Sulphate mineralization from one locality in Lozen ore field, Eastern Rhodopes

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Abstract. A suite of sulphates from a locality in Lozen ore field in the Eastern Rhodopes has been characterized by chemical analyses and X-ray diffraction. Three mineral species have been identified: epsomite (MgSO₄), pickeringite (MgAl₂(SO₄)₄•22H₂O) and alunogen (Al₂(SO₄)₃•17H₂O). An attempt was made to characterize the phase transformations that occur upon wetting of the studied samples. The results show that at high humidity, pickeringite dissolves, providing constituents for subsequent crystallization of epsomite and alunogen. Further on, upon drying alunogen loses some of its crystallization water and recrystallizes again to pickeringite including magnesium species from the surrounding medium. This study draws light on certain genetic aspects related to the mechanisms and sequence of deposition of sulphate mineralization under similar conditions.

Keywords: deposition of sulphate mineralization, epsomite, pickeringite.

Introduction

Magnesium sulphates are commonly found in evaporitic deposits, as precipitates in salt lakes, and as weathering products of ores and coals (Mauro et al., 2019; Jambor et al., 2000). Recently there has been increasing interest in the study of magnesium salts, their crystal hydrates and complexes, associated with the discovery of significant amounts of sulphate, chloride and chlorides minerals on Mars and with the consideration that such phases occur also on other planets of the Solar System (Vaniman et al., 2004; Rodriguez, van Bergen, 2016; Wilks et al., 2019). There is a wide variety of magnesium-bearing sulphate minerals, their diversity being due to the quick response of sulphate systems to the physical and chemical conditions of the environment. Therefore, there exists an interest in the moisture and temperature dependent phase transformation of sulphate hydrates (Kahlenberg et al., 2015; Ju et al., 2023). In Bulgaria, natural magnesium sulphate hydrates have not been subject to targeted research and have only been mentioned occasionally as weathering products. The following localities have been reported for the above mentioned sulphates so far: epsomite: Madzharovo, Eastern Rhodopes,
Chiprovtsi, and Milin Kamak, Srednogorie; pickeringite: Obichnik, Momchilgrad district, Chiprovtsi, Western Stara Planina, and from Pirin mine, Blagoevgrad region; alunogen: Sofia district, Pirin mine, Blagoevgrad region (Kostov et al., 2022).

This paper presents preliminary data on secondary sulphate mineralization in an abandoned exploration drift mine situated in Lozen ore field, Eastern Rhodopes. We also comment on the phase transitions that occur during the wetting and subsequent drying of the samples under investigation.

**Materials and methods**

The studied sample was kindly provided by the staff of the “Educational Museum of Mineralogy, Petrology and Economic geology”, Faculty of Geology and Geography of Sofia University “St. Kliment Ohridski” (cat. no. M7862, sample size 22 × 12 × 4.5 cm) (Fig. 1a). The specimen has been collected from a locality of Lozen lead-zinc ore field (Fig. 1c). It is embedded in the acidic rocks of the Lozen paleovolcano complex, with Priabonian age. Pyroclastites and lavas of rhyolite and trachyrhyolite composition are cut by numerous faults with NW, N and NE orientation. The rock complex is deeply hydrothermally altered within the Lozen locality (Harkovska et al., 1976). The main ore minerals are galena and sphalerite, and minor ones are chalcopyrite and pyrite. A relatively strong weathering crust has been superimposed on the hydrothermally altered rocks and ore mineralization. Sulphate mineralization was deposited within the first 15 meters on the floor and the walls of an old exploration drift mine (Fig. 1d).

A 10 g piece of the studied sample (Fig. 1a) was initially used for scanning electron microscope (SEM) and energy dispersive spectral (EDS) analyses – JEOL JSM-6010 PLUS/LA electron microscope at 20 kV accelerating voltage and vacuum medium in the range of 10–4 Pa. Subsequently it was ground and investigated by X-ray fluorescence (XRF) performed using Supermini 200 spectrometer – Rigaku, Japan. Data were collected at 50 kV and 4.00 mA, the sample was prepared without additives. The same material was subjected on powder X-ray diffraction (PXRD) performed on Empyrean, Panalytical diffractometer XRD, 2Θ range 5–100, CuKα radiation (λ = 1.54 Å).

The experiments aiming to study the phase transformation with supplemental semi-quantitative phase analyses were performed as follows: 0.1 g of the powder sample preliminary characterized by XRF was placed in a zero background holder. After the first measurement 0.5 ml of distilled water was dropped on the sample without removing it from the holding device. Two subsequent measurements were taken after 2 and 16 hours, correspondingly using the same experimental conditions.

**Results and discussion**

The studied sample is a typical weathering product in terms of its physical characteristics. It is light in color, lightweight, soft and fragile (Fig. 1a). Under an optical microscope, it appears to be relatively uniform and composed of mutually inter-grown needle shaped crystals. The SEM images magnification allows to establish that actually these are composed of bundles of similarly oriented tiny crystals (Fig. 1b).

The EDS analysis carried out on these bundles reveal energy spectra of only Mg, Al, S and Zn. The results from the XRF semi-quantitative analyses in mass % are as follows: 8.02% MgO, 17.66% Al2O3, 64.4% SO3, 7.86% ZnO, 2.01% CuO.

PXRD patterns are presented in Figure 1e. DDM semi-quantitative analyses performed with program HighScore Plus 5.2 reveal that the initial batch contains 35.7 wt % epsomite and 64.3 wt % pickeringite, which is in good agreement with the obtained chemical composition. Possibly, small amounts of zinc incorporate pickeringite and epsomite compositions, whereas copper is part of another phase that we have not been able to identify. When water has been added to the sample, a partial dissolution of pickeringite and crystallization of alunogen and epsomite on its account has occurred according to the following equation:

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\begin{align*}
n\text{MgAl}_2(\text{SO}_4)_2 \cdot 22\text{H}_2\text{O} + 2n\text{H}_2\text{O} & \rightarrow n\text{Al}_3(\text{SO}_4)_2 \cdot 17\text{H}_2\text{O} + \\
& + n\text{MgSO}_4 \cdot 7\text{H}_2\text{O} \quad (0 < n < 1) \\
& \text{pickeringite} \\
& \text{alunogen} \\
& \text{epsomite}
\end{align*}
\]

This process is found to be reversible. Two hours after the water has been added, the sample contains 41.2 wt % epsomite; 21.3 wt % pickeringite; and 37.4 wt % alunogen. After 16 hours of drying the amount of alunogen decreases to 18.2 wt % whereas those ones of epsomite and pickeringite increase up to 46.4 and 35.4 wt %, correspondingly. These data are indicative and more in-depth quantitative studies (Rietveld method) are needed to better reflect the mass transfer and balance in the sample. Either way, they indicate an increasing over time epsomite content in the sample.

The overall picture of the mineral-forming process could better be understand by comparing the crystal structures of the three considered phases (Fig. 1f). All they are composed of Mg and/or Al octahedra, SO4 tetrahedra and free water molecules in different ratios for each of them. This fact suggests kindred crystal chemical relations between these compounds and easily reversible mutual phase.
Fig. 1. a, the studied sample; b, SEM image of the studied sample; c, schematic presentation of the Lozen locality geological setting (Boyanov et al., 1992); marked with blue rectangle is the exploration drift mine d, where the sample was collected; e, PXRD patterns of the studied sample; f, arrangement of the structural units in the crystal structures of epsomite, pickeringite and alunogen.
transformations when water is added or removed. Upon drying these structures that contain the least amount of crystallization water remain stable. The results are interesting from the point of view of some genetic aspects related to the mechanisms and sequence of deposition of sulphate mineralization in the described locality. With fully expected cyclic changes in the humidity of the mineral-forming environment, it is possible that initially deposited pickeringite undergoes repeated processes of dissolution and re-deposition in the manner described by the above equation. In doing so, the unstable intermediate phase alunogen and epsomite are formed. The latter however is the most stable in this association and quantitatively accumulates over time at the expense of the other two minerals. The registered accompanying elements Zn and Cu are also involved in the described processes either isomorphously entering the structures of the main phases or by forming their own species. Crystallographic studies on these issues are in progress.

Conclusions

Secondary sulphate minerals analytical data are presented for the first time for a new locality from Eastern Rhodopes. Preliminary studies indicate that upon wetting epsomite and pickeringite start to dissolve providing constituents for formation of the intermediate phase – alunogen. Subsequent drying results in partial recrystallization of pickeringite and epsomite on the account of alunogen and with the possible participation of impurity elements such as Cu and Zn. The recrystallization process passing through intermediate products increases the amount of epsomite. Such mechanism suggests that the cyclic wetting and desiccation of sulphate minerals in similar localities results in continuous redeposition of different mineral types through time and space. Detailed studies of the crystal structures and physicochemical characteristics of the sulphate minerals from the described locality are forthcoming.

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References


