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Environmental mineralogy and geochemistry of Pb–Zn mine wastes, Northern Tunisia

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Abstract Fine-grained waste materials in the former Pb–Zn mining district of Northern Tunisia contain environmentally significant amounts of potentially toxic elements (PTE), such as Zn (6.9–13.7 g kg^{-1}), Pb (2.9–9.6 g kg^{-1}), Cd (31–106 mg kg^{-1}), As (180–837 mg kg^{-1}), and Sb (1–102 mg kg^{-1}). Mineralogical studies identified as PTE carriers' primary sulfides (galena, sphalerite, pyrite, chalcopyrite, and arsenopyrite) and sulfosalts (jordanite), and secondary oxidized minerals (cerussite and smithsonite), accompanied by sulfates (gypsum and barite), calcite, and minor clay minerals. Leaching tests with deionized water indicate a near-neutral reaction, accompanied by a comparatively high release of PTE (As 16–58.5 μg L^{-1} and Sb 1.5–60 μg L^{-1}), (Pb 222–1130 μg L^{-1}, Zn 4865–15,665 μg L^{-1}, and Cd 4–25 μg L^{-1}), and sulfate (3690–22,070 mg L^{-1}). These values are well above the recommended WHO limits for drinking waters. Therefore, these wastes represent a potential threat for the environment, and should be adequately monitored/ reclaimed.

Keywords Mine tailings · Neutral reaction · Leaching tests · PTE · Northern Tunisia

1 Introduction

Mining activity in Tunisia started with Carthaginians and Romans (Sainfeld 1952). About 600 mineral occurrences are known in the Northern part of the country; about 50 deposits were exploited, mainly from the end of the nineteenth century. The main deposits are hosted within upper cretaceous to tertiary sedimentary rocks, and consist of veins, impregnations, and replacement masses. The element association includes Pb–Zn–Fe–Ba–F, with subordinate Cd, As, Sb, and others; gangue minerals include calcite and clays. Total production adds up to 55 Mt Fe ore, 2.3 Mt Pb ore, and 2 Mt Zn ore (DGM 2005).

After mine closure, several million tonnes of flotation tailings remain confined within dams. They still contain environmentally significant amounts of potentially toxic elements (PTE), and represent a potential hazard to human health, being located close to human settlements and amidst farming lands. Several studies were devoted to the environmental aspects of these tailings (Souissi et al. 2008, 2013, 2015; Chakroun et al. 2013; Othmani et al.

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2013, 2014, 2015; Daldoul et al. 2015), but comparatively little attention was paid to semimetals, such as As and Sb. These highly toxic elements might be overlooked in mining areas, where they were not the main object of exploitation, but quite often they are of relevance for the environmental impact (e.g., Benzaazoua 1996; Casiot et al. 2007; Ashley et al. 2007; Razo et al. 2004; De Gregori et al. 2003; Hiller et al. 2012; Souissi et al. 2008, 2013).

This study deals with the former Pb–Zn mining sites of Jalta (Ja, 1903–1951), Jebel Hallouf-Sidi Bouaouane (JH-SBA, 1892–1986), and Touiref (TO, 1891–1959), located in Northern Tunisia (Fig. 1). The area is characterized by a temperate, sub humid climate [annual rainfall ranging from 333 to 1011 mm for the decade 2001–2010, with minimum in July (2–8 mm) and maximum in January (76–117 mm); average monthly temperatures from 8 to 11 °C in December through February, to 27–28 °C in July–August; INM 2011].

Ore deposits were dominated by Pb–Zn–Ba–F concentrations, hosted mainly in carbonate (limestone and dolostone) rocks, which may locally be accompanied by lesser amounts of silica, clay, gypsum, and others. Ores were extracted in open pits or underground workings. Ore processing was first based on gravimetric separation and then on flotation techniques. The latter gave rise to most of the mine tailings as they are known today, because large amounts of the former gravimetry tailings were reprocessed by flotation.

This paper reports the results of a mineralogical and geochemical study of flotation tailings at these sites. The mobility of heavy metals (Zn, Pb, and Cd) and semi-metals (As and Sb) is estimated by a static leaching test in deionized water, simulating the interaction of wastes with rain and/or surface water. The results contribute to a full assessment of environmental hazards associated with abandoned mine wastes in carbonate settings of Northern Tunisia. We emphasize the attention given to the semi-metals As and Sb.

2 Materials and methods

2.1 Sampling

As specified in Table 1, several samples of 2 kg each were collected at regular intervals from a total of nine sampling points in tailing dams of the three localities.

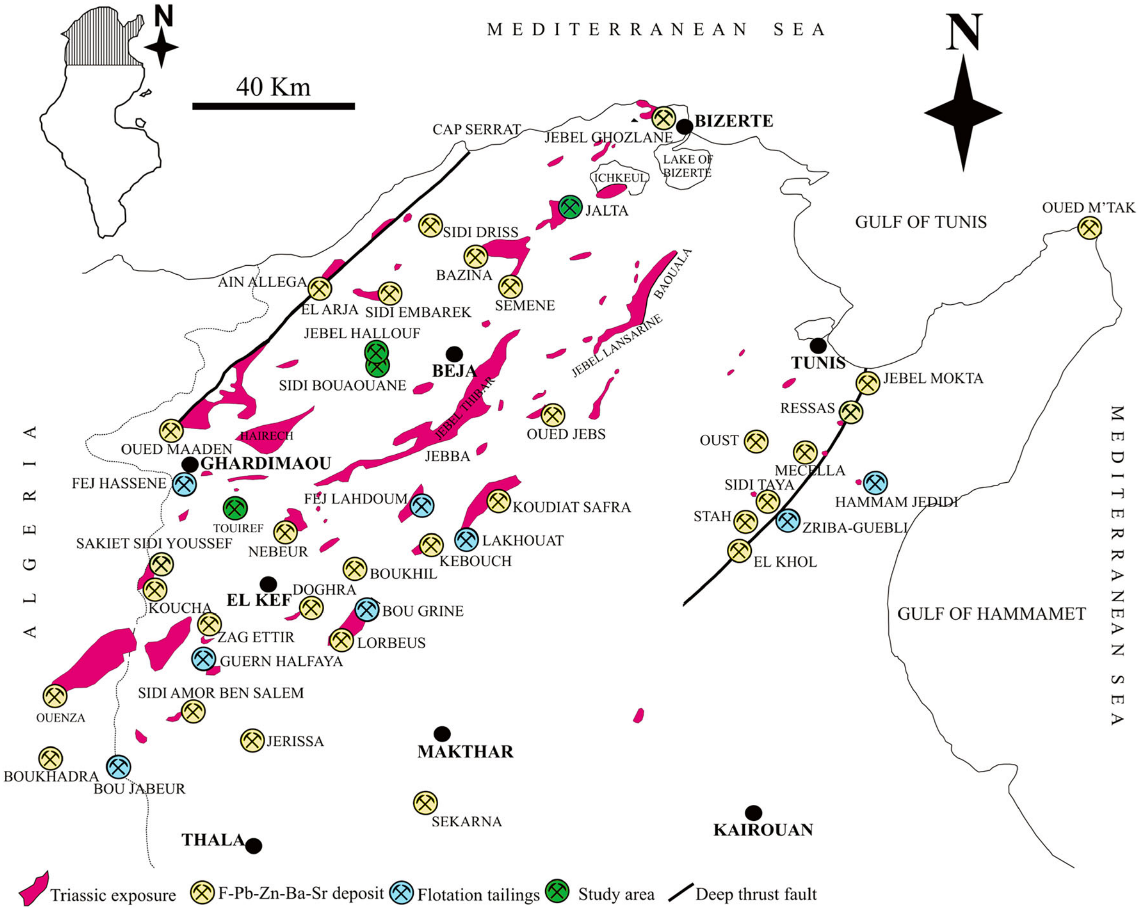

Fig. 1 Location map of the study area [adapted from Sainfeld (1952); Perthuisot (1978), by Souissi et al. (2013)]

Table 1 Characteristics of the studied samples

Mine site	Sample location	Sampling depth	Number of sampling points	d_{50} (μm)	Label
Jebel Hallouf	Slope of dam I	30 cm	12	31.6	JHD1
	Slope of dam II	30 cm	11	19.5	JHD2
	Drill core on top of dam I	0–575 cm	5	116.9	JHC
Sidi Bouaouane	Dam slope	30 cm	9	149.8	SB
Touiref	Trench	0–3.80 cm (oxidized zone)	12	120.6	ZO
		3.80–5.40 cm (transition zone)	4	160.7	ZT
		5.40–6.60 cm (sulfide zone)	11	169.7	ZF
	Dam slope	30 cm	15	119.1	TO
Jalta	Dam slope	30 cm	13	161.2	JA

Most samples were taken at 30 cm depth; however, at Touiref, it was possible to take samples at different depths corresponding to visual changes in the appearance of the material, indicating the transition from a yellowish oxidized zone (ZO) to an intermediate yellowish-grey zone (ZT) to a dark grey sulfide-bearing zone (ZS). At Jebel Hallouf, in addition to the surficial (30 cm) samples, it was possible to drill a core down to a depth of 5.75 m. Because of macroscopic homogeneity in texture and colour, five subsamples were collected from this core at ~1 m intervals, and combined into a single sample. In the laboratory, samples were dried first in open air and then in oven (45 °C for 24 h). Samples of each sampling point were then carefully mixed, homogenized, and quartered, to obtain one representative sample for each sampling point. This sampling strategy, dictated by practical limitations of the following analytical steps, does not allow recognition of subtle field scale variations, but gives for each sampling site an estimate of the overall characteristics and potential impact.

Grain-size analysis, performed at INRAP (Sidi Thabet, Tunisia) by means of a Mastersizer 2000 laser instrument, pointed out the fine-grained nature of all materials (see below); all subsequent analyses were performed on aliquots of the bulk homogenized samples, with no size distinction.

2.2 Analytical methods

Mineralogical analyses (X-ray power diffraction) were performed at the University of Cagliari by means of a Panalytical X'pert Pro instrument, and complemented by scanning electron microscopy (SEM) observation with semi-quantitative EDS microanalysis at MEMA (University of Firenze, Italy; ZEISS EVO instrument with Oxford Linkam microanalysis). Chemical analyses for major elements were performed by X-ray fluorescence (Rigaku Primus II spectrometer, CRIST, University of Firenze; raw data correction by an in-house standardless ab initio procedure). The procedure is optimized for ordinary rocks, and it is not well suited for samples with unusual composition, such as mine tailings. Moreover, while most major elements are conventionally reported as oxides, for others, there is indetermination on the chemical state (e.g., sulfur occurs both as sulfide and as sulfate). For these reasons, major element analysis is affected by an uncertainty that was estimated in the order of 10–20%.

The loss on ignition (LOI) was based on differential thermal analysis in a muffle furnace. Tailing samples begin to lose volatiles at about 110 °C; the devolatilization process was complete at about 950 °C. Calculation of LOI is based on the difference in weight of sample before and after ignition.

For an accurate determination of selected trace elements (Zn, Pb, Cd, As, and Sb) at the University of Cagliari, samples were first reacted in a microwave oven (Milestone ETHOS 1) with an HNO_3–H_2O_2–HF mixture. The resulting solutions were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES; ARL Fisons 3520B instrument); the reproducibility of analysis was checked by running several duplicates and the accuracy by analysis of the certified standard SRM 2710. Both reproducibility and accuracy are within 5%.

In the absence of a specific Tunisian regulation, leaching tests were performed according to Italian environmental law (DL 152/2006). The test is based on the UNI 10802 (2013; www.uni.com) procedure, and consists in the static treatment for 24 h by deionized water of the material (solid/liquid ratio 1:10) under agitation at 150 RPM. The leachates were analyzed by ICP-OES for Zn, Pb, and Cd, and by ICP mass spectrometry (ICP-MS; Perkin Elmer ELAN DRC-e instrument) for As and Sb.

3 Results and discussion

3.1 Grain-size distribution

As previously mentioned, all collected materials are fine-grained (100% <2 mm; >85% <0.5 mm). Specifically, the mean diameters (d_{50}) are comprised between 19.5 and 169.7 µm (Table 1); the dominant fraction can be classified as either fine sand or very fine sand, except two samples from Jebel Hallouf–Sidi Bouaouane, where the main fraction can be described as clayey silt. The fine-grained nature of these tailings testifies to a protracted grinding procedure to achieve the best liberation of the economic phases. On the other hand, this fine-grained size enhances the reactivity of the tailings, favoring the mobility of PTE (see Brill and Floc'h 2001).

3.2 Mineralogy

Table 2 shows the mineralogical composition of the nine samples as a result of the XRD patterns and SEM–EDS observations. In all samples, calcite is the most abundant mineral, in agreement with the calcareous nature of the host rocks. Primary sulfides, especially arsenopyrite and sphalerite, are always present, whereas galena and pyrite are comparatively less widespread. The widespread occurrence of jordanite, $Pb_{14}(As, Sb)_6S_{23}$, is remarkable. The mineral was identified both by the presence of its strongest reflection ($d = 2.24$ Å) in the XRD patterns, and by semiquantitative SEM–EDS microanalyses. Jordanite had previously been reported in these deposits by Rouvier (1971); Jemmali et al. (2011, 2013, 2014), and Souissi et al. (2013).

Secondary minerals are represented mainly by carbonates (cerussite and smithsonite) and gypsum, but we point out the presence of mimetite, $Pb_5(AsO_4)_3Cl$, and Sb oxides evidenced by SEM images (Fig. 2e). In the Touiref samples collected at different depths, described as "oxidized", "intermediate", and "sulfide", there are no significant changes in the overall mineralogical composition, except for the presence of galena limited to the "sulfide" zone. Figure 2 reports some SEM photomicrographs portraying the occurrence and textural relationships of some of the observed minerals.

3.3 Tailing composition

The major element contents of the studied samples are reported in Table 3. The analyses, showing the dominance of Ca (38–52%), an important loss on ignition (LOI; 25–40%), and a subordinate presence of Si, Al, Fe, and Mg are in agreement with mineralogical studies (abundance of calcite, minor quartz, Fe-oxyhydroxides, dolomite, and traces of silicates). Table 3 also includes the contents in heavy metals (Pb, Zn, and Cd) and semimetals (As and Sb) in the tailings. The contents of these elements are consistently of the same orders of magnitude in all samples, with just moderate differences among different localities: values for Pb, As, and Sb are higher at Jebel Hallouf and Sidi Bouaouane; this last deposit also shows, along with Touiref, the highest contents of Zn and Cd.

The abundance of Zn (6.9–13.7 g kg^{-1}) and Pb (2.9–9.6 g kg^{-1}) corresponds to the presence of sphalerite, smithsonite, galena, and cerussite; some Pb also occurs in jordanite and mimetite. These last two minerals are probably

Table 2 Results of the XRD semi-quantitative analysis

Mineral	Samples								
	JA	JHD1	JHD2	JHC	SB	ZF	ZT	ZO	TO
Calcite	+++	+++	+++	+++	+++	+++	+++	+++	+++
Dolomite	+	−	−	−	−	+	+	+	+
Ankérite	+	−	−	−	−	+	+	+	+
Cerussite	+	+	+	+	+	+	+	+	+
Smithsonite	+	−	−	−	−	+	+	+	+
Galena	+	−	−	−	−	+	−	−	−
Sphalerite	++	++	++	++	++	++	++	++	++
Pyrite	+	+	+	−	−	+	+	+	+
Arsenopyrite	++	++	++	++	++	++	++	++	++
Realgar	−	−	−	−	−	−	++	−	+
Jordanite	+	++	++	+	++	+	+	+	+
Gypsum	++	++	++	++	++	−	+	+	+
Barite	++	−	−	−	−	−	−	−	−
Quartz	++	++	++	++	++	++	++	++	++
Kaolinite	+	−	+	+	−	−	−	−	−
Illite	+	−	−	−	−	−	−	−	−
Mimetite	++	++	++	++	++	++	++	++	++
Iron oxyhydroxides	++	++	++	++	++	++	++	++	++

+++ abundant, ++ present, + trace, − not detected

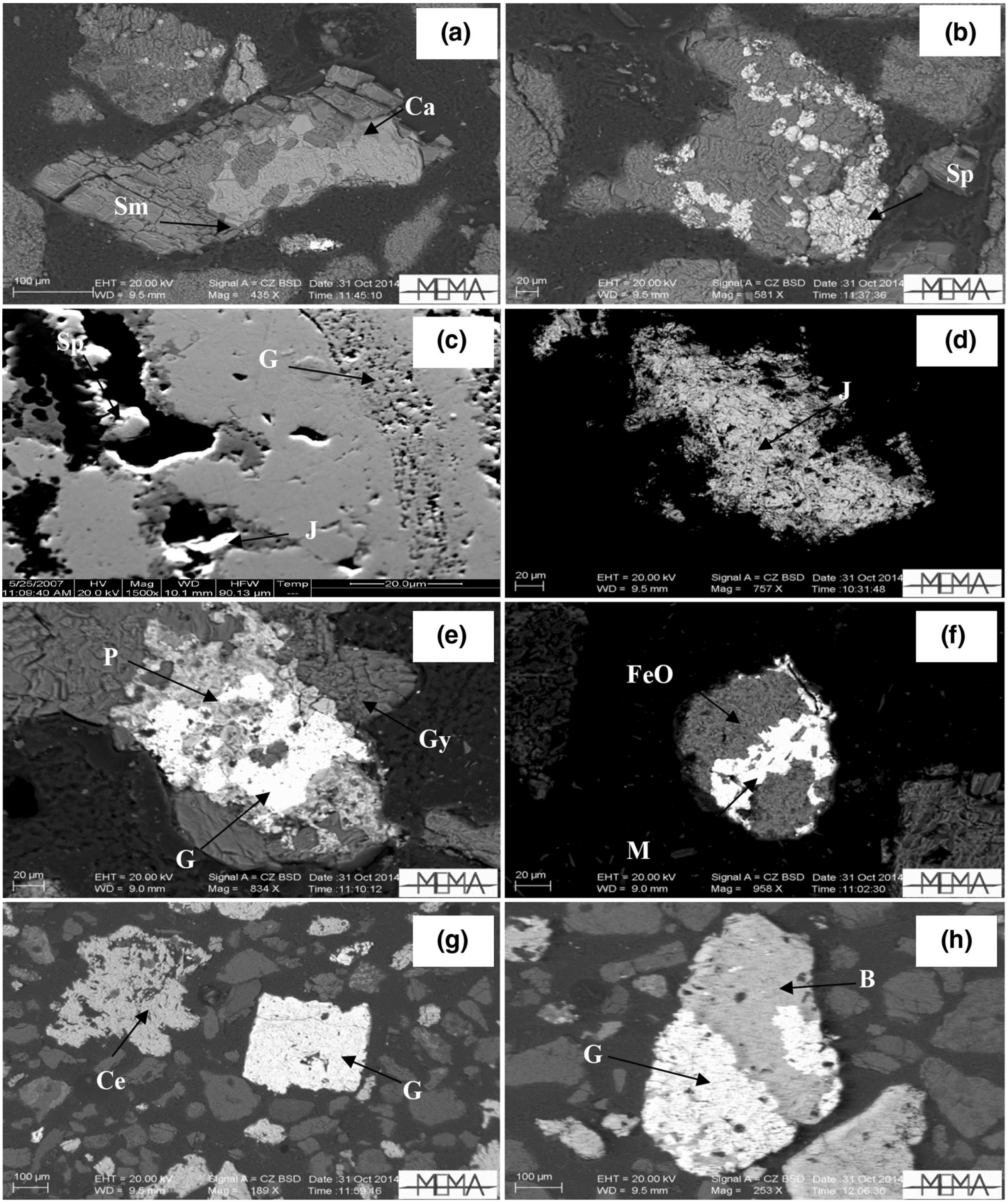

Fig. 2 SEM photomicrographs of flotation tailings from the study areas. *Sample TO* **a** smithsonite (Sm) grains in a gangue of calcite (Ca); **b** sphalerite (Sp); and **c** associated grains of galena (G), sphalerite (Sp), and jordanite (J). *Sample JHD1* **d** jordanite; notice the dark rim of (presumably) Sb-oxides **e** associated grains of galena (G), gypsum (Gy), and pyrite (P); **f** associated mimetite (M) and iron oxyhydroxides (FeO). *Sample JA* **g** galena (G) and cerussite (Ce); **h** grain with associated galena (G) and barite (B)

Table 3 Major and trace element contents of the representative tailing samples

	JA	JHD1	JHD2	JHC	SB	ZF	ZT	ZO	TO	Crustal abundance	Italian limits
Contents of trace elements (mg kg^{-1})											
Pb	5290	8070	9630	9580	8620	3190	2900	4540	4520	100	1000
Zn	8280	6900	7610	7380	13,000	13,670	11,600	13,440	11,780	79	1500
Cd	58	55	59	31	84	91	106	102	99	0.15	15
As	383	657	837	468	670	139	192	233	180	2.1	50
Sb	1	102	97	nd	93	<0.4	<0.4	<0.4	4	0.20	30
Contents of major elements (%)											
CaO	38.17	47.22	47	46.89	47	51.74	51.7	51.34	50.15		
SiO_2	12.23	5.06	5.12	6.65	7.89	3.45	2.87	2.64	3.97		
Fe_2O_3	6.31	6.11	6.45	5.39	4.22	1.61	1.44	1.95	1.61		
Al_2O_3	4.5	2.31	2.18	2.5	3.01	0.9	0.72	0.69	1.2		
MgO	1.65	0.12	0.1	0.12	0.15	0.64	0.55	0.41	0.69		
P_2O_5	0.16	0.06	0.06	0.05	0.04	0.09	0.08	0.06	0.09		
K_2O	0.71	0.19	0.09	0.15	0.25	0.06	0.05	0.04	0.07		
SrO	1.53	0.22	0.11	0.18	0.11	0.08	0.08	0.09	0.09		
BaO	4.96	0.46	0.39	0.18	0.11	<0.01	<0.01	<0.01	<0.01		
S	1.86	0.49	0.58	0.62	1.1	0.4	0.27	0.26	0.33		
LOI*	25.48	35.68	35.17	34.94	33.76	38.64	40.08	40.32	39.6		
Total	98.91	99.42	98.97	99.36	99.55	99.30	99.29	99.60	99.43		

Na_2O and TiO_2 were always <0.1%

nd not determined

* Loss on ignition

also the main carriers of arsenic (139–837 mg kg^{-1}), as suggested by the strong positive correlation between As and Pb ($R^2 = 0.82$, $p = 0.0008$); on the other hand, As is also hosted by arsenopyrite and realgar, and probably also occurs in association with Fe oxyhydroxides; correlation between As and Fe is indeed significant ($R^2 = 0.69, p = 0.006$). Jordanite is likely the main phase hosting Sb (up to 102 mg kg^{-1}), as indicated by the strong correlation of Sb with As ($R^2 = 0.84$, $p = 0.0005$) and Pb ($R^2 = 0.93$, $p < 0.0001$), whereas Cd (31–106 mg kg^{-1}) most probably substitutes for Zn in its minerals (as shown, for this district, by Souissi 1987, 2007; Ghorbel et al. 2010). This idea is reinforced by the high degree of positive correlation between Zn and Cd ($R^2 = 0.75$, $p = 0.003$).

These contents of potentially toxic elements (PTE) are obviously several orders of magnitude higher than average crustal abundances 6, and also exceed the limits established by many countries for soils (Table 3 reports the Italian limits for industrial soils as defined by DL152/2006).

3.4 Leaching tests

The composition of the solutions obtained from the leaching tests is reported in Table 4.

As expected from the calcite-dominated mineralogy, the pH of the leachates is subalkaline (7.6–8.0). The quality of leachates is otherwise rather poor if compared with international standards for waters. All relevant chemical parameters exceed the limits recommended for drinking water by the World Health Organization (WHO 2011), and most values also exceed the limits established by many countries for wastewater discharge (Table 3 reports the Italian limits according to DL152/2006).

In general, there is no correlation at a significant level ($p > 0.05$) between total contents of the elements in the solid wastes and corresponding contents in the leachates, i.e., the mobile fraction is different from one sample to another. The only exception is for Sb. For the five samples, where Sb concentrations in the leachates could be measured, there is a significant correlation ($R^2 = 0.95$, $p = 0.005$) between Sb contents in the leachates and in the solid wastes, in agreement with the dominance in all samples of a single Sb-hosting phase (jordanite).

The considered elements show different degrees of mobility in the conditions of the test. This difference can be quantified by introducing a parameter M defined as the ratio between the concentration of the element (in mg kg^{-1}) in the solid and that (in g L^{-1}) in the corresponding leachate; the lower the value of M, the more mobile the element (for the specific test conditions).

From Table 5, it can be seen that mobility of Zn and Sb is higher than that of As, Cd, and Pb. The difference between

Table 4 Composition of the solutions obtained from the leaching tests

Samples	pH	As (μg L^{-1})	Sb (μg L^{-1})	Pb (μg L^{-1})	Cd (μg L^{-1})	Zn (μg L^{-1})	SO_4^{2-} (mg L^{-1})
JA	7.8	16	2	1130	25	14,300	16,050
JHD1	7.7	43	62	730	13	12,605	11,970
JHD2	7.7	38	60	822	14	14,465	8160
JHC	7.7	48	nd	795	10	15,665	19,030
SB	7.6	59	43	874	23	24,245	22,070
ZF	8.0	27	nd	362	3	4865	4980
ZT	7.9	21	nd	222	4	7210	3690
ZO	7.7	16	nd	419	11	13,900	11,070
TO	7.5	35	10	730	7	13,000	8970
Limits WHO		10	20	10	3	3000	500
Italian limits	5.5–9.5	500	nd	200	20	500	1000

nd not determined

Table 5 Mobility ratio (*M*: see text for definition) for the analyzed PTE

	As	Pb	Cd	Zn	Sb
JA	23.94	4.68	2.32	1.73	0.67
JHD1	15.46	11.06	4.40	1.83	1.65
JHD2	22.03	11.71	4.21	1.90	1.62
JHC	9.85	12.05	3.10	2.12	nd
SB	11.45	9.86	3.73	1.87	2.16
ZF	5.25	8.81	36.40	0.36	nd
ZT	9.14	13.06	26.50	0.62	nd
ZO	14.56	10.83	9.27	1.03	nd
TO	5.14	6.18	14.14	1.10	0.40

nd not determined

the two groups (Zn–Sb vs. As–Cd–Pb) is statistically significant (Mann–Whitney *U* test, $p < 0.01$), whereas intragroup (i.e., Zn vs. Sb, and As vs. Cd and Pb) differences are not significant ($p > 0.05$). A high mobility of Zn compared to Pb, and a comparatively high mobility of semimetals, that at subalkaline pH dominantly occurs in anionic form, is a typical feature of net alkaline mine drainages (NAMD). On the other hand, Cd is less mobile than Zn, in spite of the similar geochemical behavior of the two elements, and of a strong correlation ($R^2 = 0.86$, $p = 0.0005$) between their contents in the leachates. This mobility difference was observed in other systems (e.g., Frau et al. 2015), and was ascribed to the occurrence of highly soluble secondary Zn sulfates, whereas Cd preferentially occurs in comparatively less soluble minerals, such as carbonates (e.g., Lattanzi et al. 1998). Indeed, the correlation between Zn and sulfate in the leachates is significant ($R^2 = 0.79$, $p = 0.002$); the occurrence of comparatively soluble sulfates (including gypsum) in tailings is demonstrated by the high amount of sulfates in the leachates.

In our samples, arsenic is apparently less mobile than Sb. In mine environments, As may be less or more mobile than Sb depending on the specific conditions (e.g., Ashley et al. 2003; Casiot et al. 2007), even if a higher mobility of As is more commonly reported (e.g., Flynn et al. 2003; Ettler et al. 2010; Majzlan et al. 2011). Both As and Sb can be, at least temporarily, adsorbed onto secondary Fe-oxy-hydroxides, but this mechanism seems more effective for Sb than for As (Majzlan et al. 2011). In their study of materials from the Hillgrove mine, New South Wales, Ashley et al. (2003) found that in stream sediments, mobility of Sb is higher than that of As, whereas leaching of stibnite ore concentrate released Sb and As in ratios consistent with those in the starting solid. The authors suggested that Sb mobility is essentially controlled by the rapid formation of secondary Sb oxides. In our case, we can speculate that As mobility is comparatively low, because much of this element is either still contained in primary arsenopyrite, or else it occurs in an insoluble phase, such as mimetite. This low mobility of a toxic element, such as As, is obviously good news, but, while mimetite can be considered a long-term storage of this element (e.g., Flis et al. 2011), oxidation of arsenopyrite may eventually release As into the environment, and should be monitored.

Considering the tailings of Touiref, it is possible to follow the behavior of PTE in depth according to the different zones (oxidized zone, intermediate zone, and sulfide or fresh zone). Results show (Table 5) that As and Zn have the same geochemical behavior: their mobility increases gradually with depth to reach the mobility ratio $M = 5.25$ and $M = 0.36$, respectively, in the fresh zone, while the mobility of Cd decreases with depth. The variation of Pb mobility is irregular; the highest mobility is recorded within the fresh zone.

4 Conclusions

Fine-grained waste materials in the former Pb–Zn mining districts of Northern Tunisia contain environmentally significant amounts of potentially toxic elements (PTE), such as Zn, Pb, Cd, As, and Sb. Mineralogical studies identified as PTE carriers' primary sulfides (galena, sphalerite, pyrite, chalcopyrite, and arsenopyrite) and sulfosalts (jordanite), and secondary oxidized minerals (cerussite, smithsonite, and Sb-oxides), accompanied by calcite, sulfates (gypsum and barite), and clay minerals. Because of the fine-grained nature of wastes, wind deflation and/or runoff may represent non-negligible pathways for PTE dispersion.

Leaching tests with deionized water indicate a near-neutral reaction, accompanied by a comparatively high release of PTE. These values are well above the recommended WHO limits for drinking waters, and suggest that interaction with rain and/or surface waters will produce contaminated drainage downstream mine. A specific risk is the mobilization, at the beginning of the rainy season, of comparatively soluble salts accumulated during the dry season (see Canovas et al. 2010). Moreover, the mobility of As, which is currently comparatively low, might increase in the long term because of oxidation of residual arsenopyrite.

Therefore, these wastes represent a potential threat for the environment and for the nearby human settlements. An adequate monitoring plan is advisable to exactly quantify the actual impact on environment and health. The results of monitoring could indicate the appropriate remediation measures to be undertaken.

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References

Ashley PM, Craw D, Graham BP, Chappell DA (2003) Environmental mobility of antimony around mesothermal stibnite deposits, New South Wales, Australia and southern New Zealand. J Geochem Explor 77:1–14

Ashley PM, Graham B, Tighe M, Wolfenden BJ (2007) Antimony and arsenic dispersion in the Macleay River catchment, New SouthWales, Australia: a study of the environmental geochemical consequences. Aust J Earth Sci 54(1):83–103

Benzaazoua M (1996) Caractérisation physico-chimique et minéralogique de produits miniers sulfurés en vue de la réduction de leur toxicité et de leur valorisation. Thèse de doctorat. Université de Lorraine. Laboratoire "Environnement et Minéralurgie" U.R.A. n 235 du C.N.R.S. Ecole Nationale Supérieure de Géologie Nancy

Brill H, Floc'h JP (2001) Le devenir des métaux provenant des anciennes mines: l'exemple du massif central français. Université de Limoges, Article paru en 2001 dans la revue. "Géologues" publiée par l'Union française des Géologues 130/131:233–241

Canovas CR, Olias M, Nieto JM, Galvan L (2010) Wash-out processes of evaporitic sulfate salts in the Tinto river: hydrogeochemical evolution and environmental impact. Appl Geochem 25:288–301

Casiot C, Ujevic M, Munoz M, Seidel JL, Elbaz-Poulichet F (2007) Antimony and arsenic mobility in a creek draining an antimony mine abandoned 85 years ago (upper Orb basin, France). Appl Geochem 22:788–798

Chakroun HD, Souissi F, Souissi R, Bouchardon JL, Moutte J, Abdeljaoued S (2013) Heavy metals distribution and mobility in flotation tailings and agricultural soils near the abandoned Pb-Zn district of Jebel Hallouf-Sidi Bouaouane (NW Tunisia). Carpath J Earth Environ Sci 8:249–263

Daldoul G, Souissi R, Souissi F, Jemmali N, Chakroun HK (2015) Assessment and mobility of heavy metals in carbonated soils contaminated by old mine tailings in North Tunisia. J Afr Earth Sci 110:150–159

De Gregori I, Fuentes E, Rojas M, Pinochet H, Potin-Gautier M (2003) Monitoring of copper, arsenic and antimony levels in agricultural soils impacted and non-impacted by mining activities, from three regions in Chile. J Environ Monit 5(2):287–295

DGM (Direction Générale des Mines) (2005) Annuaire statistique, mines et dérivés. Ministère de l'industrie (1997-2005), Tunis, p 30

Ettler V, Tejnecký V, Mihaljevič M, Šebek O, Zuna M, Vaněk A (2010) Antimony mobility in lead smelter-polluted soils. Geoderma 155:409–418

Flis J, Manecki M, Bajda T (2011) Solubility of pyromorphite $Pb_5(PO_4)_3Cl$-mimetite $Pb_5(AsO_4)_3Cl$ solid solution series. Geochim Cosmochim Acta 75:1858–1868

Flynn HC, Meharg AA, Bowyer PK, Paton GI (2003) Antimony bioavailability in mine soils. Environ Pollut 124:93–100

Frau F, Medas D, Da Pelo S, Wanty R, Cidu R (2015) Environmental effects on the aquatic system and metal discharge to the Mediterranean Sea from a near-neutral zinc-ferrous sulfate mine drainage. Water Air Soil Pollut 226:55

Ghorbel M, Munoz M, Courjault-Rade P, De Strigneville C, De Parseval P, Souissi R, Souissi F, Ben Mammou A, Abdeljaouad S (2010) Health risk assessment for human exposure by direct ingestion of Pb, Cd, Zn bearing dust in the former miners village of Jebel Ressas (NE Tunisia). Eur J Mineral 22:639–649

Hiller E, Lalinská B, Chovan M, Jurkovic L, Klimko T, Jankulár M, Hovoric R, Šottník P, Fľaková RZ, Ženišová Z, Ondrejková I (2012) Arsenic and antimony contamination of waters, stream sediments and soils in the vicinity of abandoned antimony mines in the Western Carpathians, Slovakia. Appl Geochem 27(3):598–614

INM (Institut National de la Météorologie) (2011) Archive des données de pluviométrie, température, évaporation et vent de la région de Bizerte, Jendouba et Kef. Website: http://www.meteo.tn/. Accessed Dec 2011

Jemmali N, Souissi F, Villa IM, Vennemann TW (2011) Ore genesis of Pb–Zn deposits in the Nappe zone of Northern Tunisia: constraints from Pb–S–C–O isotopic systems. Ore Geol Rev 40(1):41–53

Jemmali N, Souissi F, Carranza EJM, Bouabdellah M (2013) Lead and sulfur isotope constraints on the genesis of the polymetallic mineralization at Oued Maden, Jebel Hallouf and Fedj Hassene carbonate-hosted Pb–Zn (As–Cu–Hg–Sb) deposits, Northern Tunisia. J Geochem Explor 132:6–14

Jemmali N, Souissi F, Carranza EJM, Vennemann TW, Bogdanov K (2014) Geochemical constraints on the genesis of the Pb–Zn deposit of Jalta (northern Tunisia): implications for timing of mineralization, sources of metals and relationship to the neogene volcanism. Chemie der Erde Geochem 74(4):601–613

Lattanzi P, Zuddas P, Frau F (1998) Otavite from Montevecchio, Sardinia, Italy. Mineral Mag 62:367–370

Majzlan J, Lalinska B, Chovan M, Blass U, Brechet B, Gottilicher J, Steininger R, Hug K, ziegler S, gescHer J (2011) A mineralogical, geochemical, and microbiogical assessment of the antimony—and arsenic-rich neutral mine drainage tailings near Pezinok, Slovakia. Am Mineral 96(1):1–13

Othmani MA, Souissi F, Benzaazoua M, Bouzahzah H, Bussiere B, Mansouri A (2013) The geochemical behaviour of mine tailings from the Touiref Pb–Zn District in Tunisia in weathering cells leaching tests. Mine Water Environ 32:28–41

Othmani MA, Souissi F, Bouzahzah H, Bussière B, Ferreira da Silva E, Benzaazoua M (2014) The flotation tailings of the former Pb–Zn mine of Touiref (NW Tunisia): mineralogy, mine drainage prediction, base-metal speciation assessment and geochemical modeling. Environ Sci Pollut Res 22(4):2877–2890

Othmani MA, Souissi F, Ferreira da Silva E, Coynel A (2015) Accumulation trends of metal contamination in sediments of the former Pb–Zn mining district of Touiref (NW Tunisia). J Afr Earth Sci 111:231–243

Perthuisot V (1978) Dynamique et pétrogenèse des extrusions triasiques en Tunisie septentrionale. Thèse PhD, Travaux du Laboratoire de Géologie, 12, Presse de l'Ecole Normale Supérieure de Paris, France

Razo I, Carrizales L, Castro J, Díaz Barriga F, Monroy M (2004) Arsenic and heavy metal pollution of soil, water and sediments in a semi-arid climate mining area in Mexico. Water Air Soil Pollut 152:129–152

Rouvier H (1971) Minéralisations plombo-zincifères et phénomène karstique Exemple tunisien: le gisement du Djebel Hallouf. Miner Depos Springer 6(3):196–208

Sainfeld P (1952) Les gites plombo zincifères de la Tunisie. Annales des mines et de la géologie N 9. Imprimerie S.E.F.A.N, Tunis. p 285

Souissi F (1987) Etude gîtologique et conditions de formation des gisements de fluorine (Pb–Zn–Ba) du Jebel Zaghouan (J. Stah et Sidi Taya) et du Jebel Oust, Tunisie nordorientale. Thèse Université Paul Sabatier, Toulouse III, France p 220

Souissi F (2007) Minéralogie et géochimie des gîtes minéraux et leur impact sur l'environnement. Mémoire d'Habilitation Universitaire en géologie, Université de Tunis el Manar, Faculté des sciences de Tunis, Département de géologie, p 77

Souissi F, Souissi R, Bouchardon JL, Moutte J, Munoz M, Chakroun HK, Othmani MA, Ghorbel M (2008) Mineralogical and geochemical characterization of mine tailings and the effect of Pb, Zn, Cd and Cu mobility on the quality of soils and stream sediments in Northern Tunisia. International Congress of Solid Waste Management and Sustainable Development, TUNISIA Book of Abstracts 313–317

Souissi R, Souissi F, Chakroun HK, Bouchardon JL (2013) Mineralogical and geochemical characterization of mine tailings and Pb, Zn, and Cd mobility in a carbonate setting (Northern Tunisia). Mine Water Environ 32:16–27

Souissi R, Souissi F, Ghorbel M, Munoz M, Courjault-Radé P (2015) Mobility of Pb, Zn and Cd in a soil developed on a carbonated bedrock in a semi-arid climate and contaminated by Pb–Zn tailing, Jebel Ressas (NE Tunisia). Environ Earth Sci 73(7):3501–3512

World Health Organization (WHO) (2011) Guidelines for drinking water-quality, 4th edn. Switzerland, Geneva, p 564