



## Recent sulphate minerals: A result of weathering of pyrite

### Новообразувани сулфатни минерали – резултат от промяна на пирит

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#### Introduction

The mining of sulphide ores leads to the generation of large volumes of waste rocks and fine materials from the processing. The sulphide-bearing wastes commonly containing large amounts of pyrite, are a serious environmental pollutant (Rosso, Vaughan, 2006). Formed in reductive conditions, on exposure at the Earth's surface, pyrite is put to intensive alterations, with formation mostly of Fe-sulphates.

In order to establish the variety of the alteration products, natural pyrites with peculiar textures were artificially weathered and subsequent crystallization products were identified. The recent minerals and the crystallization sequence are comparable to that found in natural environments.

#### Pyrite

Natural pyrites with radial texture, which are very easily weathered under dry conditions, from hydrothermal sulphide deposits of different genesis were investigated. Such occurrences are: Madzharovo, and others vein Pb-Zn deposits in south Bulgaria; vein Pb-Zn deposits from Kratovo district, Macedonia; Magura-Hondol vein Au-Pb-Zn deposit, Romania; Rio Tinto massive polymetallic sulphide deposit, Spain, etc. The studied pyrite samples have very high radial porosity, characterized by extremely high interfacial area and intergranular spaces (Atanassova, 2008). These features determine the very high reactivity in supergene conditions, much higher than that of massive pyrite and the materials of its fragmentation.

#### Recent minerals

The pyrite samples were washed with deionised water (at T~25° C) and allowed to dry in the laboratory. After a few hours they were covered with crystalline oxidation products.

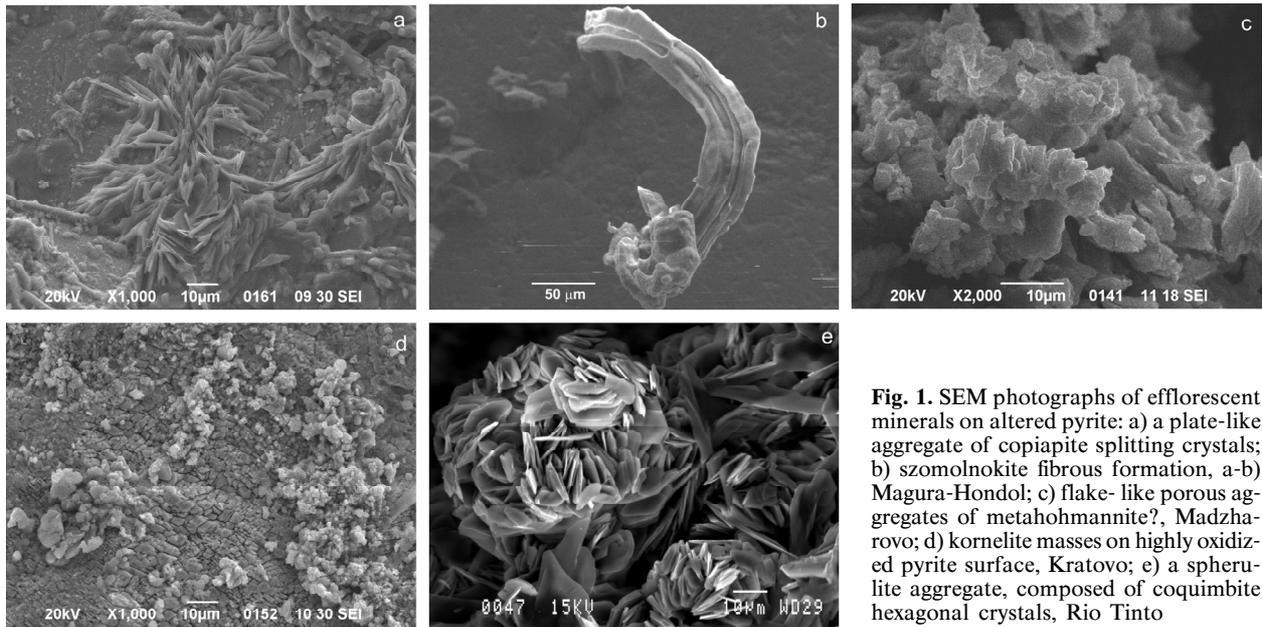
Numerous soluble Fe-sulphate salts plus gypsum and jarosite were identified (Table 1) using X-ray diffraction, Debye-Scherrer method (XRD) and Scanning Electron Microscope with Energy Dispersive Spectrometer (SEM/EDS). Although microanalyses by EDS performed on rough surfaces provide semi quantitative chemical data, the combination with used X-ray method, which allowed registration of the powder pattern from very small amounts made possible the identification of the minerals.

Nearly all iron sulphate minerals are hydrous and the number of waters of hydration is controlled by relative humidity and temperature (Rimstidt, Vaughan, 2003). Therefore, it is not surprising that some of the samples consist of a mixture of phases. Some trace amounts of As and Al were recorded in coquimbite group minerals.

Macroscopically, the observed minerals form fine fibrous incrustations, botryoidal coatings and granular or porous masses on the pyrite surfaces. The

*Table 1. Idealized chemical formulae and methods of identification of the sulphate minerals*

Minerals:	Chemical formulae:	Methods:
<i>Melanterite group</i>		
Szomolnokite	Fe <sup>2+</sup> SO <sub>4</sub> .H <sub>2</sub> O	XRD, SEM/EDS
Rozenite	Fe <sup>2+</sup> SO <sub>4</sub> .4H <sub>2</sub> O	XRD
Melanterite	Fe <sup>2+</sup> SO <sub>4</sub> .7H <sub>2</sub> O	XRD
<i>Coquimbite group</i>		
Rhombochase	(H <sub>3</sub> O)Fe <sup>3+</sup> (SO <sub>4</sub> ) <sub>2</sub> .3H <sub>2</sub> O	XRD, SEM/EDS
Lausenite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .6H <sub>2</sub> O	XRD
Kornelite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .7H <sub>2</sub> O	XRD, SEM/EDS
Coquimbite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .9H <sub>2</sub> O	XRD, SEM/EDS
Quenstedtite	Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .10H <sub>2</sub> O	XRD, SEM/EDS
<i>Butlerite group</i>		
Metahohmannite	Fe <sup>2+</sup> (SO <sub>4</sub> ).1.5H <sub>2</sub> O	SEM/EDS
<i>Copiapite group</i>		
Copiapite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>4</sub> (SO <sub>4</sub> ) <sub>6</sub> (OH) <sub>2</sub> .20H <sub>2</sub> O	XRD, SEM/EDS
Bilinite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> .22H <sub>2</sub> O	XRD
Römerite	Fe <sup>2+</sup> Fe <sup>3+</sup> <sub>2</sub> (SO <sub>4</sub> ) <sub>4</sub> .14H <sub>2</sub> O	XRD, SEM/EDS



**Fig. 1.** SEM photographs of efflorescent minerals on altered pyrite: a) a plate-like aggregate of copiapite splitting crystals; b) szomolnokite fibrous formation, a-b) Magura-Hondol; c) flake-like porous aggregates of metahohmannite?, Madzharovo; d) kornelite masses on highly oxidized pyrite surface, Kratovo; e) a spherulite aggregate, composed of coquimbite hexagonal crystals, Rio Tinto

recent minerals are mostly white, yellowish, and greyish to pale green in colour. Under high magnification, it is revealed that sulphates occur as fibrous or thick tabular crystals, plate-like, spherulite or rosette-like aggregates, etc. (Fig. 1). In samples from the Magura-Hondol deposit also rhomboclase was found as plate-like crystals with bipyramidal forms. Copiapite is one of the most common phases. The detailed investigation under SEM reveals that the newly formed phases, including coquimbite, quenstedtite, bilinite, and others are preferably formed on pyrite octahedral faces. Regardless of the exact surface structure, our observations confirm the accepted notion that reaction rates of non-equivalent crystallographic orientations may differ significantly. The results imply that crushed pyrite used in batch experiments represents an ensemble of crystals with different crystallographic orientations and, therefore, different reactivity rates.

## References

- Atanassova, R. 2008. Environmental impact of pyrite with different textures in mining areas. – In: *33<sup>rd</sup> International Geological Congress*, August 6–14, 2008, Oslo, Norway, Abstract CD-ROM.
- Jambor, J. L., D. K. Nordstrom, C. N. Alpers. 2000. Metal-sulphate salts from sulphide mineral oxidation. – In: Alpers, C. N., J. L. Jambor, D. K. Nordstrom (Eds.). *Sulfate Minerals: Crystallography,*

## Conclusions

The radial-fibrous pyrites with very high reactivity, much higher than that of massive varieties (Atanassova, 2008) exposed to atmosphere undergo alterations resulting in formation of highly soluble products. Diverse porous Fe-sulphates occur very fast when pyrite were artificially weathered in the laboratory.

The dissolution of these efflorescent minerals can generate acid mine drainage with high concentrations of metals (Jambor et al., 2000). This phenomenon is common at mine waste sites and is an important cause of contamination of the surface waters and soils.

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- Geochemistry, and Environmental Significance. – *Rev. Mineral. Geochem.*, 40, 303–350.
- Rimstidt, J. D., D. J. Vaughan. 2003. Pyrite oxidation: A state-of-the-art assessment of the reaction mechanism. – *Geochim. Cosmochim. Acta*, 67, 873–880.
- Rosso, K. M., D. J. Vaughan. 2006. Sulfide mineral surfaces. – In: D. J. Vaughan (Ed.). *Sulfide mineralogy and geochemistry*. – *Rev. Mineral. Geochem.*, 61, 505–556.