	141.3
3.5	–	0.31	–	*	36.0	2.0	4.0	0.32	58.4
2.5	0.001	0.37	0.07	*	24.4	2.4	4.4	0.73	68.2
6.4	0.009	9.92	1.09	*	97.4	27.3	6.2	2.56	142.9
4.2	0.001	1.24	0.77	0.20	6.0	43.9	57.9	6.40	225.8
2.1	–	1.70	0.10	*	30.0	2.7	5.3	0.68	59.7
1.1	–	0.53	0.07	*	16.4	3.4	0.8	0.49	67.7
17.6	0.051	2.77	1.35	*	97.8	31.3	34.8	0.20	211.3
18.7	0.008	0.32	0.18	0.07	44.0	35.6	87.1	0.10	241.7
8.8	0.006	0.09	–	*	45.2	10.6	35.4	0.33	128.8
12.6	0.012	0.08	–	*	48.0	21.9	34.1	23.48	198.0
17.1	0.050	2.97	0.19	*	94.2	14.2	60.1	0.50	283.1
16.6	0.017	0.67	–	0.09	70.8	20.4	69.1	0.60	216.7
4.8	0.002	0.04	–	*	33.2	4.4	23.1	0.13	90.1
3.5	0.001	0.33	–	*	21.2	8.4	11.8	5.62	79.5
50	0.050	0.20	0.05	0.001	**	25.0	250.0	**	1500.0
**	0.100	5.00	0.20	**	**	70	575.0	50.00	**
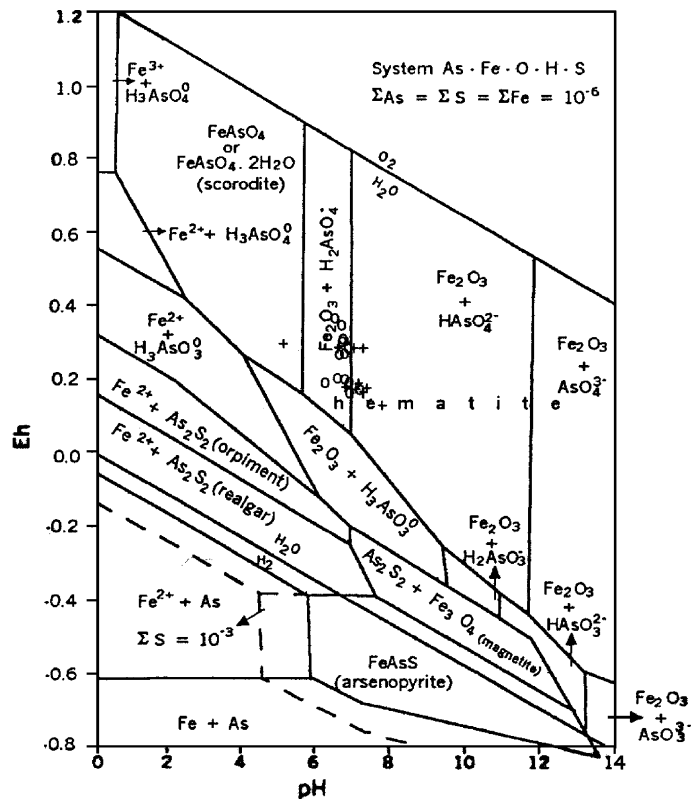
Fig. 6. Plot of water samples from Segura on the Eh–pH diagram for the system As–Fe–O–H–S (Vink, 1996). Symbols: water samples associated with O—Sn–W quartz veins, +—Ba–Pb–Zn quartz veins.

plot mainly in the $Fe_2O_3 + HAsO_4^{2-}$ field because commonly they have the highest pH values. Therefore, arsenopyrite and scorodite are not stable at Eh and pH values of the water samples from Segura. Arsenopyrite of Sn–W quartz veins was oxidized and scorodite precipitated as found (Table 3). There was dissolution of some arsenopyrite and scorodite from these veins and arsenopyrite and mimelite from Ba–Pb–Zn quartz veins, mine tailings and waste heaps. The waters associated with the Sn–W quartz veins and As anomalies in soils have higher As contents than the waters associated with the Ba–Pb–Zn quartz veins. Generally, arsenic content decreases in waters from springs to wells and to streams associated with

Sn–W quartz veins with increase in oxidizing Eh values (Table 5) because As is easily adsorbed by Fe oxyhydroxides at relatively high Eh values (Nickson et al., 2000).

The waters with the highest As concentrations also have high Fe and Mn contents (Table 5), but correlations are poor because the largest Fe and Mn concentrations were found in waters associated with Ba–Pb–Zn quartz veins, while the highest As concentration was found in waters associated with Sn–W quartz veins. The poor correlation between As and Fe was also found by Nickson et al. (2000). The highest Fe content may also have been derived by dissolution of pyrite, which is more abundant than arsenopyrite in
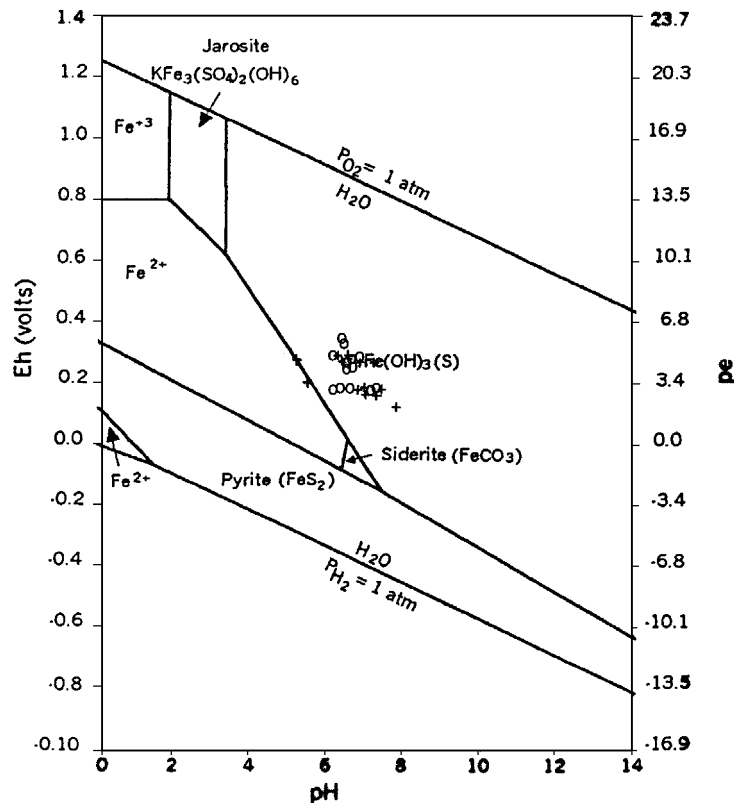
Fig. 7. Plot of water samples from Segura on the Eh–pH diagram for iron species (Deutsch, 1997). Symbols as in Fig. 6.

these veins. Most of the water samples from Segura plot in the Fe(OH)$_3$ field (Fig. 7). Therefore, precipitation of Fe(OH)$_3$ seems to control the Fe concentration.

The highest Ba content of 1.6 mg l^{-1} (Table 5) was found in water samples 4 and 5, which are close to a quartz vein with barite, galena and sphalerite cutting the schist–metagraywacke complex. Barium content is low because barite has a low solubility at neutral to alkaline pH conditions (Appelo and Postma, 1993). However, these samples have the lowest pH (5.20), specific conductance and ionic concentration (Table 5).

Sn, B, Cu and Pb were not detected in waters from Segura (Antunes, 1999), but they were found in stream sediments and soils (Table 4), which may be explained by their low solubility in water. Their contents in stream sediments and soils probably result

mainly by erosion of cassiterite, tourmaline, chalcopyrite and galena (Table 3) from mineralized quartz veins. Anglesite, mimetite and kintoreite were found in Ba–Pb–Zn quartz veins (Table 4) as alteration products of galena, but they are anhydrous.

The pH of the analyzed waters ranges between 5.20 and 8.25 (Table 5) and, consequently, there is no significant acid drainage associated with the old mine workings at Segura, which is generally responsible for problems of water pollution associated with other mine tailings (Bell, 1998). Commonly, sulphide minerals react with oxygen and water to form sulfuric acid, which reduces the pH of the system and causes dissolution of metallic compounds and, consequently, large metal concentrations. However, it will not occur if the sulphide minerals are nonreactive or if the rock contains materials to neutralize the acidity and pH values of water may be near neutral (Bell, 1998). The

Sn−W quartz veins and Ba−Pb−Zn quartz veins from Segura are small and contain some sulphides. These veins mainly intersect the schist−metagraywacke complex containing marble intercalations, which probably neutralized acid waters derived from reaction with sulphide minerals and, consequently, the metal concentration is relatively low as found in others (Rahn et al., 1996).

Generally, the waters from wells and streams have lower concentrations of As, Fe and Mn during winter than during summer, which may be due to dilution effect. However, waters from springs have generally higher concentrations of As, Fe and Mn during winter than during summer, which may be due to the higher volume of infiltrated water, which promotes chemical dissolution of ore minerals. Generally, waters should not be used for human consumption and agriculture due to their As, Fe and Mn concentrations (Table 5).

5. Conclusions

(1) At Segura, there are granitic pegmatite veins containing cassiterite and lepidolite, quartz veins with cassiterite and wolframite and quartz veins with barite, galena and sphalerite which fill late- to post-tectonic Hercynian faults, cutting the Cambrian schist−metagraywacke complex and Hercynian granites.

(2) Cassiterite from Li-bearing granitic pegmatite veins from Segura is zoned and darker zones have Nb>Ta and Mn>Fe and are richer in Nb and Ta than lighter zones. The darker zones show exsolutions of manganocolumbite.

(3) Cassiterite from Sn−W quartz veins is unzoned, does not show any exsolutions and is richer in Ti and poorer in Nb and Nb + Ta than cassiterite from Li-bearing granitic pegmatite veins.

(4) Single crystals of wolframite from Sn−W quartz veins at Segura have a dominant ferberite component.

(5) At Segura, the Sn−W quartz veins contain sulphides (pyrrhotite, arsenopyrite, pyrite, sphalerite, chalcopyrite and stannite) and sulphosalts (matildite and schapbachite), while the sulphides found in the Ba−Pb−Zn quartz veins are cobaltite, pyrite, sphalerite, chalcopyrite and galena. Arsenopyrite is locally altered to scorodite, while anglesite, mimetite and kintoreite are associated with the galena alteration.

(6) Sphalerite from Ba−Pb−Zn quartz veins is richer in Zn and poorer in Fe than sphalerite from Sn−W quartz veins. Chalcopyrite from Ba−Pb−Zn quartz veins has more Cu and Fe than chalcopyrite from Sn−W quartz veins.

(7) The Ba−Pb−Zn quartz veins from Segura contain 20−30% of barite, which has a homogeneous composition and only up to 1.82 wt.% of SrO.

(8) In parent rocks, Sn, W, Cu and Zn occur in micas and Ba and Pb are retained in K-feldspar and micas. In waste heaps, mine tailings and stream sediments, Sn and W are mainly concentrated in cassiterite and wolframite, respectively, B is retained in tourmaline, As is concentrated in arsenopyrite, Cu and Zn are retained in chalcopyrite, Zn, Pb and Ba are concentrated in sphalerite, galena and barite, respectively.

(9) Stream sediments and soils from Segura are generally enriched in metals with respect to parent granite and schist.

(10) The Sn, W, B, As and Cu anomalies in stream sediments and soils at Segura are mainly associated with quartz veins containing cassiterite and wolframite and old mining activity on them.

(11) At Segura, the Ba, Pb and Zn anomalies in stream sediments and soils are related to quartz veins with barite, galena and sphalerite and old mining activity on them.

(12) The mechanical process was the most important for Sn, W and B in stream sediments and soils, which are sinks of metals. The abandoned mines increased the mobility of trace elements from mineralized veins to soils, stream sediments and water.

(13) Trace element contents decrease from soils to stream sediments and to water due to their relatively low mobility, particularly shown by the absence of Sn, B, Cu and Pb in waters.

(14) At Segura, there is no significant acid drainage associated with old mine workings, which is mainly attributed to the marble intercalations in the schist−metagraywacke that neutralized the acid waters due to reaction of sulphides with water and oxygen.

(15) Soils must not be used for agriculture and human residences due to the large content in Sn, B, As and Ba and As concentration forbids to use them even for industrial settings.

(16) At Segura, waters associated with Sn−W quartz veins and As anomalies in soils are the richest in As, but there is a decrease in As content in waters

from springs, well and streams with increase in Eh values.

(17) The richest waters in Fe and Mn are related to the Ba–Pb–Zn quartz veins. Waters associated with the mineralized veins and old mining activities at Segura have As, Fe and Mn concentrations, which forbid their use for human consumption and agriculture.

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References

Allen, S.K., Allen, J.M., Lucas, S., 1996. Concentrations of contaminants in surface water samples collected in west-central Indiana impacted by acidic mine drainage. Environ. Geol. 27, 34–37.

Antunes, I.M.H.R. 1999. The impact of abandoned mines on the environment at Segura (central Portugal). MSc thesis. University of Coimbra, Portugal, 162 pp.

Appelo, C.A.J., Postma, D., 1993. Geochemistry, Groundwater and Pollution. A.A. Balkema, Rotterdam, pp. 485–502.

Bell, F.G., 1998. Environmental Geology—Principles and Practice. Blackwell Science, Oxford, pp. 415–458.

Boulet, M.P., Larocque, A.C.L., 1998. A comparative mineralogical and geochemical study of sulphide mine tailings at two sites in New Mexico, USA. Environ. Geol. 33, 130–142.

Brooks, R.R., 1972. Geobotany and Biogeochemistry in Mineral Exploration. Harper and Row, New York, 290 pp.

Canadian Council of Ministers of the Environment, 1991. Interim Canadian environmental quality criteria for contaminated sites. CCME EPC-CS34, 1–20, Manitoba.

Deutsch, W.J., 1997. Groundwater Geochemistry, Fundamentals and Applications to Contamination Lewis Publishers, Boca Raton.

Instituto Geológico e Mineiro, 1988. Reports from a prospecting project for tungsten, tin and associated minerals from Góis–Segura. Metallic Mineral Prospecting Section. Oporto, Portugal, 10 pp.

Marszalek, H., Wasik, M., 2000. Influence of arsenic-bearing gold deposits on water quality in Zloty Stok mining area (SW Poland). Environ. Geol. 39, 888–892.

Neiva, A.M.R., Neiva, J.M.C., Silva, M.M.V.G., 1990. Geochemistry of gold quartz veins walls from Jales (northern Portugal). Chem. Geol. 82, 217–251.

Neiva, A.M.R., Silva, M.M.V.G., Antunes, I.M.H.R., Ramos, J.M.F., 2001. Phosphate minerals of some granitic rocks and associated quartz veins from northern and central Portugal. J. Czech. Geol. Soc. 46, 35–43.

Nickson, R.T., McArthur, J.M., Ravenscroft, P., Burgess, W.G., Ahmed, K.M., 2000. Mechanism of arsenic release to groundwater, Bangladesh and West Bengal. Appl. Geochem. 15, 403–413.

Portuguese law, 1998. Decree No. 236/98—Portuguese Legislation on Water Quality. I-A, 980–1024, Portugal.

Rahn, P.H., Davis, A.D., Webb, C.J., Nichols, A.D., 1996. Water quality impacts from mining in the Black Hills, South Dakota, USA. Environ. Geol. 27, 38–53.

Rösner, U., 1998. Effects of historical mining activities on surface water and groundwater—an example from northwest Arizona. Environ. Geol. 33, 224–230.

Vink, B.W., 1996. Stability relations of antimony and arsenic compounds in the light of revised and extended Eh–pH diagrams. Chem. Geol. 130, 21–30.