PHOSPHATE-BEARING MINERALS IN ADVANCED ARGILLIC ALTERATION ZONES OF HIGH-SULPHIDATION ORE DEPOSITS IN THE CARPATHO-PANNONIAN REGION

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Abstract: Ca-bearing Al-sulphate-phosphate (APS) minerals with REE elements were found in hydrothermal alunite of advanced argillic alteration zones in the high-sulphidation type epithermal systems of Velence Mountains (Hungary) and Klokoč, Podpolom (Slovakia). Their occurrence together with alunite indicates extensive leaching of apatite in the host rock by strongly acidic, sulphate-bearing magmatic-hydrotermal fluids with fluctuating characteristics.

Key words: high-sulphidation, advanced argillic alteration, APS minerals, phosphates, alunite

Introduction

During the examination of a Palaeogene and a Neogene high-sulphidation type epithermal deposit sulphate-phosphate (APS) minerals were detected, which have not been mentioned from the examined areas until now. APS minerals were found in the advanced argillic alteration zones of the systems, mostly in alunite, but sometimes separately as well. The characteristics and proposed genesis of these phosphate-bearing minerals from the eastern part of the Velence Mountains (Hungary) and the Podpolom gold deposit (Klokoč, Slovakia) are discussed below.

Geological background

In the eastern part of the Velence Mountains (situated about 50 km SW to Budapest) hydrothermal alteration zones are developed in an andesitic stratovolcanic sequence of Eocene-Lower Oligocene age located above a subvolcanic diorite intrusion. The vuggy silica bodies surrounded by alunite-quartz-pyrite(-hematite)-kaolinite alteration assemblage appear in the near-surface portion of the alteration zones, 300 to 500 m above the intrusive body and represent a typical high-sulphidation type environment. Tabular alunite crystals of up to 1 mm size occur in the cavities formed after leached phenocrysts of the porphyry andesite (Fig. 1). Sulphur isotope composition of alunite indicates magmatic-hydrothermal origin.

The Podpolom high-sulphidation type epithermal deposit (Štohl et al, 1999) is located at the center of the Javorie andesite stratovolcano, a part of the Central Slovakian Volcanic Field, formed from the Badenien through Pannonian. It is one of the hydrothermal centers related to the stock-like-form dioritic bodies that intruded the andesitic stratovolcanic sequence. The gold mineralization occurs in a ferruginous breccia that has developed in the central core of a barren silicified zone. Abundant tabular alunite crystals up to 0.1 mm in size, in association with pyrite or limonite appear rimming the cavities of the vuggy silica or form patches in the matrix of the siliceous breccia (Fig. 2).

Appearance of phosphate-bearing (APS) minerals

The phosphate-bearing minerals can be detected only by scanning electron microscope. They appear mostly as bright, irregular-ragged portions in hydrothermal alunite (Fig. 3, 4, 5) or form cores of alunite crystal groups. They also occur in the silica matrix, separate from the alunites (Fig. 6). The rim of phosphate minerals can be discrete or diffuse, their irregular shape suggest dissolution. These minerals in the Velence Mountains are mostly Ca-dominant Al-sulphate-phosphates or -phosphate-sulphates with variable amount of Ba, K and Sr (Fig. 7). REE (Ce, La) enrichment occurs usually at the rim of some minerals. At Podpolom they are composed mainly of (K-Ca-Ba)-Al-(S-P) and (Ca-Ba-K-Sr)-Al-(P-S) elements, respectively (Fig. 8). The Ca-dominant phosphate-sulphate minerals also contain REE elements at the rims or sometimes in the core.

The APS minerals seem to be solid solutions of different end-member minerals of the alunite, woodhouseite and crandallite mineral groups (Ca-bearing woodhouseite and crandallite, Sr-bearing svanbergite and goyazite, Ba-bearing gorceixite, the REE-bearing florencite and K-bearing alunite). Several cations can be present due to the possible complete solid solution within the woodhouseite mineral group and limited solid solution between alunite and woodhouseite mineral groups and woodhouseite and crandallite mineral groups, respectively (Wise, 1975, Stoffregen & Alpers, 1987).

Genesis of the phosphate-bearing minerals

The presence of phosphate-bearing minerals in close connection with hydrothermal alunite indicates the hydrothermal origin of these phases. In high sulphidation systems primary alunite is formed by acidic magmatic-hydrothermal fluids, which are produced by the condensation of magmatic HCl, SO_2 and HF gases into groundwater (Hedenquist & Arribas, 1999). Dissolution of magmatic apatite by these acidic fluids at high temperatures can induce the precipitation of APS minerals (Stoffregen & Alpers, 1987). The early formation of sulphate-phosphate minerals sometimes with REE followed by dissolution and subsequent precipitation of alunite shows the fluctuating characteristics of hydrothermal fluids.

Similar APS minerals (woodhouseite, svanbergite, florencite, crandallite) were also found in the core of magmatic-hydrothermal alunite from other high-sulphidation ore deposits, e. g. Summitville, Colorado, USA (Stoffregen & Alpers, 1987), Baguio district, Philippines (Aoki et al., 1993), Nansatsu, Japan (Hedenquist et al., 1994), Rodalquilar, Spain (Arribas et al., 1995) and Lepanto, Philippines (Hedenquist et al., 1998). In the Carpathian-Balkan region APS minerals were described from the alunite- and/or pyrophyllite-quartz alteration zones of the Asarel porphyry copper deposit in Bulgaria (Velinov et al., 1991). The presence of phosphate-bearing minerals in the core of alunite is not typical for steam-heated or supergene alunite; however, a small amount of sulphate-phosphates can also occur together with these types of alunites (e. g. Szakáll & Kovács, 1998).

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Fig. 1. Alunite infillings in a vug after phenocryst. Andesite with advanced argillic alteration, Velence Mountains. Transmitted light, +N

Fig. 2. Alunite, intergrown with pyrite and quartz, filling a vug of the silicified matrix. Siliceous breccia, Podpolom deposit, R4-79.5 m. Transmitted light, +N

Fig. 3. Phosphate-bearing mineral with diffuse edge (light grey-white) in alunite (dark grey). Andesite with advanced argillic alteration, Velence Mountains. BSE image

Fig. 4. Phosphate-bearing mineral with discrete edge (white) in alunite with oscillatory zoning (dark grey). Andesite with advanced argillic alteration, Velence Mountains. BSE image

Fig. 5. Irregular Ca-Al-phosphate (light grey) in alunite (dark grey) with REE enrichment at the rims. Siliceous breccia, Podpolom deposit, R4-79.5 m. BSE image

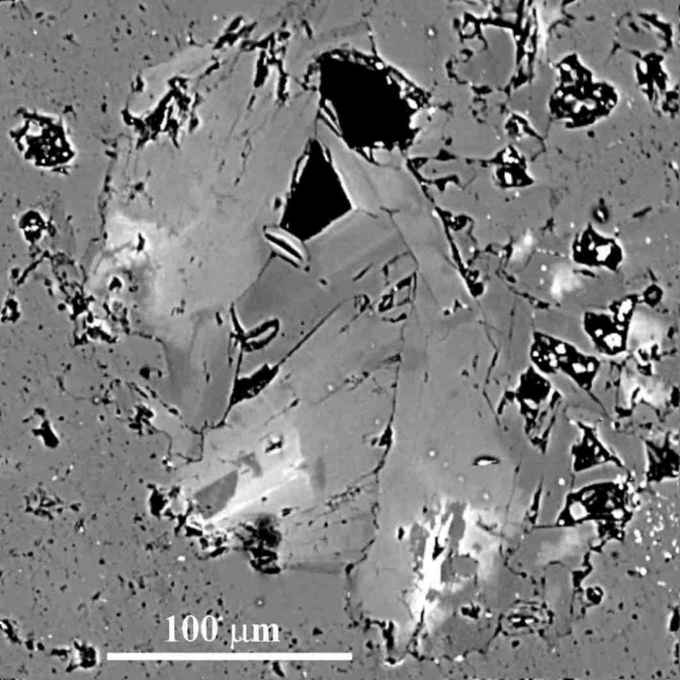
Fig. 6. Irregular Ca-Al-phosphate (light grey) in quartz (dark grey). The lighter parts mark the REE enrichment. Siliceous breccia, Podpolom deposit, R4-79.5 m. BSE image

Fig. 7. EDS spectra of phosphate-bearing minerals, Velence Mountains

Fig. 8. EDS spectra of phosphate-bearing minerals, Podpolom deposit


1 mm


200 μm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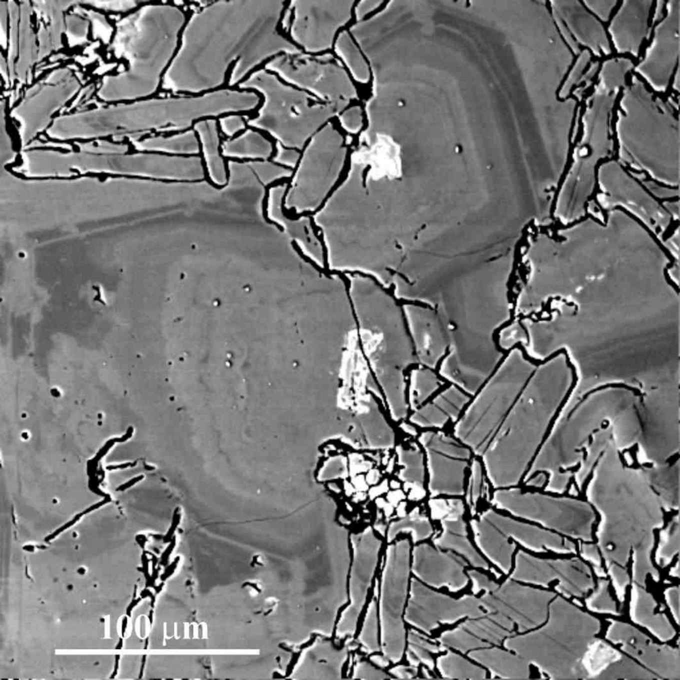
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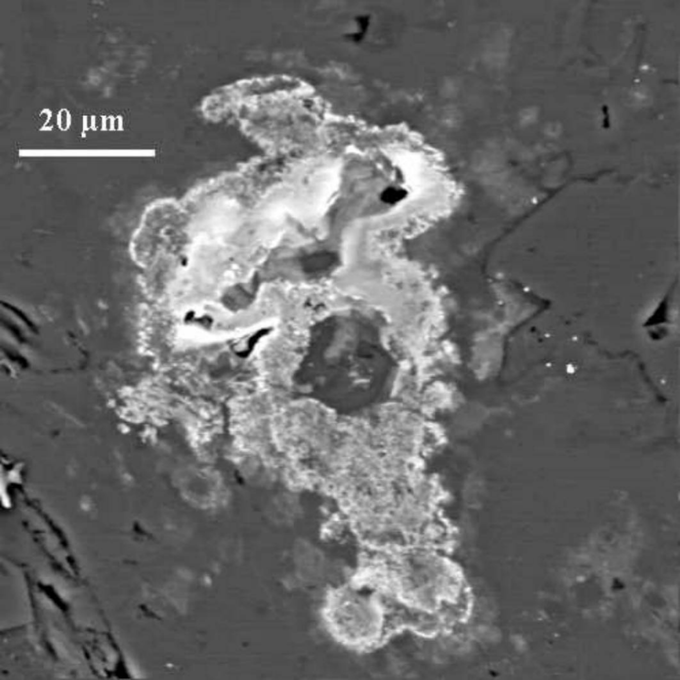
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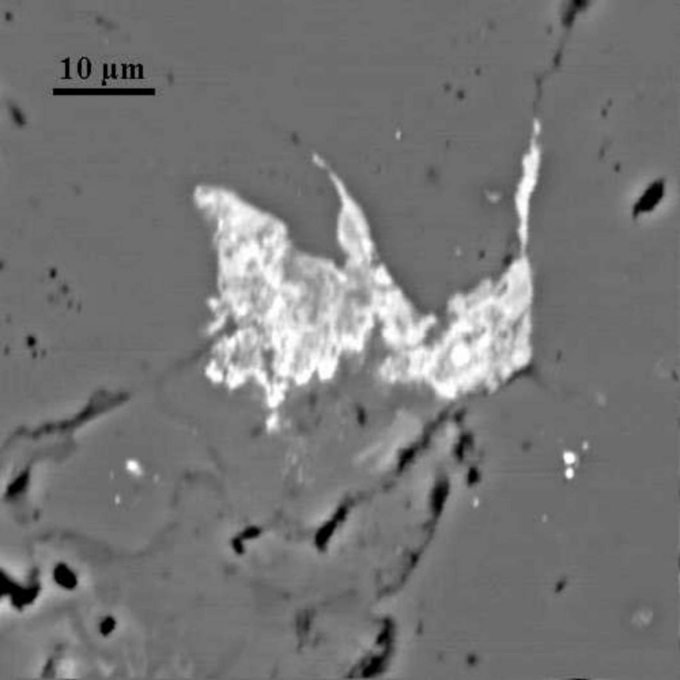
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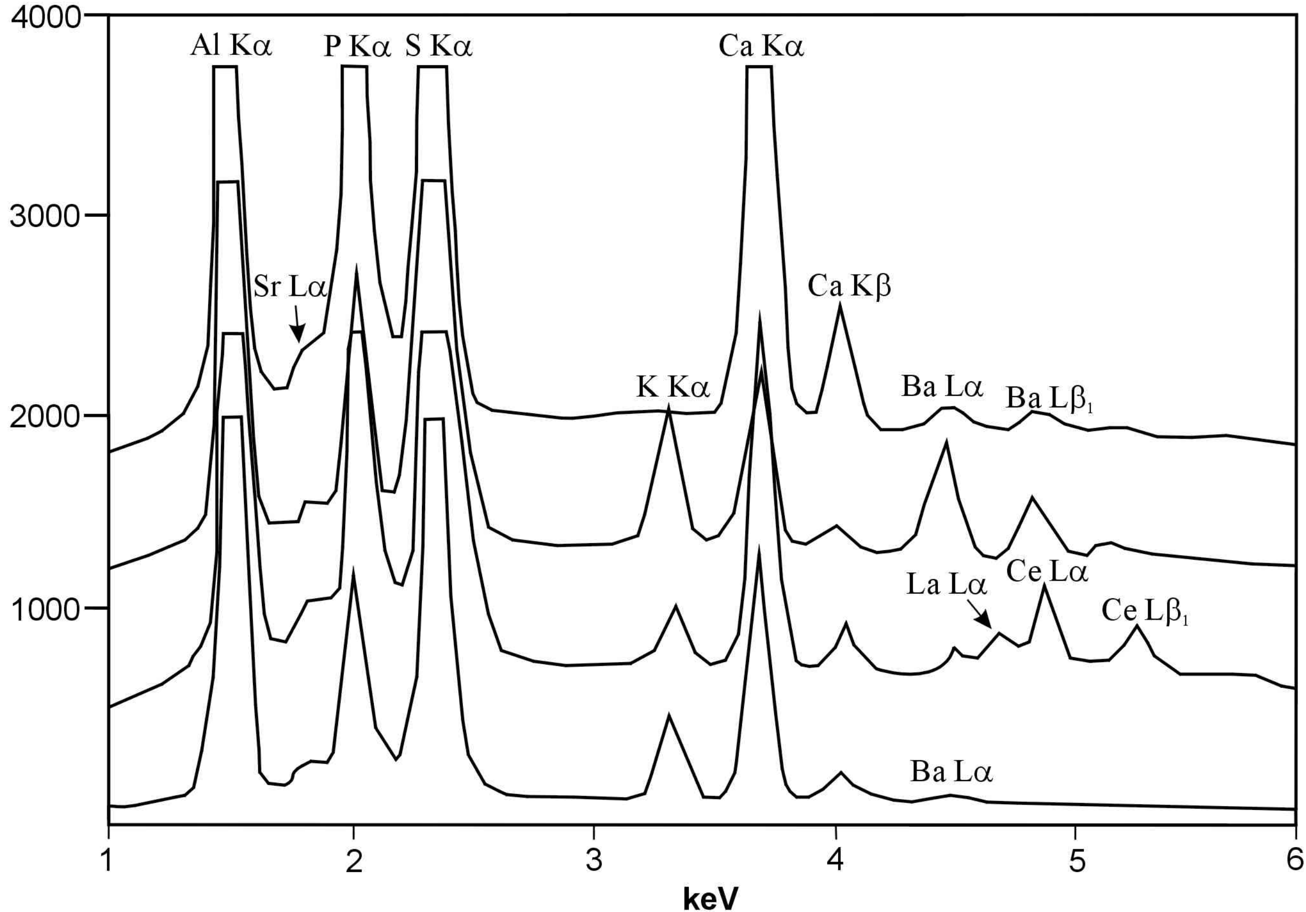
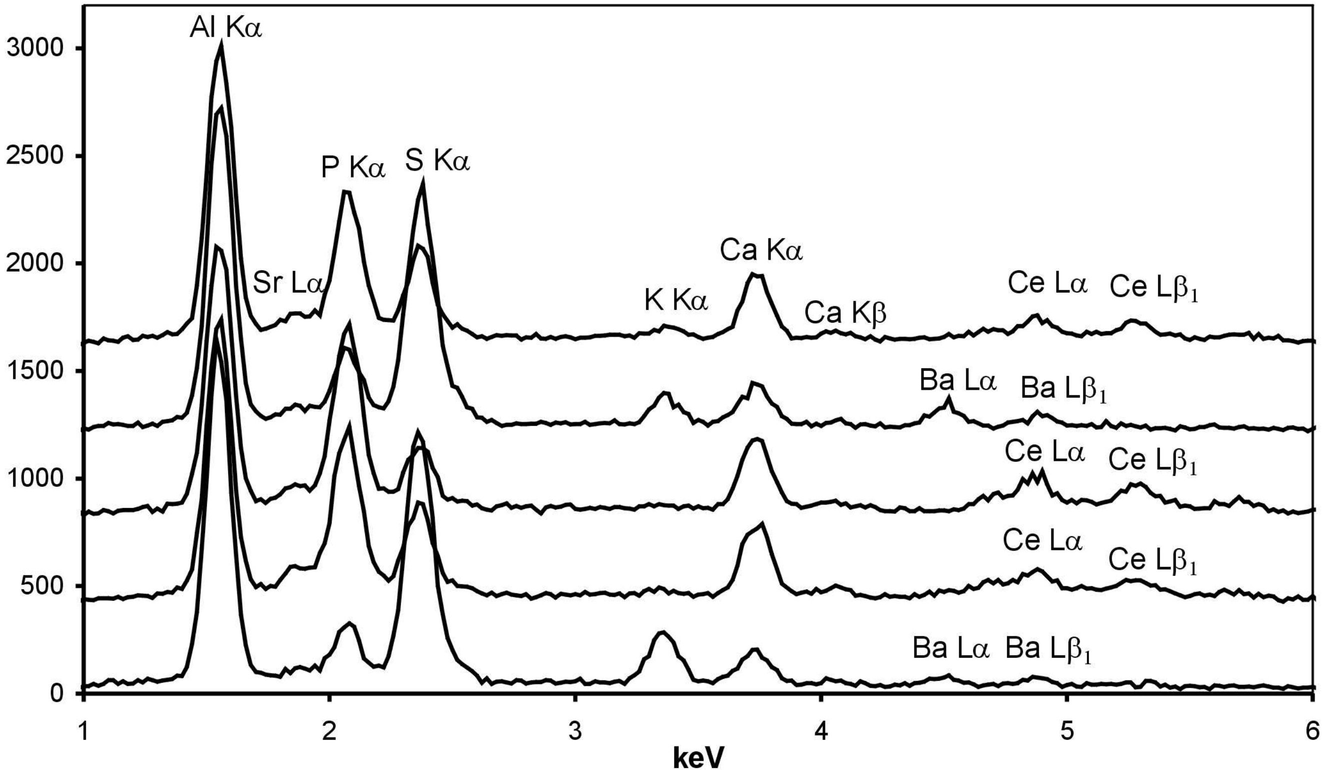


4000
3000
2000
1000
Al Kα
P Kα
S Kα
Ca Kα
Sr Lα
Ca Kβ
K Kα
Ba Lα
Ba Lβ1
La Lα
Ce Lα
Ce Lβ1
Ba Lα
1
2
3
4
5
6
keV



Al Kα
P Kα
S Kα
Sr Lα
Ca Kα
K Kα
Ca Kβ
Ce Lα
Ce Lβ1
Ba Lα
Ba Lβ1
Ce Lα
Ce Lβ1
Ce Lα
Ce Lβ1
Ba Lα
Ba Lβ1
3000
2500
2000
1500
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0
1
2
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5
6
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