THE ABANDONED COPPER-MINE OF FUNTANA RAMINOSA (SARDINIA): PRELIMINARY EVALUATION OF ITS IMPACT ON THE AQUATIC SYSTEM

Rosa Cidu and Luca Mereu
Department of Earth Sciences, Via Trentino 51, 09127 Cagliari, Italy

Abstract

Copper-lead deposits at Funtana Raminosa in Central Sardinia were exploited mostly underground since 1917. Flotation tailings were dumped nearby the mine plant. Mining operations ceased in 1987; the mine drainage observed later from several galleries was circumneutral, due to the availability of carbonate minerals able to buffer the acidy produced by the oxidation of Fe-bearing sulphides. The chemistry of mine waters was characterized by dissolved SO_4, F, Zn, Cd, Pb, Mn and Mo contents higher than those observed in uncontaminated spring and stream waters in the area. Drainage from the oldest flotation tailings showed concentrations of Zn, Cd and Pb much lower than those generally observed in mine waters. Drainage from the recent flotation tailings had the highest SO_4, Zn and Cd dissolved contents (1600, 30 and 0.8 mg/L, respectively) when sampled in the dry season. In the Rio Saraxinus, a stream that drains the whole mining area, the water showed a relatively low level of contamination (concentrations of 170 μg/L Zn, 7 μg/L Cd and 0.9 μg/L Pb).

Introduction

The Funtana Raminosa area has been an important mining site for copper exploitation since the Bronze age. It is located in Central Sardinia (Fig. 1) and is part of the Sardinian Geomining Park (*Parco Geominerario Storico e Ambientale della Sardegna*). Geological setting consists of Palaeozoic volcano-sedimentary sequences affected by low-grade metamorphic processes (metavolcanic rocks, quartzite, metasandstone, metalimestone and black shale; Carmignani et al., 2001). Hercynian post-orogenic subvolcanic events caused transformations of country rocks; the main products were quartz-feldspatic hornfels in terrigenous units, and garnet-pyroxene skarn in carbonate sequences; later hydrothermal alteration produced hydrothermalite rocks consisting mainly of chlorite, epidote, quartz and calcite (Protano et al., 1996). Small outcrops of Jurassic carbonate rocks and Recent covers occur in the study area. Ore deposits are generally hosted in hydrothermalite rocks, with minor occurrence in skarn (Garbarino et al., 1984; Protano et al., 1996). Veins of Cu-Pb ores were exploited intensively from 1917 to 1983. Among a large variety of minerals (Stara et al., 1999), including the rare mineral creedite (Frau et al., 1998), the main exploited minerals were chalcopyrite, galena and sphalerite.

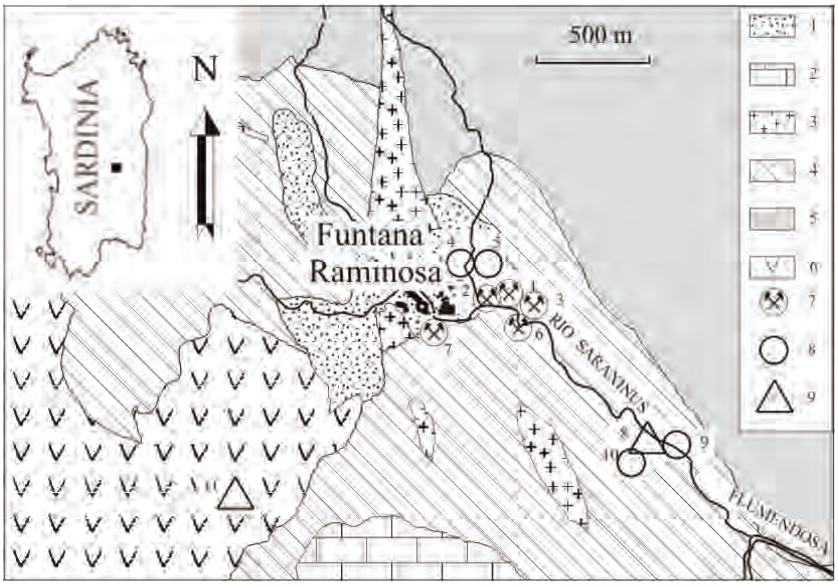

Figure 1. Schematic geology at Funtana Raminosa and locations of water samples. Legend. 1= Recent sediments; 2= Jurassic carbonate rocks; 3= Subvolcanic rocks (Permo-Trias); 4= Silurian-Devonian black shale and metacarbonate hosting ore-bearing horizon; 5= Metasandstone, quartzite, phyllite (Barbagia Metamorphic Complex); 6= Middle Ordovician metavolcanic rocks ; 7= Mine water samples; 8= Spring and stream water samples; 9= Tailings drainages.

The mine was closed in 1987. Flotation tailings were left nearby. The Tialesi tailings were dumped from 1970 to 1980, downstream of the mine plant at about 400 m a.s.l. (close to No. 8 in Fig. 1); while the Taccu Zippiri tailings were dumped in 1982-1983 upstream of the mine plant, about 700 m a.s.l. (close to No. 11 in Fig. 1).

The study area has a semi-humid climate, with dry summers and rainfall variable from year to year, mostly occurring from November to April. Data of precipitation and temperature collected from 1922 to 1992 at stations close to the study area show a mean annual precipitation of 790 mm, and a mean annual temperature of 14 °C (R.A.S., 1998). The elevation of mined areas ranges between 600 and 400 m a.s.l.; the flotation plant was located at 430 m a.s.l.

Spring waters are scanty and usually have low flow (<0.5 L/s). The Rio Saraxinus stream, the only perennial stream in the area, is a tributary of the Flumendosa river. The Flumendosa system, comprising several reservoirs, supplies water for domestic and irrigation uses to a large part of population in Southern Sardinia. This water resource needs to be protected from potential contamination, therefore, a hydrogeochemical survey was carried out to evaluate the impact of past mining at Funtana Raminosa on the aquatic system. Preliminary results are reported here.

Methods

Water sampling was carried out in September 2004 at the end of the dry season under low-flow conditions. Waters sampled out of the mines comprise one spring (No. 5) and three streams (Rio Brebegargiu No. 4, Rio Sarraxinus No. 9, Rio Tialesi No. 10); the latter is the only water flowing outside of the mineralized area. Five samples are waters collected inside the mine (Brebegargiu No. 1, Yvonne No. 6, Ribasso VI No. 7) or at the outflow of galleries (S. Eugenio No. 2, Galleria Romana No. 3). Two samples drain flotation tailings, the old ones at Tialesi (No. 8) and those more recent at Taccu Zippiri (No. 11). The tailings drainage No. 11 was sampled again in September 2005 under low-flow condition, and in February 2006 under high flow condition. The location of water samples is shown in Figure 1.

At the sampling site, temperature, pH, redox potential (Eh) by platinum electrode, conductivity and alkalinity were measured; water samples were filtered (0.4 µm) and acidified with HNO_3 for cation analyses. Anions were determined by ionic chromatography, major cations by ICP-OES and trace elements by ICP-MS (Perkin Elmer Elan5000, REE by ElanDRC). An aliquot of filtered sample was acidified with HCl for the determination of As and Sb by on-line hydride generation ICP-MS. Dissolved components refer to concentrations measured in the filtered sample. The ionic balance was always less than 5%; both precision and accuracy were estimated at ≤10% by analyses of randomly duplicate samples and standard reference solutions (NIST1643 d, e).

Table 1. Physical and chemical parameters and major ions dissolved in waters at Funtana Raminosa.

No.	Date	Flow	T	Eh	pH	Cond	Ca	Mg	Na	K	HCO_3	Cl	SO_4	F
		L/s	°C	mV		mS/cm	mg/L							
spring														
5	Sept.04	0.10	16	470	7.2	0.62	72	16	35	3.1	143	68	75	0.8
streams														
4	Sept.04	0.01	17	470	8.0	0.63	82	14	27	2.8	148	36	120	2.0
9	Sept.04	100	16	470	8.0	0.63	80	18	29	2.7	179	45	102	0.8
10	Sept.04	0.05	24	450	7.8	0.63	80	30	24	3.9	326	40	37	0.4
mine waters														
1	Sept.04	0.10	15	470	7.6	0.83	47	7.8	103	8.6	182	44	160	4.3
2	Sept.04	0.33	17	490	8.0	1.08	150	40	27	3.0	210	41	330	1.7
3	Sept.04	0.08	16	510	7.8	1.57	235	41	54	4.5	99	25	760	2.3
6	Sept.04	1	16	490	7.5	0.58	67	17	30	3.0	145	39	110	1.3
7	Sept.04	0.1	18	460	7.8	0.70	91	15	38	3.6	159	34	170	1.6
tailings drainages														
8	Sept.04	0.1	16	480	7.8	1.01	150	38	27	2.8	360	39	200	0.5
11	Sept.04	0.03	18	580	7.2	2.64	515	43	44	9.1	104	20	1590	2.1
11	Sept.05	0.04	12	510	7.1	2.53	600	48	43	10	75	19	1680	2.7
11	Feb.06	2	10	460	7.2	0.17	12	3.3	14	1.7	25	26	22	0.3

Results and Discussion

The physical-chemical characters and the major dissolved components in waters sampled at Funtana Raminosa are reported in Table 1. Waters have low flow, except the Rio Sarraxinus No. 9 that is the larger stream in the area. The water temperature reflected the air temperature during the sampling seasons.

The pH was neutral or slightly alkaline (7.1-8.0), which was consistent with the large availability of carbonate minerals in the area. The redox potential values (Eh ranged from 450 to 580 mV) indicated oxidising conditions. The conductivity was <0.7 mS/cm in spring and streams; it increased in mine drainages; the highest values were observed in waters draining the tailings No. 11. Dissolved Ca was the dominant cation, except in the water No. 1 where Na prevailed; Ca concentrations increase with increasing conductivity. Dissolved Mg, Na and K were not correlated to conductivity. Dissolved Cl was generally much lower than HCO_3 and SO_4. Figure 2 shows that spring and stream waters had a prevalent bicarbonate component, while some drainages from mines and tailings had a dominant sulphate component. Dissolved SO_4 increased with increasing salinity (Fig. 2b). Since Ca was the dominant cation (see Table 1), two groups of waters can be distinguished, namely Ca-HCO_3 at low salinity and Ca-SO_4 at higher salinity. The former group comprises waters related to a circulation in carbonate-bearing formations; the latter consists of waters interacting with sulphide-bearing materials (ore minerals and tailings). All waters were at equilibrium or supersaturated with respect to calcite, while gypsum equilibrium was only observed in the water No. 11.

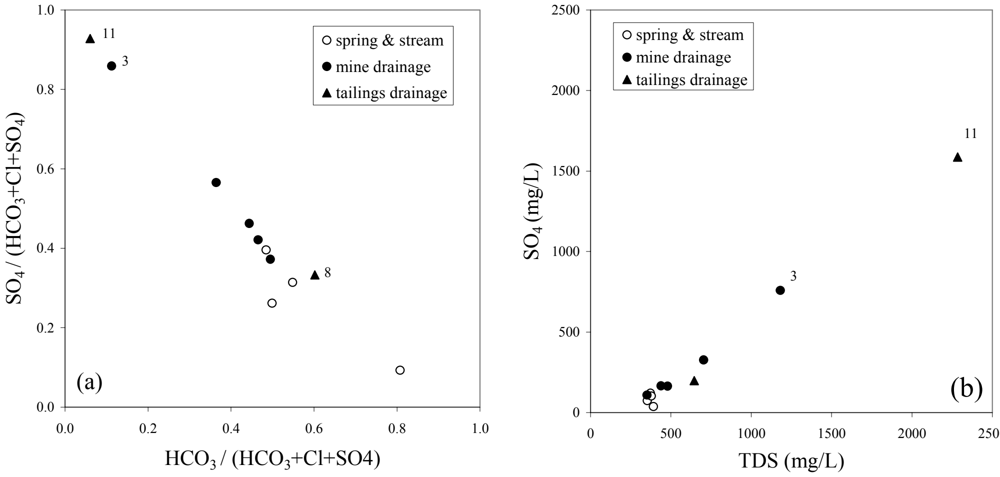

Figure 2. Dissolved bicarbonate versus sulphate, both normalized to the sum of major anions (a), and sulphate versus total dissolved solids, TDS (b).

Data reported in Table 1 also show that dissolved F was high in many waters (F > 1 mg/L); F concentrations increase as dissolved SO_4 increases; all mine waters and the tailings drainage No. 11 are at equilibrium or slightly supersaturated with respect to fluorite. The high values of F in these waters are consistent with the occurrence of fluorite in the ore mineral assemblage and host rocks. Previous studies had already showed that dissolved F, combined with dissolved SO_4, was an efficient hydrogeochemical indicator in the prospecting of sulphide deposits hosted in Palaeozoic formations of Central Sardinia (Bertorino et al., 1987).

Considering other analyzed components (not reported in Table 1 and 2), SiO_2 (9 to 16 mg/L) and NO_3 (1 to 6 mg/L) did not show large differences among different water samples. Detectable PO_4 (1 mg/L) was only found in the mine water No. 1. Dissolved Sr, in the range of 100-3000 µg/L, was correlated with Ca (R^2 = 0.90). Dissolved Ba (10 to 40 µg/L) increased with increasing SO_4 until supersaturation with respect to barite was reached in the tailings drainage No. 11. Mine waters had the highest values of Li and Rb (up to 100 and 20 µg/L, respectively). Dissolved As was always <0.7 µg/L; Sb was detected (1.7 µg/L) in the mine water No. 2 only; Co, Cr and V were below the analytical detection limits (0.5, 3 and 5 µg/L, respectively). Nickel was in the range of 1 to 23 µg/L; the highest values were observed in the mine water No. 3 and in the tailings drainage No. 11. Mercury was below 0.5 µg/L, except in samples No. 1 and 11 (1.7 and 1.3 µg/L Hg, respectively).

A selection of dissolved elements, comprising the toxic heavy metals Cd and Pb and others with a potential environmental concern, is reported in Table 2. Among the water samples collected in the Funtana Raminora area, the Rio Tialesi stream No. 10 showed the lowest concentrations of Zn, Cd and Pb. Dissolved concentrations of Fe, Mn, Cu, Zn and REE in this water are close to mean values reported for worldwide rivers, while dissolved

Cd, Pb, Mo and U are significantly higher. Considering that this water does not drain the mineralized area, and taking into account the low value of dissolved SO_4, the concentrations of metals observed in the water No. 10 probably represent the background values in the area surrounding the mineral deposit. Dissolved Zn, Cd and Mo in the spring No. 5 and streams No. 4 were much higher than in worldwide rivers and one order of magnitude higher than the median values observed in Sardinian river waters (Cidu and Frau, 2007). Although these samples do not flow out of mines and flotation tailings, they reflect a circulation in the mineralized area.

Concentrations of metals in the mine waters showed large variations. The highest concentrations of Fe, Mn and Mo were observed in the mine water No. 1, the highest Cu occurred in No. 6, dissolved Zn and Cd were higher in No. 3, dissolved U was highest in No. 2 and 3, while the REE ($\sum$La-Lu) were higher in No. 6 and 7. Since pH and Eh values did not show large variations, the differences in metal contents observed in the mine waters probably reflect the large variations that occur in the ore mineral assemblage (Stara et al., 1999).

Table 2. Concentrations of Fe, Mn, Cu, Zn, Cd, Pb, Mo, U, Y and rare earth elements (REE=$\sum$La-Lu) dissolved in waters at Funtana Raminosa, and mean values in worldwide rivers.

No.	Date	Fe	Mn	Cu	Zn	Cd	Pb	Mo	U	Y	REE
		µg/L									
spring											
5	Sep.04	29	3	3.4	123	2.4	1.1	2.8	0.5	0.07	0.10
streams											
4	Sep.04	70	6	3.8	140	4.5	4.2	24	1.4	0.06	0.17
9	Sep.04	8	2	6.0	172	6.9	0.9	5.0	1.1	0.06	0.12
10	Sep.04	44	11	2.1	13	0.3	0.6	4.2	1.7	0.03	0.24
mine waters											
1	Sep.04	605	320	1.8	12	0.2	1.1	148	0.6	0.04	0.20
2	Sep.04	29	4	5.4	396	4.1	1.3	88	18	0.05	0.08
3	Sep.04	54	180	32	4600	135	7.9	35	13	0.13	0.24
6	Sep.04	27	120	172	940	24	2.3	14	1.0	0.27	1.40
7	Sep.04	43	69	3.8	27	0.9	1.5	16	2.3	0.06	1.60
tailings drainages											
8	Sep.04	15	5	41	87	1.8	0.7	4.0	1.9	0.10	0.22
11	Sep.04	16	71	13	34200	850	6.1	6.4	2.6	1.3	8.50
11	Sep.05	20	92	11	30000	760	4.6	5.5	2.5	1.1	7.50
11	Feb.06	250	18	5.0	120	1.6	5.0	0.1	0.1	0.55	3.80
worldwide rivers[a]		40	8	1.5	30	0.02	0.1	0.5	0.24	-	0.24

[a]: Chester, 1990

Concentrations of toxic elements in drainage from the oldest tailings (sample No. 8) were relatively low, i.e. Cd, Pb, Hg, As, Ni and Cr below the guidelines established by the World Health Organization for drinking water (WHO, 2006). These tailings appear to be sufficiently stabilized to minimize the release of potential contaminants to the aquatic system. In contrast, very high concentrations of Zn, Cd, Y and REE were observed in the drainage from recent flotation tailings (No. 11). The release of metals, especially Zn and Cd, from these tailings was higher under low-flow condition; the sample collected in February 2006 during the rainy season showed much lower SO_4 (Table 1), as well as Zn and Cd (Table 2) but dissolved Pb was similar to concentrations observed at low-flow. Table 2 shows that dissolved Mo in waters draining the flotation tailings is much lower than values measured in mine waters. This is consistent with the ore processing used at Funtana Raminosa where Mo was recovered in the chalcopyrite-galena-sphalerite concentrate, so that its concentration decreased in the tailings.

The Rio Saraxinus stream (sample No. 9) receives all drainages from the Funtana Raminosa mines and tailings, and can be used to estimate the influence of past mining on the local surface waters. It was sampled about 1 km far from the downstream border of the mining area, at its confluence with the Flumendosa river. At the time of sampling, i.e. under low-flow condition, concentrations of Zn and Pb in the Rio Saraxinus water were relatively low (170 and 0.9 µg/L, respectively), while dissolved Cd was 7 µg/L.

Conclusions

This study shows that mine waters and drainages from flotation tailings derived from past mining and processing at Funtana Raminosa are sources of potential contamination for the aquatic system. The recent flotation tailings showed the highest potential for the release of metals, especially Zn and Cd, to the aquatic system. High concentrations of sulphate and metals occur at near-neutral pH condition. The contaminated waters flow into the Rio Saraxinus stream; this stream is a tributary of the Flumendosa river, which is an important water resource of southern Sardinia. Sampling of the Rio Saraxinus about 1 km downstream of the mine area, before its confluence with the Flumendosa river, showed a relatively low level of contamination under low flow condition. More data are necessary to evaluate the dispersion of contaminants at Funtana Raminosa. In particular, hydrogeochemical surveys should be carried out under different seasonal condition to evaluate the overall impact of past mining on the aquatic system.

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References

Bertorino G., Caboi R., Caredda A.M., Fanfani L., Gradoli M.G., Zuddas P. (1987). Prospezione idrogeochimica mineraria nell'aria di Gadoni-Seulo (Sardegna Centrale): il significato di solfati e fluoruri disciolti. Rend. Soc. It. Miner. Petrol. 42, 47-58.

Carmignani L., Barca S., Oggiano G., Pertusati P.C., Salvadori I., Conti P., Eltrudis A., Funedda A., Pasci S. (2001). Geological map of Sardinia. Scale 1:200000. Litografia Artistica Cartografica, Firenze.

Chester R. (1990). Marine geochemistry. Unwin Hyman, London.

Cidu R., Frau F. (2007). Influence of fine particles on the concentration of trace elements in river waters. Proceedings WRI-12, July 31-August 5, 2007, Kunming, PR China. Balkema (in press).

Frau F., Rizzo R., Sabelli C. (1998). Creedite from Sardina, Italy: the first European occurrence. N. Jb. Miner. Mh. 11, 495-504.

Garbarino C., Grillo S.M., Marini C., Mazzella A., Melis F., Padalino G., Tocco S., Violo M., Maccioni M., Fiori M. (1984). The Paleozoic metallogenic epochs of the Sardinian microplate (Western Mediterranean): an attempt of synthesis on geodynamic evolution and mineralizing processes. Rend. Soc. It. Miner. Petrol. 39, 193-228.

Protano G., Riccobono F., Sabatini G. (1996). Magmatism and hydrothermal processes in the Funtana Raminosa ore district (Central Sardinia, Italy): petrographic and geochemical features. Miner. Petrogr. Acta 39, 135-158.

R.A.S. (1998). Nuovo studio dell'idrologia superficiale della Sardegna. Regione Autonoma della Sardegna, (Assessorato della Programmazione, Bilancio ed Assetto del Territorio), Ente Autonomo del Flumendosa, Cagliari.

Stara P., Rizzo R., Sabelli C., Ibba A. (1999). I minerali di Funtana Raminosa (Gadoni, Sardegna centrale). Rivista Mineralogica Italiana 1, 10-27.

WHO (2006). Guidelines for drinking water quality, 3rd edition. World Health Organization, Geneva.