

## IN VITRO WEATHERING PRODUCTS OF PYRITE

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## ABSTRACT

Fine grained natural pyrite concretions oxidize spontaneously under laboratory conditions. A solution of oxidation products in distilled water yields the following crystallization products upon evaporation (in order of formation): melanterite, rozenite, szomolnokite, rhomboclase, coquimbite, roemerite, a slightly basic ferric sulphate, and voltaite. The crystallization sequence is comparable to that found in natural environments where pyrite ores are oxidizing.

## INTRODUCTION

Natural pyrite concretions, which are frequently found in clays of marine and coastal environments of all ages, are very easily weathered when exposed to the atmosphere.

Under dry weather, conditions concretions are frequently covered with white, crystalline oxidation products. X-ray diffraction analysis of these products reveals that they consist of a mixture of ferrous and ferric sulphates. In order to establish the sequence and variety of these weathering products of pyrite, natural pyrite concretions were artificially weathered in the laboratory and subsequent crystallization products were identified.

## METHODS

Experiments were done with pyrite concretions from Middle Oligocene clays and with pyritized wood of Late Pliocene age, both from The Netherlands. Samples were X-rayed, and pyrite was found to be the only crystalline phase in both materials.

Pieces of each of the samples were washed, in order to remove adhering clay, put in a beaker with distilled water and kept at 25°C for one week.

After this week the fluid was filtered through a paper filter, pured into petri discs and allowed to evaporate. Crystallization products were hand-picked and identified with the aid of X-ray diffraction analysis (quadruple Guinier-de Wolff camera, Co K-alpha radiation).

Samples for X-ray diffraction analysis were powdered and mounted in grease as to prevent dehydration.

Some crystalline phases were artificially prepared from pure solutions.

## RESULTS

The first crystallization products were green, rhombohedral crystals, identified as *melanterite* ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). When these crystals were allowed to dry for a few moments, a mixture of melanterite and *rozenite* ( $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ ) was found. When crystallization proceeded, only rozenite was formed, and melanterite was converted into rozenite. This was also observed in a synthetic solution of ferrous sulphate in dilute sulphuric acid. Initially melanterite was formed, with crystals as large as 1 cm  $\phi$ . After a few days, these crystals (still in the solution) redissolved, and smaller crystals of green rozenite were formed.

Upon further evaporation (concentration of the brine), rozenite converted into *szomolnokite* ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). Siderotil ( $\text{FeSO}_4 \cdot 5\text{H}_2\text{O}$ ) was found only once, as an intermediary phase between melanterite and rozenite.

The szomolnokite, that covered the bottom of the petri discs, was soon intimately mixed with *rhomboclase* ( $\text{FeH}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ ).

On this groundmass, yellow and rosa efflorescences were formed identified as: a slightly basic ferric sulphate ( $\text{Fe}_7(\text{SO}_4)_9 (\text{OH})_3 \cdot n\text{H}_2\text{O}$ ) and as *roemerite* ( $\text{Fe}^{++}\text{Fe}_2^{+++}(\text{SO}_4)_4 \cdot 12\text{H}_2\text{O}$ ) respectively.

Szomolnokite and rhomboclase were partially overgrown with white, spherulitic *coquimbite* ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ).

The last phase to appear existed of pitch black regular crystals and rosettes that were identified as *voltaite* ( $\text{K}_2\text{Fe}_5^{++}\text{Fe}_4^{+++}(\text{SO}_4)_{12} \cdot 18\text{H}_2\text{O}$ ). (Fig. 1) These aggregates never exceeded 1 mm, while single crystals were smaller than 0.5 mm.

The pH in the solution was below 1 during the whole experiment.

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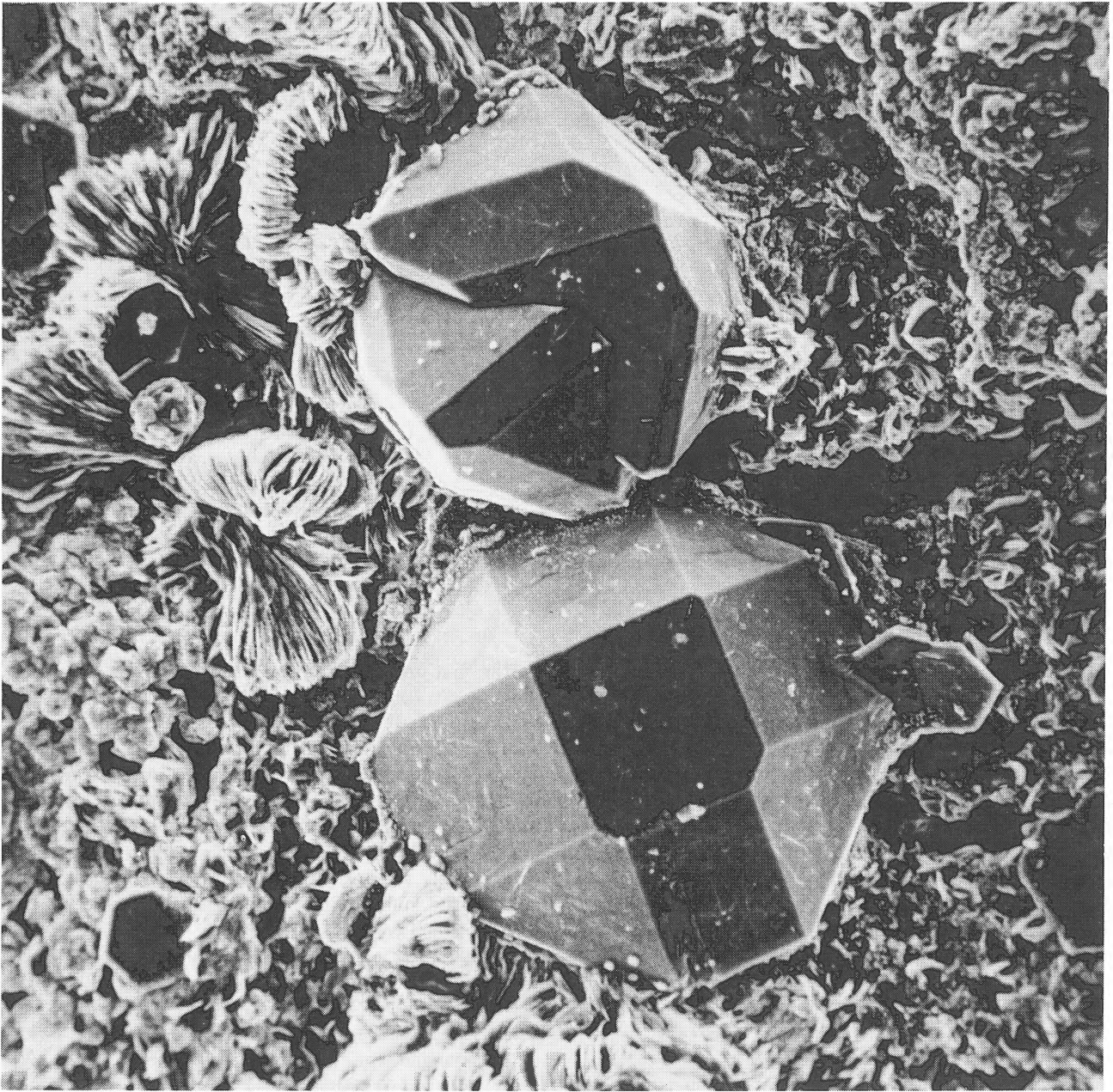


Fig. 1  
Scanning electron micrograph of voltaite crystals. 262 x, TFDL 340-8

At the time that the experimental part of this project was carried out, (1972/73) an appropriate X-ray diffraction pattern of rhomboclase was not yet available. Therefore the mineral was prepared artificially by mixing ferric sulphate with sulphuric acid in molar ratio's 2:1, 1:1, 1:2 and 1:3. Rhomboclase was the only crystalline phase formed in this trial, after evaporation of the solution. It formed euhedral crystals in the 1:3 solution, but not in the other ones. (fig. 2).

Recently, an X-ray diffraction pattern of rhomboclase was published by Van Tassel (1974). This pattern coincides very well with the data obtained by the present author.

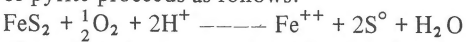
Szomolnokite too was prepared artificially by evaporation of a solution of ferrous sulphate in sulphuric acid. Well shaped crystals were formed. (fig. 3).



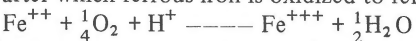
Fig. 2  
Scanning electron micrograph of rhomboclase (synthetic). 3500 x, TFDL 340-3

#### DISCUSSION

According to van Breemen (1973), the initial oxidation of pyrite proceeds as follows:

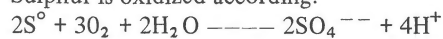


after which ferrous iron is oxidized to ferric iron:



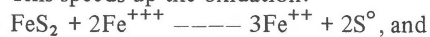
The second reaction is very slow, unless oxidizing bacteria are present, which is very unlikely at the given pH.

Sulphur is oxidized according:



The weathered part of the pyrite nodules had not been removed before the experiment, so that there is a fair amount of  $\text{Fe}^{+++}$  ions in solution.

This speeds up the oxidation:



so that the overall reaction in this case will be:

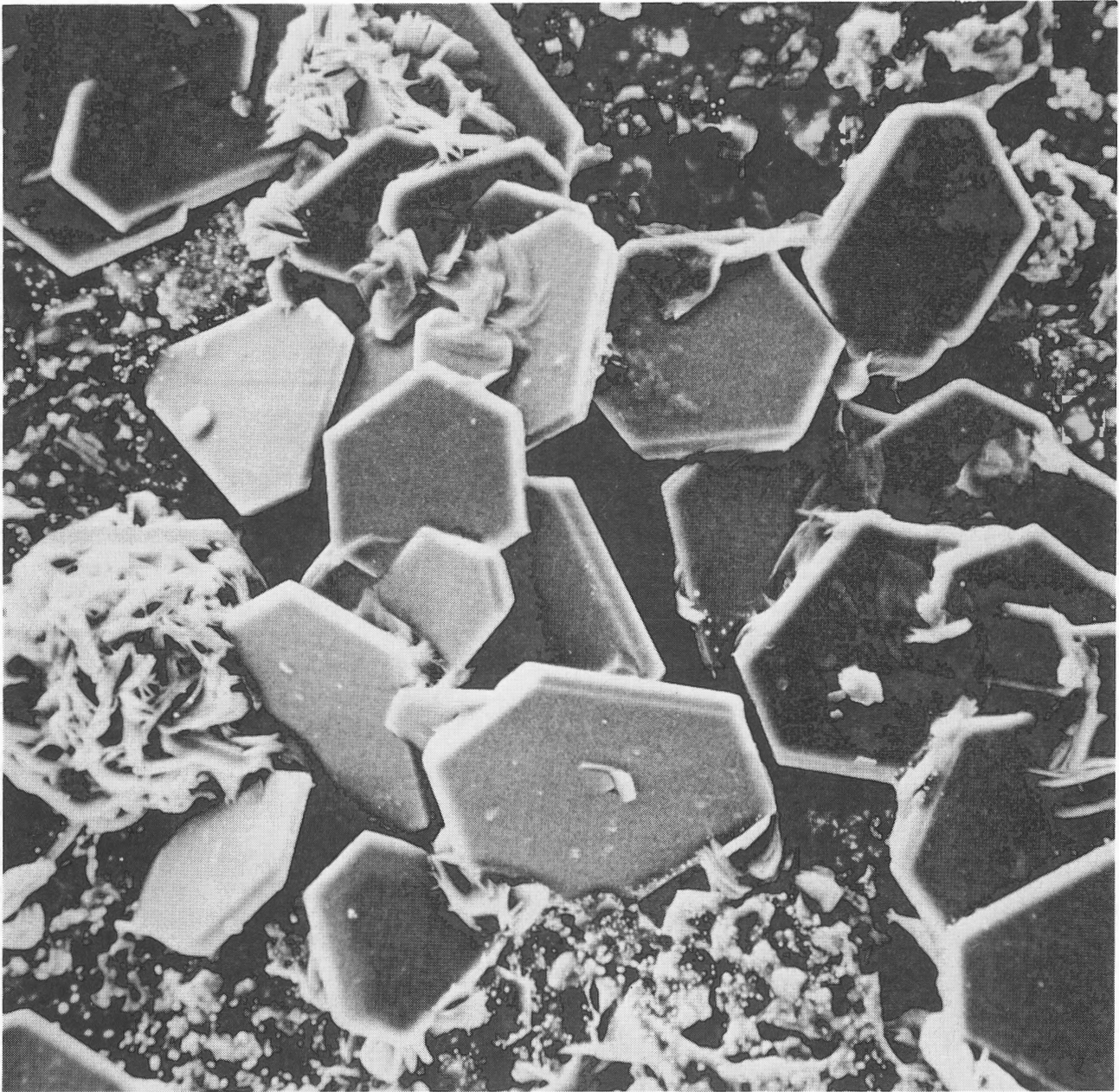


Fig. 3  
Scanning electron micrograph of szomolnokite (synthetic). 525 x, TFDL 340-6

$\text{FeS}_2 + 14\text{Fe}^{+++} + 8\text{H}_2\text{O} \text{-----} 15\text{Fe}^{++} + 2\text{SO}_4^{--} + 16\text{H}^+$   
In absence of bacteria, the oxidation of  $\text{Fe}^{++}$  to  $\text{Fe}^{+++}$  is very slow, so that  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{SO}_4^{--}$  and  $\text{H}^+$  are the dominant ion species in the solution. When this solution is left to evaporate, the following crystallizations occur:

$\text{Fe}^{++} + \text{SO}_4^{--} + 7\text{H}_2\text{O} \text{-----} \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  (*melanterite*)

Because of the very high ionic strength of the solution, which is still increasing upon evaporation of the water, the activity of  $\text{H}_2\text{O}$  in the solution decreases. Nor melanterite,

nor hexa- and pentahydrates are stable, and rozenite is formed at the expense of melanterite:

$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} \text{-----} \text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  (*rozenite*) +  $3\text{H}_2\text{O}$   
and from the solution:

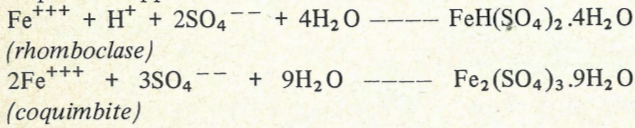
$\text{Fe}^{++} + \text{SO}_4^{--} + 4\text{H}_2\text{O} \text{-----} \text{FeSO}_4 \cdot 4\text{H}_2\text{O}$  (*rozenite*)

Upon further dessiccation, rozenite becomes instable and loses part of its water: szomolnokite is formed:

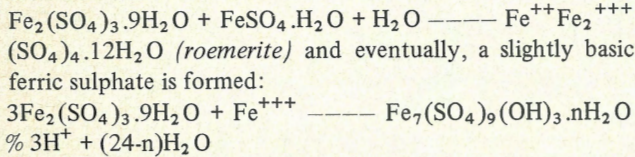
$\text{FeSO}_4 \cdot 4\text{H}_2\text{O} \text{-----} \text{FeSO}_4 \cdot \text{H}_2\text{O} + 3\text{H}_2\text{O}$

In this stage of the evaporation, the ion product of rhom-

boyclase is reached. In an acid environment, acid sulphates are more stable than neutral sulphates, and therefore neutral sulphates are not formed before part of the H<sup>+</sup> is incorporated in acid sulphates. Thus first rhomboclase and then coquimbite appear:

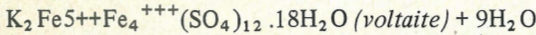
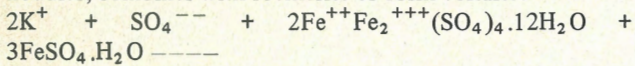


Part of the coquimbite combines with szomolnokite to form roemerite:



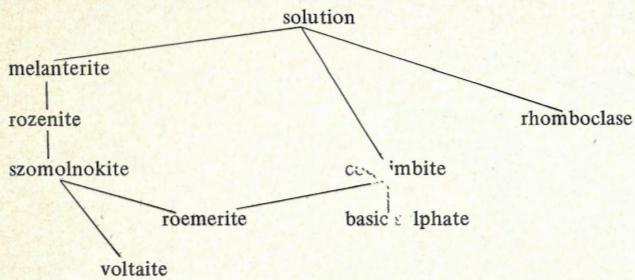
The formation of roemerite is hindered by the fact that it consumes H<sub>2</sub>O. Further formation of basic sulphates, such as hohmannite, amarantite or butlerite is inhibited by the slightly acid environment.

Potassium, till now in solution, and probably present as a result of the dissolution of impurities (clay) in the pyrite nodules, combines with roemerite to form voltaite:



This reaction will probably proceed till K<sup>+</sup> in solution is exhausted, because the formation of voltaite produces water instead of consuming it.

The overall crystallization scheme is probably as follows



As thermodynamic properties of most of the crystalline components involved are not known at present, and activity coefficients in the highly concentrated brine are not easily calculated, it is not yet possible to construct stability diagrams of this system.

The sequence of crystallization described here is very similar to the zonation around weathering pyrite in Chilean sulphate deposits (Bandy, 1938). When the aluminium sulphates are omitted, the initial part of Bandy's oxidation sequence is:

pyrite-szomolnokite-roemerite-quenstedtite-coquimbite-copiapite voltaite

This sequence describes the zonation around oxidizing pyrite and it is therefore a reflection of the oxygen pressure in the deposit.

In the present paper, roemerite is described as a combination of coquimbite and szomolnokite, because both these phase appear earlier, while in Bandy's sequence, roemerite is the oxidation step between szomolnokite and quenstedtite (Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·10H<sub>2</sub>O). Quenstedtite was not formed in the present trial, because of the low H<sub>2</sub>O activity.

Bandy's sequence proceeds with a series of basic ferric sulphates and, finally, ferric hydroxides. In the present investigation the sequence cannot stretch so far, because it is not an open system where leaching occurs. Petri-discs with fully crystallized material, that were kept for two years at approximately 20°C, did not show any further evolution.

As all the sulphates encountered in the present investigation are very soluble in water, accumulation of vast amounts of these around pyrite concretions in the field will hardly ever occur. Nevertheless, because the weathering of pyrite can be quite rapid, and evaporation of the solvent water may occur within days, we will occasionally find freshly weathered pyrite concretions covered by a mixture of hydrated ferrous sulphates, ferric sulphates, and intermediates, as described in this paper.

REFERENCES

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