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## GEOCHEMICAL INVESTIGATION AND MODELLING OF AN ACID PIT LAKE FROM A HIGH SULFIDATION ORE DEPOSIT: KIRKI, NE GREECE

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### Abstract

*Open pit mining of a high sulfidation epithermal type deposit at Kirki (Thrace, NE Greece) resulted in the formation of an acid pit lake by infilling of the open cast by rain and drainage waters after mine closure. The acidic and oxidative pit lake waters show high concentrations of trace metals largely due to the high toxic metals content of the ore, the limited buffering capacity of host rocks and the direct exposure of the ore zone to weathering. The floor of the pit lake is covered by a fine-grained mineral precipitate that comprises mainly detrital minerals, originating from erosion of the rocks exposed on the walls of the open pit. Secondary anglesite, several species of the jarosite-group, rozenite, melanterite, gypsum, bukovskyite, beaverite, scorodite and minor goethite are also detected. The mineral precipitate presents significant heavy metal content indicating effective removal of metals from the acidic waters. The speciation/mass transfer computer code PHREEQC-2 and the MINTEQA database were employed for geochemical modelling of the equilibrium between the acidic pit lake waters and the secondary phases of the mineral precipitate.*

**Key words:** Acid pit lake, mineral precipitate, high-sulfidation ore, geochemical modelling, Kirki.

### 1. Introduction

Pit lakes are unique water bodies. They are developed as a result of open cast mining. When the activity ceases, the open pit is back filled with groundwater and surface water (Lu et al., 2003). The rate of filling is defined by climatic and geologic conditions, as well as the regional hydrologic characteristics.

Assessment of the environmental risks of pit lake development is an imperative for the mining industry and the public, especially in cases of high sulfidation deposits that are characterized by high concentrations of toxic metals (Plumlee et al., 1999). Pit lakes forming from such deposits pose a significant threat to the environment since they are often acidic containing elevated concentrations of metals (e.g. Fe, Al, Pb, Cu, Zn, Mn, Cd) and metalloids (e.g. As, Sb), and show high acid generation potential and very low buffering capacity (Latanzi et al., 2008; Sperling & Grandschamp, 2008; Shevenell et al., 1999).

Quantification, prediction and evolution of pit lake systems require the use of numerical models (such as PHREEQC), which take into account the relevant thermodynamic, mineralogical and geochemical data, as well as other parameters such as changes in pit lake volume, effects of seasonal



**Fig. 1:** View from north of the Kirki (Ag. Filippos) acid pit lake.

weather patterns, processes occurring on pit walls above the lake surface (Gimber et al., 2008). The aim of this paper is to provide information on the function of the small pit lake developed at the abandoned Kirki (Agios Filippos) high sulfidation mine. The results of this study can be used for future evaluation of various remediation options for the pit lake.

## 2. Site description

The Kirki (Agios Filippos) high sulfidation deposit is hosted into the Eocene-Oligocene volcano-sedimentary rock sequences of SE Evros county and is associated with orogenic calc-alkaline to shoshonitic magmatism. The high sulfidation epithermal type mineralization is developed between two sub-parallel fault zones that form the western and the eastern part of the open pit. The ore is rich in base-metals sulfides and various Pb- and As-bearing sulfosalts (Skarpelis, 1999). Galena shows the highest degree of weathering among other sulfides and sulfosalts. The low degree of oxidation of pyrite and sphalerite is reasonably explained by their rather chemical purity (Triantafyllidis & Skarpelis, 2004). Studies by Triantafyllidis (2006) showed that in the upper part of the oxidation zone sulfates, hydrosulfates and sulfoarsenates are the predominant secondary mineral phases. Anglesite is the major oxidation product, followed by lower proportions of osarizawaite, beaverite, linarite and beudantite (Triantafyllidis & Skarpelis, 2004). At lower levels of the oxidation zone, carbonates are additionally identified. Secondary carbonates include cerussite, hydrocerussite, smithsonite, azurite and rosasite. The mineralogy of efflorescences appearing on the walls of the open pit is indicative of highly acidic and oxidative conditions. Efflorescences of Fe-bearing (e.g. siderotile, copiapite, rhomboclase) and Cu-bearing sulfates (e.g. chalcantite), arsenates (scorodite) and sulfoarsenates dominate over Pb and Zn sulfates.

Since mine closure in 1997, an acid pit lake has been formed by infilling of the open pit by rain and drainage waters (Fig. 1). The height of the water column fluctuates, depending on the annual rainfall. The waters from the pit lake show low pH, high Eh values and increased concentrations of dissolved toxic metals through the year (Triantafyllidis & Skarpelis, 2006). The topography of the mine prevents overflow and dispersion of acidic waters into the drainage system of the area.

A yellowish to orange-yellowish, fine-grained, unconsolidated mineral precipitate with an average thickness of 20cm covers the floor of the pit lake and yields significant heavy metal content. The mineral precipitate comprises mainly detrital quartz, dickite/kaolinite, pyrophyllite and feldspar, origi-

nating from erosion of the rocks exposed on the walls of the open pit. Semiquantitative analyses indicate that Fe-bearing sulfates (jarosite group minerals, melanterite, rozenite, butlerite), sulfoarsenates (bukovskyite) and arsenates (scorodite) dominate over other secondary minerals (e.g. anglesite, beaverite, wroewolfeite and gypsum) (Triantafyllidis & Skarpelis, 2006).

### 3. Sampling - analytical methods

Drill core samples down to a depth of 200m from the surface were used for the mineralogical investigation of secondary mineral phases. Samples of mineral precipitate from the open pit and efflorescences from the mine walls were collected and dried at room temperature. Water samples from the open pit were collected in September 2001, June 2003 and December 2004, applying standard sampling techniques. Temperature, pH and Eh were measured on site using a WTW pH 320/Set-2 electronic pH-meter. Water samples were filtered through a 0.45 µm Millipore filter and acidified with 1 M HNO<sub>3</sub>. Details of the analytical technics implemented in this study can be found at Triantafyllidis (2006), Triantafyllidis & Skarpelis (2006) and Triantafyllidis et al. (2007).

### 4. Analytical data used

The physicochemical data for the pit lake waters, the geochemical data of the mineral precipitate, and the mineralogy of the precipitate are given in Tables 1, 2, and 3 respectively (Triantafyllidis & Skarpelis, 2006).

**Table 1.** Physicochemical characteristics of pit lake waters (Dissolved ions in mg/l, Eh in mV) (from Triantafyllidis & Skarpelis, 2006).

	pH	Eh	SO <sub>4</sub>	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
September 2001											
<b>Mean</b>	3.1	235	2300	3.82	0.26	16.2	7.5	169.7	1.76	2.24	425.5
<b>Stan. Dev.</b>	0	1.58	130	0.07	0.01	0.25	0.26	3.4	0.03	0.03	1.22
June 2003											
<b>Mean</b>	2.9	248	1700	2.71	0.14	12.1	27.1	112.0	1.30	0.90	282.5
<b>Stan. Dev.</b>	0.06	4.62	75	0.06	0.01	0.13	1.04	1.91	0.04	0.02	3.4
Ag, Hg, As, Sb below detection											
Total Radioactivity: 16.48 – 151.62 pCi/l											

**Table 2.** Chemical analyses of the mineral precipitate (Major elements and Fe in wt %, trace elements in ppm) (from Triantafyllidis & Skarpelis, 2006)

	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Cr <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	MgO	Na <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	TiO <sub>2</sub>	LOI
<b>Min</b>	30.9	12.72	0.4	0.02	1.82	0.6	0.16	0.1	0.43	11.4
<b>Max</b>	59.5	22.71	0.63	0.03	3.1	0.91	0.37	0.19	0.64	22.9
<b>Mean</b>	43.8	17.5	0.52	0.02	2.39	0.76	0.28	0.14	0.55	18.4
<b>Stan. Dev.</b>	12.1	4.4	0.09	0.01	0.58	0.14	0.09	0.03	0.1	5.16
LOI: Loss on ignition										

**Table 2 continued.**

	Fe	Pb	Zn	Cu	Mn	As	Cd	Ni	Sb	Co	Ag	Bi	U
<b>Min</b>	6.21	3219	3195	473	591	497	22	22	26	b.d.	7.2	84	b.d.
<b>Max</b>	20.78	6748	4789	958	2017	1582	46	31	38	20	11.3	136	11
<b>Mean</b>	11.38	5087	4231	710	1256	889	32	25	31	4	8.9	98	6
<b>Stan. Dev.</b>	5.91	1050	621	147	577	475	7.3	3	5.6	6.6	1,5	28	4.4
Hg: below detection limit b.d.: below detection													

**Table 3.** Semiquantitative analyses of secondary minerals identified in the mineral precipitate (from Triantafyllidis & Skarpelis, 2006).

Jarosite group minerals (jarosite, hydronium jarosite)	$(K, H_3O)Fe_3(SO_4)_2(OH)_6$	XXX
Wroewolfeite	$Cu_4(SO_4)(OH)_6 \cdot 2H_2O$	X
Beaverite	$PbCu(Fe, Al)_2(SO_4)_2(OH)_6$	XX
Gypsum	$CaSO_4 \cdot 2H_2O$	XX
Anglesite	$PbSO_4$	XX
Scorodite	$FeAsO_4 \cdot 2H_2O$	X
Bukovskyite	$Fe_2(AsO_4)(SO_4)(OH) \cdot 7H_2O$	X
Goethite	$Fe(OH)_3$	XX
Melanterite	$FeSO_4 \cdot 7H_2O$	X
Rozenite	$FeSO_4 \cdot 4H_2O$	X
Butlerite	$FeSO_4(OH) \cdot 2H_2O$	X
Mineral abundances: XXX very abundant, XX medium, X low		

## 5. Application of PHREEQC geochemical code

The correlation between the chemistry of the acidic pit lake waters and the mineralogy of the mineral precipitate was investigated with the use of the geochemical code PHREEQC-2 (Parkhurst & Appelo, 1999) and in particular the 2.12 edition.

There are two basic approaches to geochemical modeling: chemical equilibrium and chemical kinetics, with the first, and most common, being employed in this study. In general, equilibrium models can be divided into the following categories: forward (reaction path models) and inverse.

Forward models are used for prediction of water chemistry evolution. In this case the starting water chemistry is defined and an attempt is made to model water evolution by precipitation of mineral phases. During each step the program transfers a small amount of mass from reactant to products. Then it calculates mass distribution among the products and saturation indices of pre-determined phases. Then, the program checks whether the water is supersaturated relative to those phases.

Inverse models are based on mass balance calculations for solid phase and dissolved species in a geochemical system. In this case, we examined the precipitation of the mineral phases identified in the pit lake after mixing of two different water types.

**Table 4.**

Physicochemical characteristics of the solutions used for PHREEQC modeling			
Solution 1 (meteoric waters)		Solution 2 (acidic pit lake waters)	
Temperature	25°C	Temperature	25°C
pH	6	pH	3
pε	4	pε	4
density	1gr/cm <sup>3</sup>	density	1g/cm <sup>3</sup>
		S (as SO <sub>4</sub> )	2300 mg/L
		Cu	16 mg/L
		Mn	170 mg/L
		Zn	425 mg/L
		Fe	7 mg/L
		Pb	2 mg/L
		Na	10 mg/L
		K	2 mg/L

## 6. Geochemical modeling

Thermodynamic data was taken from MINTEQ database (Allison et al., 1991). Imported parameters in the system involved: Fe (total), Pb, Zn, Cu, Mn, SO<sub>4</sub><sup>2-</sup> and pH. Cobalt was not taken under consideration since it is not included in the MINTEQ database. Several different scenarios were employed for the system “*acidic pit lake waters – precipitate mineralogy*”.

### 6.1 Forward modeling

The first scenario involved the possibility of direct precipitation of the identified secondary phases, as a result of supersaturation due to evaporation, or excessive input of toxic metals, sulfates and arsenates to the pit lake, at a given time period. Application of the PHREEQC geochemical code showed that direct precipitation is impossible largely due to the low heavy metal and sulfate load of the pit lake waters.

### 6.2 Inverse modeling

Inverse modeling was applied to verify hypotheses on the origin of the identified secondary phases in the mineral precipitate. Two cases were examined. The first case involved the study of the chemical characteristics of a theoretical solution that resulted after mixing slightly acidic meteoric water (Table 4, solution 1) with a potential acid drainage in several ratios, to check if that solution is in equilibrium with the secondary phases identified in the precipitate. For the second case, the acidic pit lake waters were used as the potential acid drainage (Table 4, solution 2). Once more, the behavior of mixing the slightly acidic rain water with the potential acid drainage in several ratios was investigated.

**1<sup>st</sup> case:** The potential acid drainage was based on thermodynamic data from MINTEQ database. The mineralogy of the Kirki high sulfidation deposit is very complex with a diversity of sulfides and sulfosalts and, unfortunately, for most of these minerals there is no data. This geochemical model showed that potential acid drainage with thermodynamic data only for pyrite, galena and sphalerite cannot sufficiently interpret the secondary mineralogy of the precipitate.

**Table 5.**

Saturation indices of secondary minerals in equilibrium with the acidic pit lake waters, based on the PHREEQC-2.12 geochemical code		
Mineral	Saturation index (MINTeq)	Formula (MINTeq)
Anglesite	0.66	PbSO <sub>4</sub>
Bianchite	-4.93	ZnSO <sub>4</sub> ·6H <sub>2</sub> O
Cerussite	-1.62	PbCO <sub>3</sub>
Ferrihydrite	-1.58	Fe(OH) <sub>3</sub>
Goethite	2.82	FeOOH
Goslarite	-4.74	ZnSO <sub>4</sub> ·7H <sub>2</sub> O
Hematite	10.64	Fe <sub>2</sub> O <sub>3</sub>
H3O-jarosite	0.94	(H <sub>3</sub> O)Fe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Jarosite	1.87	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Na-jarosite	-0.89	NaFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
Larnackite	-3.42	PbOxPbSO <sub>4</sub>
Lepidocrocite	1.94	FeOOH
Maghemite	0.24	Fe <sub>2</sub> O <sub>3</sub>
Magnetite	5.07	Fe <sub>3</sub> O <sub>4</sub>
Melanterite	-5.91	FeSO <sub>4</sub> ·7H <sub>2</sub> O
Smithsonite	-4.33	ZnCO <sub>3</sub>

**2<sup>nd</sup> case:** Development of this model with PHREEQC, for mixing of the aforementioned solutions in ratio 95:5 (95% solution 1 and 5% solution 2), leads to a final solution that is in equilibrium with the majority of the secondary phases identified in the pit lake mineral precipitate (e.g. anglesite, goethite, jarosite), as well as other secondary phases that cannot be detected with X-ray Diffraction (e.g. ferrihydrite) (Table 5).

It is worth mentioning that similar results arise with different mixing ratios (e.g. 99 to 1). Another characteristic of this model is the thermodynamic equilibrium of several secondary Fe phases, while the concentration of Fe in the acidic pit lake water are relatively low (7.5 to 27 mg/L).

## 7. Conclusions

The Kirki (Agios Filippou) high sulfidation deposit is rich in base metals sulfides (e.g. pyrite, galena, sphalerite) and sulfosalts (e.g. enargite, tennantite, jordanite). Lead and Cu-bearing sulfates and hydrosulfates dominate in the upper part of the oxidation zone of the Kirki deposit, whereas at lower levels supergene carbonates are present. During the last ten years, an acid pit lake was formed by infilling of the open pit by rain and drainage waters. The highly acidic pit lake waters show high concentrations of dissolved toxic metals. The pit lake waters are characterized by increased toxic metal concentrations as a result of:

- Oxidation of sulfides and sulfosalts and the partial release of their toxic load to the environment due to the presence of mildly acidic and oxidative meteoric and drainage waters.

- Washing and dissolution of soluble secondary phases (efflorescences) formed on the walls of the open pit.
- The direct contact of the highly acidic and oxidative waters of the pit lake with grains of sulfides and sulfosalts present at the level of pit lake water.

The model developed with PHREEQC for the Kirki pit lake system shows that meteoric waters plays a key role in deposition of secondary phases in the pit lake. In particular, mixing of slightly acidic meteoric waters with the acidic pit lake waters in ratio 95:5 or higher, may successfully lead to the formation of anglesite, goethite, jarosite group minerals, hematite and ferrihydrite. On the other hand, due to lack of thermodynamic data, there are no conclusions concerning beaverite, scorodite, bukovskyite, wroewolfeite and siderotile.

Finally, it is very important to state that the aforementioned model for the Kirki pit lake system is based on a critical limitation, being the organic activity within the pit lake waters. It is known that the role of aerobic bacteria is critical in the initial oxidation/weathering of primary sulfides and sulfosalts (Stokes, 1954; Walsh & Mitchell, 1972; Trafford et al., 1973; Ivarson & Sojak, 1978; Crepar et al., 1979; Evangelou, 1983), as well as their catalytic behavior in the formation of secondary phases present in pit lakes precipitates. Further study aims to shed light on the role bacteria play for the evolution of the Kirki pit lake system.

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