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FORECASTING AND ASSESSING EUROPE'S
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WP7 Historic Mine Sites revisited

Case Study

Kirki Mines in Greece

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This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 731166





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1 INTRODUCTION

Kirki Public Mine is located in Evros and Rhodope Prefectures, Thrace. The mine site occupies an area of 118,000 km². It's the main mine site in Thrace and one of the most important ones in Northern Greece.

The 'Kirki mines' include a group of mines 20 km north of Alexandroupoli city (capital of Evros prefecture). The most important of these mines is the Agios Philippos Mine (St. Phillip Mine), also known as "Kirki mine" because of the nearby located Kirki village. Other important well-known mines in Kirki area, besides Agios Philippos, are the Aberdeen, King Arthur and Latridis mines as well as Acha Tarla and some other smaller mines.

Exploration works at Agios Filippos Pb-Zn sulfide ores date back to 1890 (under Turkish occupation). Mining activity in the mines ceased in the 1990's.

1.1 Site Location

The Kirki mine site is located in the Region of Eastern Macedonia and Thrace, Evros and Rhodope prefectures. The district is situated North of Kirki Village, East of Erimohori and about 2km West of Leptokarya and to the West reaches up Konos.

The St. Phillip Mine is located 20 km NNW of Alexandropolis, 8 km east of Sappes and 4 km north of Kirki village.

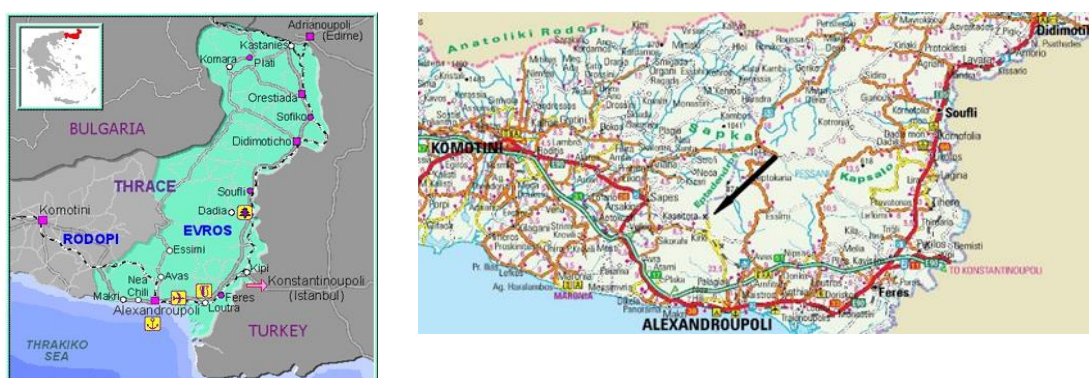


Figure 1: Location of Kirki mine sites (black arrow)

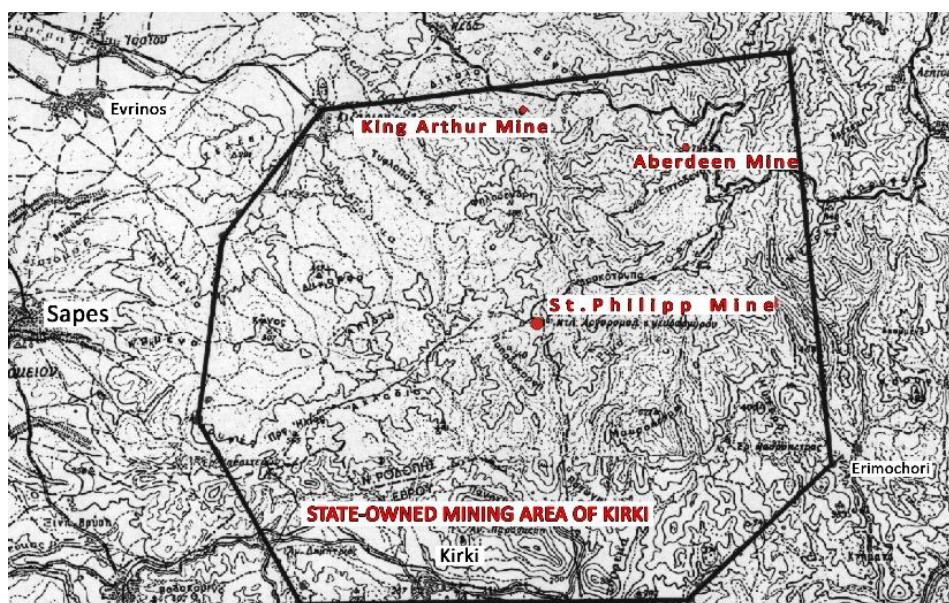


Figure 2: Historic mines in the state owned mining area

2 History of the mines

Kirki Mines belong to the Kirki-Essimi "primary" basin that was formed by intense tectonic activity during paleogen and belongs to the SW part of the metamorphic complex of Rhodope massif. Kirki mines were well known for their mixed sulfide potential.

Exploration works at Agios Filippos Pb-Zn sulfide deposit commenced in 1890. In 1932, the English mining company "Thracian Union Trust Ltd.", which gained the rights for Kirki Mine, started small scale underground exploitation resulting in the production of a total amount of 20.000 tons of ore.

In 1936 the mining rights of this company were transferred to a newly established English company named "Kirka Mines Ltd", therefore, English name are used for the new mines (St. Phillip, King Arthur, Aberdeen). The length of the newly excavated mine galleries was about 3000 m.

During World War II, the German company "Thrazische Bergwerke" carried out maintenance works in the galleries. Between 1942 and 1944 additional exploitation galleries of 3500 m length were opened (excavated), and surface facilities, such as an air cable ore transportation system, was installed. Crushing, milling, and flotation facilities were constructed at the southern slope of a hill close to Kirki village and the Alexandroupolis–Thessaloniki railway line.



Operations ceased after 1953 and restarted in 1973. Between 1973 and 1981 ore extraction was carried out with underground mining and resulted in the production of approximately 130,000 tons of ore containing 4% to 10% combined Pb and Zn content. The ore was processed by flotation for the production of galena and sphalerite concentrates which were exported to smelters in the Balkans and central European countries. (7,8,14)

After an interruption of 8 years, exploitation was resumed mainly with surface mining operations leading to the production of additional 120,000 tons of ore between 1989 and 1992 (Greek Mining Company – Evros Mine Co.). Although there were several long interruptions, ore exploitation and processing continued from 1990 to 1997 with an estimated additional extraction of 70,000 ton of sulphide ore. Since 1997 the mine has been abandoned and without any reclamation and/or rehabilitation of the afflicted area. Today it is owned by State of Greece.

The Agios Philippos mine (underground galleries and open pit) is located in a narrow valley in an area of low mountains. As mentioned before, base metal ores were extracted by underground mining and later by open-cast mining at Kirki.

Open pit exploitation took place at an elevation of +430 to +345m above sea level. The open pit has an ellipsoidal shape and covers a total surface area of approximately 4700m². A small lake, with a depth varying between 2 and 8m, fills the pit with water from rainfall and drainage. Overburden and waste rock generated by the mining operations were disposed along the bed of Kirkalon stream between elevations of +400 m and +320 m, and close to the open pit. The area disturbed by the mining operations, covers a surface of approximately 77 ha. (14)

3 Geological Setting

The Agios Filippos (Kirki) base metal and Ag mineralization is hosted by the Eocene-Oligocene rock sequences of southeast Evros county, in northeastern Greece, and is associated with orogenic calc-alkaline to shoshonitic magmatism. The high sulfidation epithermal type mineralization is developed between two sub-parallel fault zones forming the western and the eastern part of the pit. An advanced argillic alteration with alunite and pyrophyllite followed an early pervasive gray silicification of the rocks. The base metal sector has been exposed due to erosion of the upper part of the epithermal system (Skarpelis, 1999).



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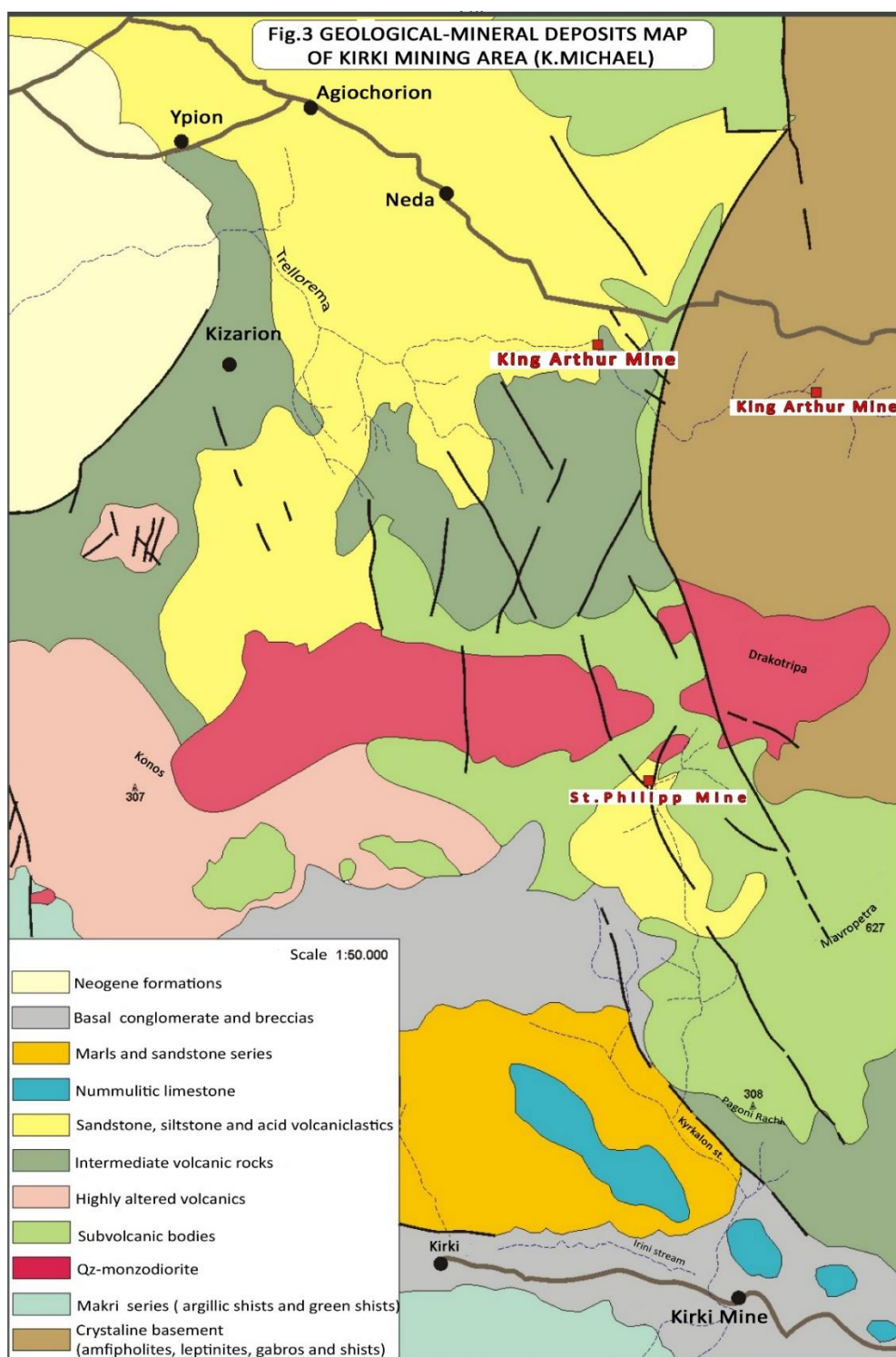


Figure 3: Geological map of “Kirki Mines” (Michael, 2003)



The regional geological structure of the broad study area (Eastern Rhodope zone) comprises three geotectonic units (Michael 2006):

- The pre-Mesozoic crystalline basement of highly metamorphic rocks (gneisses, amphibolites, marbles),
- The Mesozoic crystalline basement of metamorphic rocks (schists, marbles) and
- The Tertiary basins occupied by volcanic (andesites, dacites, rhyodacites, rhyolites, shoshonites, latites) and sedimentary rocks, intruded by granitic bodies and acid dykes.

The extensive Eocene–Oligocene magmatic activity resulted from the subduction of the African plate beneath the southern margin of the Eurasian plate and is attributed to a slab break-off mechanism.



Figure 4: Neogene banded breccio conglomerate



Figure 5: Neogene mollasic series. Alternation of silt stone, sand stone, micro-conglomerates

Molasse-type sediments are found in the north and the west, consisting of alternating layers of breccio-conglomerate, sandstones, shales and marls with a thin lignite horizon. Flysch formations also occur in the northwestern part of the area, consisting mainly of sandstone and shale with minor intercalations of micro-breccias. There is relatively little tectonic structure, with only a few vertical normal faults and very wide joint sets.



As shown on the geological map, the northern parts are covered by alluvial deposits, consisting of silty sands with gravels and recent loose deposits along the stream beds. Various mining wastes, including tailings pond materials and stock piles of unprocessed ore, have been placed on the underlying tertiary clastic basin deposits and on the late Holocene colluvial deposits.

Part of the study area is covered by alluvial deposits, consisting of silty sands with gravels and recent loose deposits along the stream beds.

The main minerals phases of Agios Philippos mine according to Dimou (2005) are shown in table 19.

Table 1: The main minerals phases of Agios Philippos mine according to Dimou (2005)

Mineral	Chemical formula	Remarks
Pyrite	FeS_2	on surface and in depth
Sphalerite	ZnS	high Mn content
Wurtzite	$(\text{Zn}, \text{Fe})\text{S}$	high, sometimes higher than sphalerite
Galena	PbS	frequently altered to cerussite
Kirkiite	$\text{Pb}_{10}\text{Bi}_3\text{As}_3\text{S}_{17}$	very similar to galena- higher than galena content occasionally
Iordanite and Bi-iordanite	$\text{Pb}_{14}\text{As}_6\text{S}_{23}$ $\text{Pb}_{14}\text{BiAs}_5\text{S}_{23}$	Abundant – often more than galena
Tennandite	$\text{Cu}_{12}\text{As}_{14}\text{S}_{13}$	increases in depth
Costerite	$\text{Cu}_2\text{ZnSnS}_4$	only in drill core samples
Chalkopyrite	CuFeS_2	minor
Markasite	FeS_2	
Bismouthinite	Bi_2S_3 (drill core samples)	
Cozalite	$\text{Pb}_2\text{Bi}_2\text{S}_5$	
Enargite	Cu_3AsS_4 (galena inclusion)	
Louzonite	Cu_3AsS_4	



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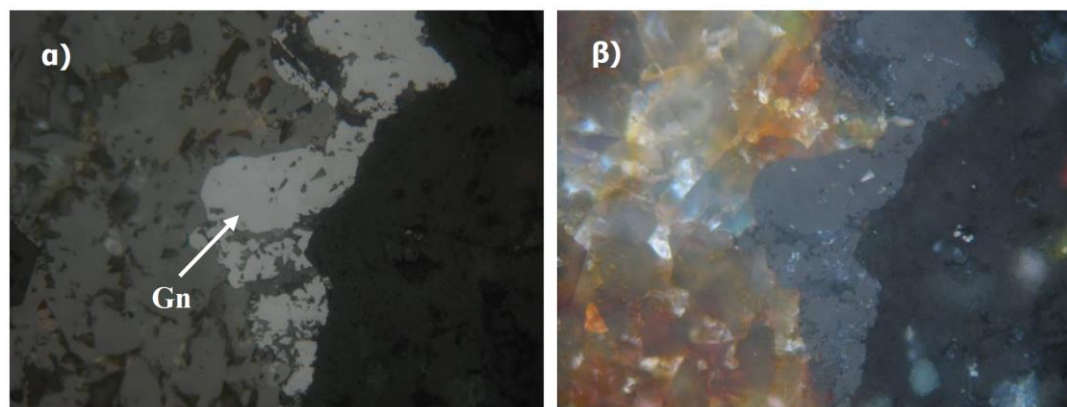


Figure 6: Scattered mineralization of Galena (optical microscopy -transmitted light polarised and not) of sample KI - 43 (19)

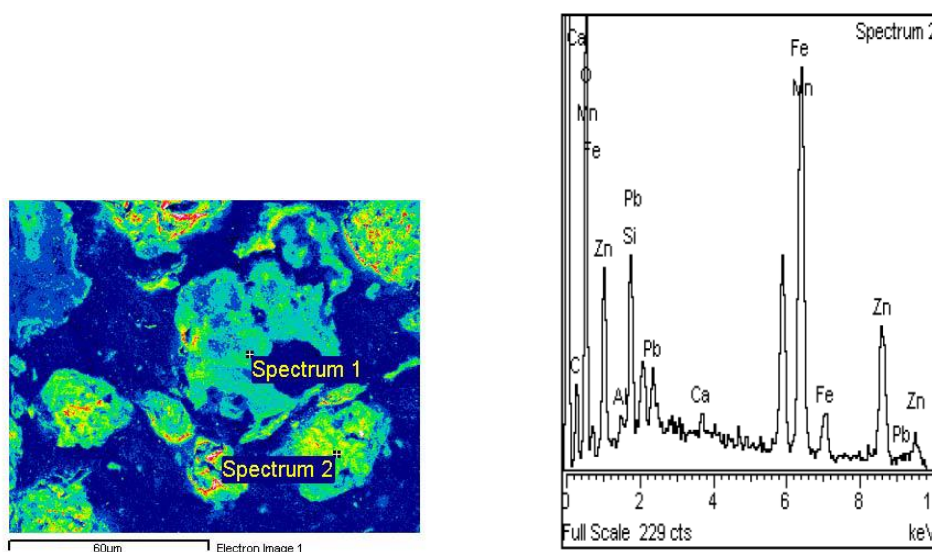


Figure 7: Combined analysis - SEM, Mn and Zn oxides with Pb carbonates (19)

4 Mining and processing activities

The old flotation plant and the surrounding tailings ponds are founded on tertiary clastic sediments. The southeastern part of the study area is occupied by a breccio-conglomerate of polygenetic origin (gneisses, leptinites, granitic gneisses, quartz etc.) components up to 150 mm in size. This mixed sulphides mine and the old flotation plant are located close to Kirki village, between 12 and 18 km north of the city of Alexandroupolis, northern Greece.



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A total amount of 252,000 tons raw ore were extracted between 1973 and 1992. Extraction waste, including barren rock, low-grade ore and some high-grade ore, was stored as unmanaged piles in the immediate vicinity of the open pit on the downstream course of drainage water (5,7,11, 13, 16).

Waste piles are currently exposed to weathering processes that lead to the dissolution of sulphides and other minerals, the formation of efflorescences and crusts of sulphates such as alunite and natralunite as well as AMD. The total lack of any vegetation and soil coverage on the sulphidic waste piles increases erosion rates. Both sheet and gully erosion can be so intense that fine-grained material, including sulphides and sulphates, are washed away by rainstorms.

The ores were beneficiated by flotation in a plant located 5 km south of the mine. A typical Zn concentrate composition was (in wt.%): Zn 50; Pb 1.5; Ag 0.012; As 0.12; Sb 0.02; Bi 0.01; Cd 0.60; Fe, 7.8; S total, 26.1 (S as SO_4 , 3.0); Cu, 0.3; SiO_2 , 1.7; Al_2O_3 , 1.0; whereas a typical Pb concentrate composition was (in wt.%): Pb 55; Zn 5; Ag 0.07; Cu 2.5; As 1.3; Sb 0.33; Bi 0.95 and total S 17 (Michael and Exioglou, 2003).



Figure 8 Historic photograph with miners in Kirki mine

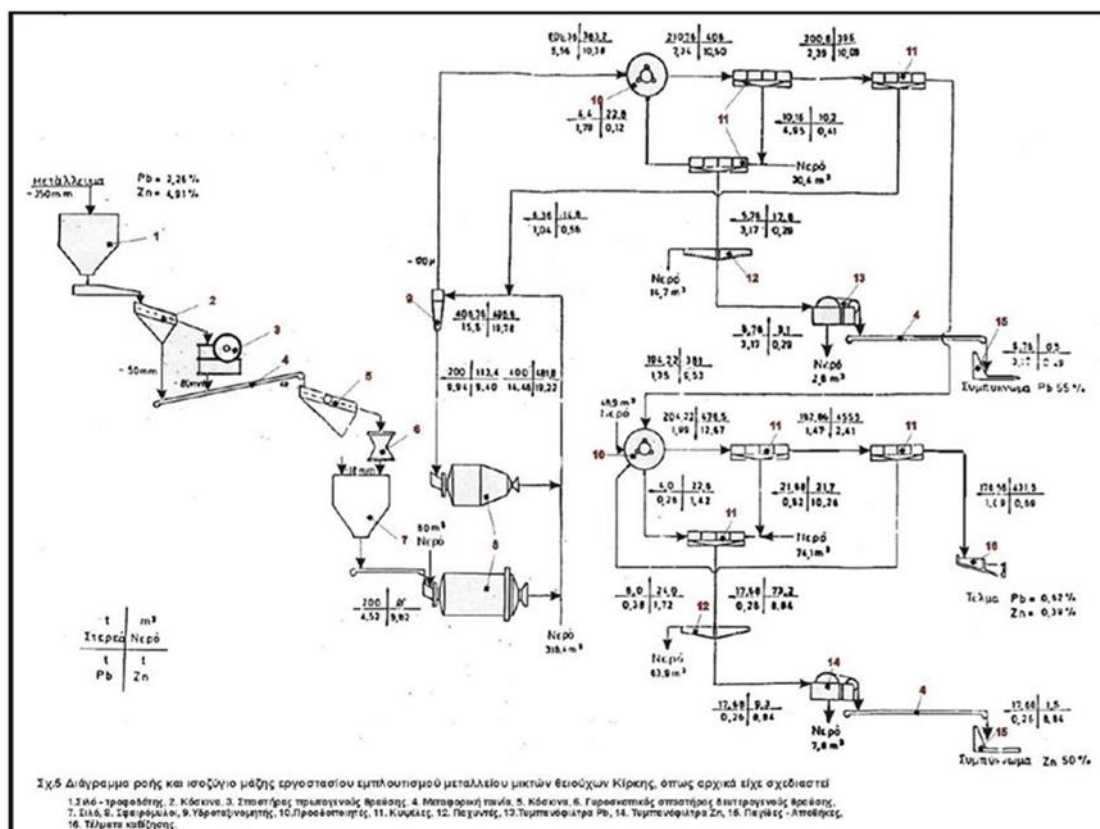


Figure 9: Schematic Flow-sheet and mass balance of Kirki's mixed sulfide ores mineral processing (Constantinides et al., 1988)

Table 2: Production Quantities Kirki mines

Mine Site	Period	Product	Quantities (tn)
St.Phillip Mine	1926-1939	Mixed sulfide	15,000
	1973-1981	"	132,445
	1989-1992	"	120,000
King Arthur	1932-1939	Mixed sulfide	d.n.a.*
Aberdeen	Antiquity-Turkish occupation	Copper sulfide	d.n.a.
d.n.a.: data not available			

Processing waste materials, which are fine-grained tailings (ore flotation residues), were disposed in eight basins around the plant near the courses of the Kirkalon and Eirini River.



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The construction of the dams was initially performed by using uncompacted soil material, sand and conglomerates, arising from the neighborhood talus cone and also from the excavation of the pits. Direct deposition of mud, in order to increase the height of the embankments, is suspected in most of the tailings ponds (Michael and Dimadis, 2006b; Liakopoulos, 2009; Loupassakis and Konstantopoulou, 2009). The maximum height of the embankments varies from 5 to 10m. The area of the tailings ponds varies from 400m² to 8000m². The exact volume of their contents cannot be calculated accurately without drilling or geophysical investigations (Loupassakis and Konstantopoulou, 2009). A tailings thickness of 2.60 to 3.25m was measured in dam no. 4, by using sampling drill hole equipment (Papasiopi et al., 2007).

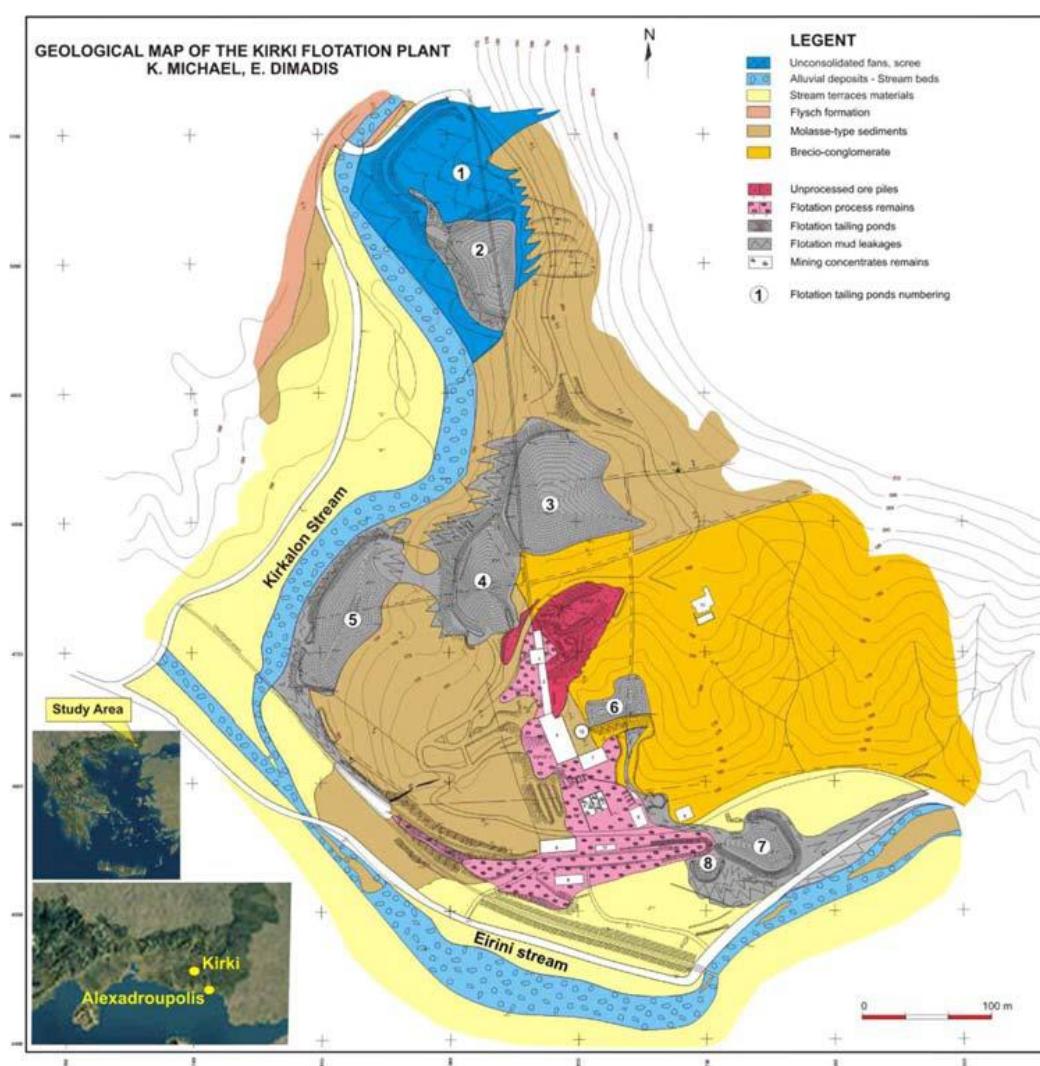


Figure 10: Geological map of flotation plant and surroundings 1:1000 (Michael and Dimadis, 2006)



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Overburden and waste rock generated by the mining operations were disposed along the bed of Kirkalon stream, between elevations +400 m and +320 m, and close to the open pit. The area disturbed by the mining operations, covers a surface of approximately 77 ha.

The beneficiation plant was constructed close to the Kirki village, during World War II. More than 200,000 tons of tailings were produced from the operation of the plant and disposed in several ponds around the mineral processing facilities.

Both Agios Filippos mining area and Kirki's beneficiation plant are the two principal sites where most of the potentially polluting hotspots, e.g. excavation works, waste rock piles and flotation tailings ponds, are located. Several studies have been carried out for the environmental characterization of these abandoned mining sites, as well as for the evaluation of their impact on the quality of nearby natural receivers, i.e. surface and ground waters, soils and sediments. (7,8,9,10,11,12,13,14,16,17)



Figure 11: Google map with sampling points in the area of mineral processing plant

HSGME has collected and evaluated data from older publications and exploration reports within nationally funded projects as well as European ones (Promine Data Base of Anthropogenic secondary ore sources, ProSum, Minerals4EU). (19)



In order to proceed in the estimation and evaluation of CRM's in abandoned mines a nationally funded project started in 2018 to sample and analyse samples from all over Greek territory. Environmental characterization was programmed, too. Extensive fieldwork in combination with laboratory work was carried out and is still in progress. GIS maps are produced with points of sampling, which will be further populated with chemical, mineralogical and environmental data. A field campaign was designed within FRAME project, too. Due to CoVID 19, several programmed works have been postponed.

5 New analysis of Kirki mine samples

The following table gives the chemical analyses of samples collected within the FRAME project. The chemical analyses were carried out by ICPMS. The samples collected are currently being mineralogically analysed, but results were delayed because of difficulties related to the Coid restrictions.

Table 3: Chemical analyses of Kirki mine site samples (wastes and raw material - w = waste; o = ore)

Sample	[mg/Kg in dry matter]									
	Be	Pb	Cr	Mn	Ni	Cu	Zn	Ga	As	Bi
KI-43 (w)	1	5600	110	685	20	139	6522	62	130	29
KI-44 (w)	1	500	90	9800	121	20	>10000	20	20	1
KI-45 (w)	1	3650	102	9805	93	249	6500	38	208	28
KI-46 (w)	1	8200	135	456	9	31	2300	29	119	28
KI-47 (w)	1	3500	105	143	68	861	100	49	1396	767
KI-49 (o)	1	10900	52	4594	33	386	8650	134	310	108
KI-50 (o)	1	2300	109	312	13	134	4500	38	73	36
KI-51 (o)	2	8200	106	716	30	162	6000	63	174	21
	Sc	Y	La	Ce	Pr	Nd	V	Co	Gd	
KI-43 (w)	21	4	13	25	3	10	90	2	4	
KI-44 (w)	29	5	20	33	4	15	87	24	4	
KI-45 (w)	25	25	34	52	17	28	97	11	3	
KI-46 (w)	29	6	17	23	6	10	57	11	4	
KI-47 (w)	7	2	12	23	4	10	57	1	4	
KI-49 (o)	18	6	21	29	6	16	61	9	4	
KI-50 (o)	40	8	22	43	4	16	56	1	4	
KI-51 (o)	26	7	22	43	5	19	131	3	6	



	Au	Hf	Pd	Ir	Pt	Ru	Rh	LOI	
KI-43 (w)	<1	<1	<1	<1	1	<1	<1	5,5	
KI-44 (w)	<1	1	1	<1	1	<1	<1	7,1	
KI-45 (w)	<1	1	1	<1	1	<1	<1	9,15	
KI-46 (w)	<1	<1	<1	<1	<1	<1	<1	5,26	
KI-47 (w)	<1	1	1	<1	1	<1	<1	5,91	
KI-49 (o)	<1	<1	<1	<1	1	<1	<1	6,85	
KI-50 (o)	<1	<1	<1	<1	<1	<1	<1	7,44	
KI-51 (o)	<1	1	1	<1	<1	<1	<1	6,38	

Environmental characterisation was carried out applying EN12457 characterisation protocol as well as paste pH measurements, EN14405 protocol, NAG test e.t.c. In the following table indicative results of eluates analysis (produced out of EN 12457 tests) regarding the above mentioned samples are presented.

Table 4: Chemical analyses of EN 12457 tests (all: liquid phase-eluate from EN12457 leaching test)

	mg/ml (ppb)								
	V	Cr	Mn	Co	Ni	Cu	Zn	Ga	As
KI-43B	<1	<1	9,360	16	1321	1	20,000	2	<1
KI-50	<1	<1	1,780	2	11	27	955	3	<1
KI-52	<1	<1	7,480	4	21	1	450	1	<1
KI-51	<1	<1	7,200	8	74	1	63,00	3	<1
KI-43A	<1	<1	12,300	19	121	1	14,000	2	2
KI-44A	<1	<1	440	<1	3	1	135	<1	<1
KI-46	<1	<1	1,700	4	40	4	4,300	1	<1
KI-47	<1	<1	3,150	4	9	<1	110	2	27
KI-49	<1	<1	18,200	34	55	64	12,000	5	<1
KI44B	<1	<1	93	<1	<1	<1	24	<1	<1
	Rb	Sr	Mo	Ag	Cd	Ba	Pb	U	
KI-43B	16	69	<1	<1	340	52	4,000	1	
KI-50	16	3	<1	<1	7	65	680	<1	
KI-52	12	27	1	<1	15	16	60	<1	
KI-51	12	74	<1	<1	195	81	1,500	<1	
KI-43A	15	103	<1	<1	177	58	3,200	<1	
KI-44A	27	12	1	<1	4	1	37	<1	
KI-46	12	26	<1	<1	29	19	10,000	3	
KI-47	<1	670	<1	<1	<1	50	140	<1	
KI-49	13	94	1	<1	145	115	5,000	1	
KI44B	22	7	5	<1	<1	1	26	<1	



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6 Conclusion

The historic Kirki mine could be of interest for exploitation. Ore samples as well as waste sample show elevated values of Pb, Zn and Mn. Further studies are needed for the estimation of the orebody dimensions and the quality of the ore. This would involve sampling campaigns of the tailings, mine waste and ore as well as further mineralogical and geochemical analysis.



Figure 12: Kirki open pit lake



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Figure 13: Mineral processing – flotation plant Kirki Mine



Figure 14: Sampling of bulk sample from wastes



Figure 15: Sampling from of bulk sample from tailing pond



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Figure 16: View of waste disposal sites



Figure 17: Views of the mining area



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Figure 18: Sampling mine wastes at Kirki mine



Figure 19: Processing plant and tailing ponds



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Figure 20: Examples of old galleries at Kirki mines



Figure 21: Flotation Plant and wastes



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