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Geochemical control of Acid Mine Drainage in abandoned mines: The case of Ermioni Mine, Greece

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Abstract

Acid mine drainage is an extensively documented environmental issue, commonly originated by the weathering of sulfide ores both in active and abandoned mining sites. Even though national and international regulations obliged mining companies to handle this problem in active mines, in the abandoned ones it is usually regarded as a major environmental thread. Natural attenuation is a term that is used to describe a combination of in situ physical, chemical and biological processes that under some specific conditions, act without human interventions in order to reduce the mass, toxicity, mobility and concentration of metals in soil or groundwater" (USEPA, 1999). For those processes, the local lithology may plays a key role, when contributing to an alkaline environment, consequent the precipitation of metals in the form of hydroxides. Despite of the fact that in Ermioni, Greece, a mixed sulfide ore mine had been operational since 1928, it has been abandoned after 1978 and no restoration actions have been implemented. Dispersed ore tailings have been deposited near the galleries, being exposed to atmospheric conditions. Soil and mine-water samples were collected from the region of that abandoned mine. The soil was collected from tailings at superficial points near the mining galleries, while water was sampled from canals, which drain from the mining galleries to the nearby Roros River. The mineralogical composition of the soil samples was studied by X-ray Diffraction Spectroscopy and Scanning Electron Microscopy, while Flame Atomic Adsorption Spectroscopy was applied for the determination of the Fe, Zn, Cd, Cu, Pb, Mn, Ni, Co, Cr and Hg concentrations in the water samples.

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Keywords: natural attenuation, acid mine drainage, sulfide ore, limestone, gypsum.

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The results from our field and laboratory study indicated that, the acid mine drainage, produced by the oxidation of the sulfide minerals (primarily pyrite), has been geochemically controlled by the lithological formations. A series of geochemical reactions between the sulfuric acid derived from the oxidation of pyrite in the presence of O2 and H2O, diluted in groundwater, and the calcareous carbonate minerals of the wall rock and the neighboring lithological formations (limestone and flysch) have led to the neutralization of the acidity and the formation of secondary sulfate minerals such as gypsum and jarosite. The initial acidity and the contamination of water by toxic elements, like Fe, Al, Mn, Cr, As, Pb, Zn etc., originated by the chemical weathering of the ores by the sulfuric acid, seems to be remediated by the elevation of the pH that leads to the precipitation of those elements. Moreover, gypsum has been identified as the main mineralogical component of the soil in that area (up to 95 vol.%) accompanied by small amounts of quartz, jarosite and residual, partially oxidized, pyrite grains.

1. Introduction

Acid mine drainage (AMD) refers to the outflow of low-pH (1.5-3.5) water from active or abandoned mining sites and metallurgical industries. It is originated by the oxidation of sulfide ores due to the combined action of air, water and bacteria.

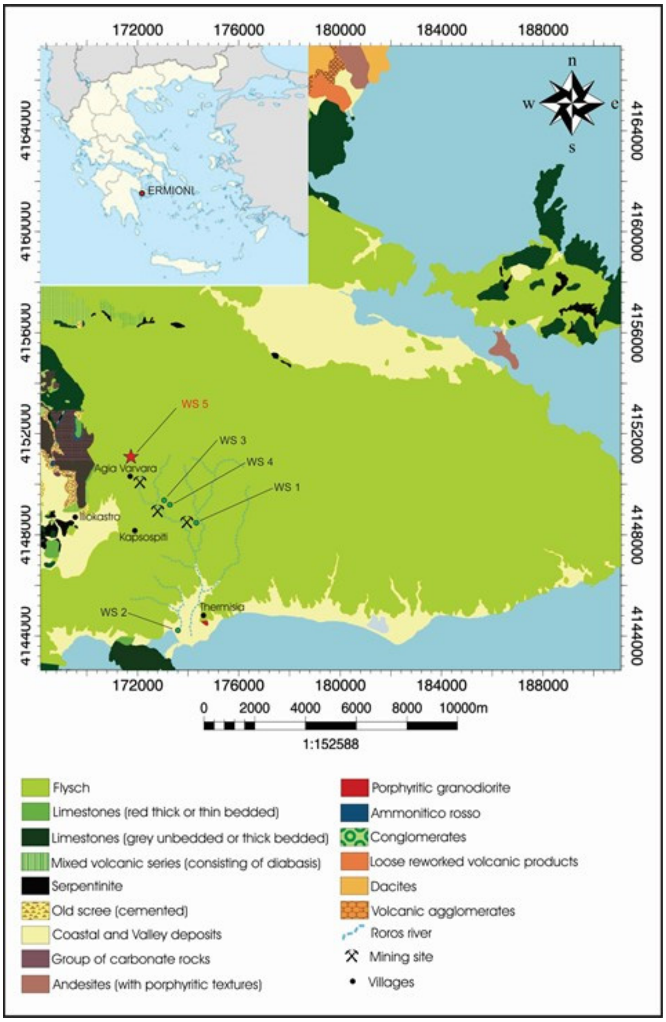

Figure 1. Geological map of the region of Ermioni, (modified after Suesskoch, 1963) showing the sampling sites.

It is characterized as a dilute solution of sulfuric acid, of low-pH (1.5-3.5), carrying significant amounts of dissolved Fe and high concentrations of heavy and toxic metals, such as Cu, Zn, Pb, harmful for any biological activity (e.g. Ash et al., 1951, Kontopoulos et al., 1996). Usually, AMD is produced by pyrite oxidation, which occurs due to the presence of O_2 and H_2O (Măicăneanu et al. 2013). Even though national and international regulations obliged mining companies to handle this problem in active mines, in the abandoned ones it is usually regarded as a major environmental thread. USEPA (1999) refers "Natural Attenuation" as a term used to describe a combination of in situ physical, chemical and biological processes that under some specific conditions, act without human interventions in order to reduce the mass, toxicity, mobility and concentration of metals in soil or groundwater". For those natural processes, the local lithology may be the controlling factor, as it can lead or contribute to create an alkaline environment, consequent the precipitation of metals in the form of hydroxides (Meck et al., 2011).
Ermioni is a small seaside town, which is located in the southeastern part of Argolis, in the eastern Peloponnese, in Greece (Figure 1). In the region of that town, a mixed sulfide ore mine had been operated since 1928 and it was abandoned after 1978 but no action for restoration has been implemented, a fact that is obvious from the dispersed ore tailings that have been deposited near the galleries. The main galleries that had been used for the exploitation of the mine were "Gallerie 90", "Stoa Rorou", and "Stoa Agias Varvaras". Canals drain from the mining galleries to the nearby Roros River (Figure 1.).
The relief of the area is characterized as scalable from the mountain crest of Aderes to the sea and comprises mainly rural areas and deep gorges, like Roros, in which the majority of the mining galleries exist (Kalatha 2005). The mine tailings have been exposed to atmospheric conditions for more than 35 years. The predominant lithological formations of the region are limestones and flysch (Figure 1). The major part of the region is covered with flysch that consists of marls (reddish in the bigger part), sandstones, breccia and conglomerates. Within the flysch formation, there are limestone bodies of Upper Cretaceous age, in forms of alternating thick and thin bedded lenses. The sulfide ore deposits of the area are spatially related to the intrusion of basic igneous rocks. The ore bodies are shaped as irregular lenses with various thickness (few centimetres to a few meters). These deposits are similar to metalliferous sediments that are found at mid-ocean ridges and island arcs, and are associated with ophiolite complexes (Varnavas and Panagos 1984). The aim of the present study is to investigate the phenomenon of possible natural attenuation in the case of Ermioni abandoned mine and to determine how this may effect the pH and heavy metal consecration in the natural waters of that area.

2. Materials and methods

Five soil samples (THERM1 to THERM5) were collected from tailings at superficial points near the mining galleries, while water was sampled from five canals which drain from the mining galleries (WS1 to WS5), (Figures 1 & 2). A portable multimeter (Consort 561 Multiparameter Analyzer) was used for the on-site measurement of the pH values. The laboratory tests were performed at the Laboratory of Economic Geology and Geochemistry, National and Kapodistrian University of Athens and at the Centre for Research and Technology of Hellas. The mineralogical composition of the soil samples was studied by means of X-ray Diffraction Spectroscopy (Siemens D5005).and Scanning Electron Microscopy (JEOL JSM 5600 equipped with an OXFORD ISIS 300 Energy Dispersive Electron Microprobe Analytical System). Flame Atomic Adsorption Spectroscopy (FAAS) (Perkin Elmer 1100 B), was applied for the determination of the Fe, Zn, Cd, Cu, Pb, Mn, Ni, Co and Cr concentrations in the water samples. Hg was measured by Graphite Furnace Atomic Adsorption Spectroscopy (FAAS) (SHIMATZU AA-6300).

Figure 2. XRD pattern of a representative soil sample (THERM1) from Ermioni. Where Gp: gypsum; Jar: Jarosite; Qtz: quartz; Cal: calcite; Py: pyrite.

3. Results and discussion

The pH measurements of the water samples which were collected from the canals near the mining galleries are shown in Table 1, along with the heavy metal content of them.

Table 1. Analytical results for the water samples from Ermioni area.

Para-meter	Unit	WS1	WS2	WS3	WS4	WS5
pH		7.2	8.3	7.0	6.6	2.7
Fe		0.12	0.09	0.14	0.60	49.50
Zn		0.02	0.01	0.01	0.03	27.20
Cd		bdl	bdl	bdl	bdl	0.05
Cu		0.02	0.01	0.01	0.02	5.63
Pb	$mg.L^{-1}$	bdl	bdl	bdl	bdl	bdl
Mn		bdl	bdl	0.03	1.14	13.10
Ni		bdl	bdl	bdl	bdl	0.48
Co		0.04	0.04	0.05	0.05	1.08
Cr		bdl	bdl	0.03	bdl	0.10
Hg	$\mu g.L^{-1}$	bdl	bdl	0.3	0.3	0.70

It is easily observed that almost all samples, exhibited neutral to slightly alkaline pH values ranging between 6.5 and 8 and negligible heavy metal concentrations. Only the WS5 that was sampled from a waste water canal, which drains from the is the Agia Varvara mining gallery presented an acidic pH of 2.7 and high metal concentrations.

Since no remediation actions have been implemented in the mining area the only explanation that could justify these results including the pH rise, is the neutralization of acidity by natural factors like the geological formations of the region, that could contribute to an alkaline environment. The results obtained by the mineralogical analysis of the soil samples are supporting the above suggestion (Table 2).

Table 2. Mineralogical phases identified in the soil samples by the XRD and SEM/EDS methods (+++: intense presence of mineral phase, +: minor presence of mineral phase).

mineral	THERM1	THERM2	THERM3	THERM4	THERM5
Gypsum	+++	+++	+++	+++	++
Quartz	+	+	+	+	+
Jarosite	+	+	+	+	+
Pyrite	+	+	+	+	+
Calcite			+	+	
Quartz				++	+
Clays		+		+	++

The predominant mineralogical phase in the soil was gypsum ($CaSO_4 \cdot 2H_2O$) **(**Figure 3**)**, which contributed up to 95% vol, in the soil composition. As aforementioned, the principal lithological formations in the study area are flysch, limestones, etc. that contain vast quantities of calcite. As the acid mine water flows away from the galleries through the water canals, it reacts with these formations, resulting not only the natural neutralization of the acidity by increasing the pH values from 2.7 to 7 or higher but also decrease of the of toxic metals concentrations. According to Kedziorek et al. (2013), geochemical mechanisms, such as precipitation and adsorption that occur under some specific conditions (e.g neutral pH) may be responsible for the phenomenon of self-remediation or natural attenuation of toxic metals. Gypsum has been formed by the reaction of the sulfuric acid of the AMD with the carbonate minerals (calcite) that leaded to the neutralization of the solution: $CaCO_3 + H_2SO_4 + 2H_2O \rightarrow CaSO_4.2H_2O + CO_2$.

Small amounts of jarosite ($KFe_3^{+3}(SO_4)_2(OH)_6$), quartz (SiO_2), calcite ($CaCO_3$) and pyrite (FeS_2) were detected in the samples (Table 2, Figure 3). Calcite and quartz are the common minerals of the local lithology and pyrite is originated from the ore deposit. Jarosite is a secondary mineral phase, frequently found in the oxidized zones of sulfide deposits, formed by the reaction of dilute sulfuric acid in ground water, with gangue minerals and wall rock in the deposit: $K^{-} + 3Fe^{3+} + 2H_2SO_4 + 6H_2O \rightarrow KFe_3^{+3}(SO_4)_2(OH)_6 + 10H^{+}$.

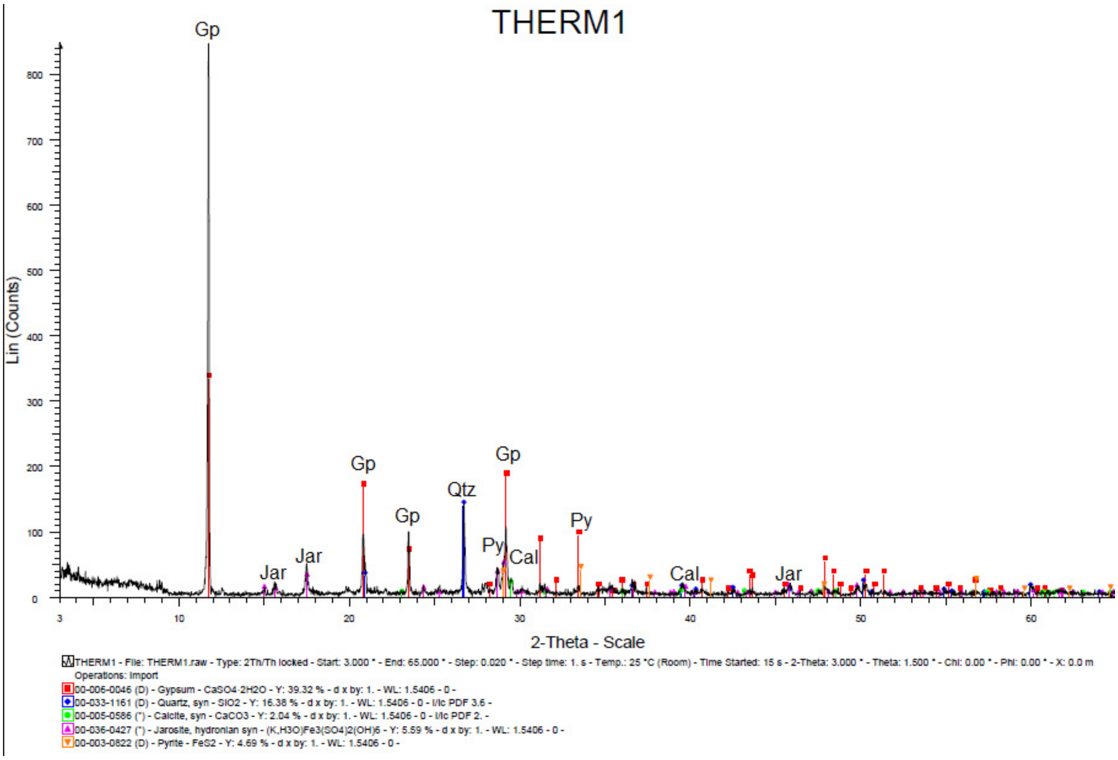

Figure 3. Results of analysis.

The traditional treatment methods of AMD aquatic discharges remediation, such as reduction precipitation, ion exchange, electrochemical reduction, reverse osmosis etc, are methods involving large exposed liquid surface area and long detention periods as well as high capital cost, usually not-affordable for small-scale industries (Alexopoulos et al. 2013). The case of natural remediation taking place in Ermioni region, has significant effects to the environment and to the economy, because a vast amount of money, that would otherwise been used for the implementation of treatment methods on sites, is saved (Meck et al., 2011).

4. Conclusions

Geochemical reactions that occur readily in nature can control the acid mine drainage from abandoned mine sites and restrain its environmental impact. Our field and laboratory results have indicated that, the acid mine drainage, produced by the oxidation of the sulfide minerals, has been geochemically controlled by the lithological formations.
A series of geochemical reactions between the sulfuric acid derived from the oxidation of pyrite in the presence of O_2 and H_2O, diluted in groundwater, and the calcareous carbonate minerals of the wall rock and the neighboring lithological formations have led to the neutralization of the acidity and to the formation of secondary sulfate minerals. The contamination of water by toxic elements seems to be remediated by the elevation of the pH that caused their precipitation.
Ermioni abandoned mine is demonstrated to be an example natural attenuation. The local lithology and its mineralogy have played a key role by contributing to an alkaline environment, consequent the formation of secondary minerals and the metals' precipitation.

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