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

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ABSTRACT

Ca-dominant, Al-phosphate-sulphate (APS) minerals with minor Ba, Sr, K, Na and REE contents were found in hydrothermal alunite or separately in advanced argillic alteration zones associated with high-sulphidation type epithermal systems in Hungary (Velence Mountains) and Slovakia (Podpolom deposit, Klokoč). Electron microprobe analyses show that these APS minerals are woodhouseite with SO_4^{2-} and PO_4^{3-} molar ratio varying between 1:3 and 2:1.

The occurrence of APS minerals in close association with alunite and other hydrothermal minerals indicates a hypogene origin for these phases. Extensive leaching of magmatic minerals (apatite, feldspar) in the host rock by strongly acidic magmatic-hydrothermal fluids induced the formation of phosphate-bearing minerals. Changing physico-chemical characteristics of the hydrothermal fluids with time resulted in zoning and multiphase formation of these alunite-type minerals, with a common late phase dominated by pure sulphate (alunite). This is the first detailed documentation of hydrothermal APS minerals in alteration systems of the Carpatho-Pannonian region.

Key words: Carpatho-Pannonian region, Velence Mountains, Podpolom deposit, advanced argillic alteration, high-sulphidation, phosphate, Al-phosphate-sulphate mineral, woodhouseite, sulphate, alunite

INTRODUCTION

Alunite-type minerals in epithermal deposits can form under different conditions, from high-temperature acid-sulphate hydrothermal alteration to low-temperature secondary weathering. The hydrothermal alunite-type minerals characteristically display compositional heterogeneity. This is a result of the change in the physico-chemical parameters (e.g. pH, temperature, salinity) of the parent fluids in time and space, which can be influenced by several processes (Aoki, 1991).

Calcium-dominant Al-phosphate-sulphate (shortly APS) minerals, which are the subject of this study, were detected in Tertiary high-sulphidation type epithermal systems (Bajnóczi et al., 2002; Seres-Hartai 2001). The APS minerals were found in the advanced argillic alteration zones of the deposits, mostly in alunite, but separately as well.

The APS minerals studied belong to the alunite family (or supergroup). This isostructural group has the general formula $AB_3(XO_4)_2(OH, H_2O)_6$, where A represents cations like Na^+, K^+, NH_4^+, H_3O^+, Ca^{2+}, Ba^{2+}, Sr^{2+}, Pb^{2+} and REE elements. B site is occupied by the cations Al^{3+}, Fe^{3+}, Cu^{2+} and Zn^{2+}. In nature, the anion (XO_4) is SO_4^{2-}, PO_4^{3-} and AsO_4^{3-} (Scott, 1987). The characteristics, mineralogy and proposed genesis of the phosphate-bearing minerals from the eastern part of the Velence Mountains (Hungary) and the Podpolom gold deposit (Klokoč, Slovakia) are discussed below.

## GEOLOGICAL SETTING AND MINERALOGY

Velence Mountains

In the eastern part of the Velence Mountains (situated about 50 km SW to Budapest), several hydrothermal alteration zones

occur in andesitic volcanic rocks deposited within a stratovolcanic sequence of Eocene-Lower Oligocene age which occurs adjacent to a Palaeozoic granite (Fig. 1). The andesitic stratovolcano sequence is located above a subvolcanic diorite intrusion, which was identified in a 1200 m deep drill hole in the north-western foreground of the Zsidó Hill. Silica bodies surrounded by an alunite-quartz-pyrite(-hematite)-diaspore-kaolinite(-pyrophyllite) alteration assemblage occur in the near-surface portion of the hydrothermally altered areas, 300 to 500 m above the intrusive body in the western zones (Templom, Nyíri and Csúcsos Hills). Closer to the subvolcanic intrusion (Csekély and Cseplek Hills) and in the deeper zones of Zsidó Hill, an assemblage composed of pyrophyllite, diaspore, zunyite and topaz is more abundant in the advanced argillically altered areas (Darida-Tichy et al., 1984; Nemecz 1984; Darida-Tichy, 1987).

The alteration mineralogy and the fluid inclusions of these hydrothermally altered areas in the Velence Mountains represent a typical high-sulphidation epithermal environment with estimated formation temperatures of 220 to 380 °C (Molnár, 1996). Although no economic ore mineralization has been found, some of these altered areas are enriched in Cu, Pb, Zn, Ag, Sn and Mo compared to unaltered rocks (Ódor et al., 1982). In addition, a gold enrichment up to 1 ppm has been observed in parts of quartz-alunite alteration zones (Koch, 1985).

Samples for study from the Velence Mountains were taken from the advanced argillic alteration zones of each of the volcanic hills, which are interpreted to represent separate paleo-hydrothermal centres. In the area of Zsidó Hill, surface and drill core (Pt-3 at 147.6–148.7 m) samples were studied (Fig. 1B).

B. Bajnóczi et al.
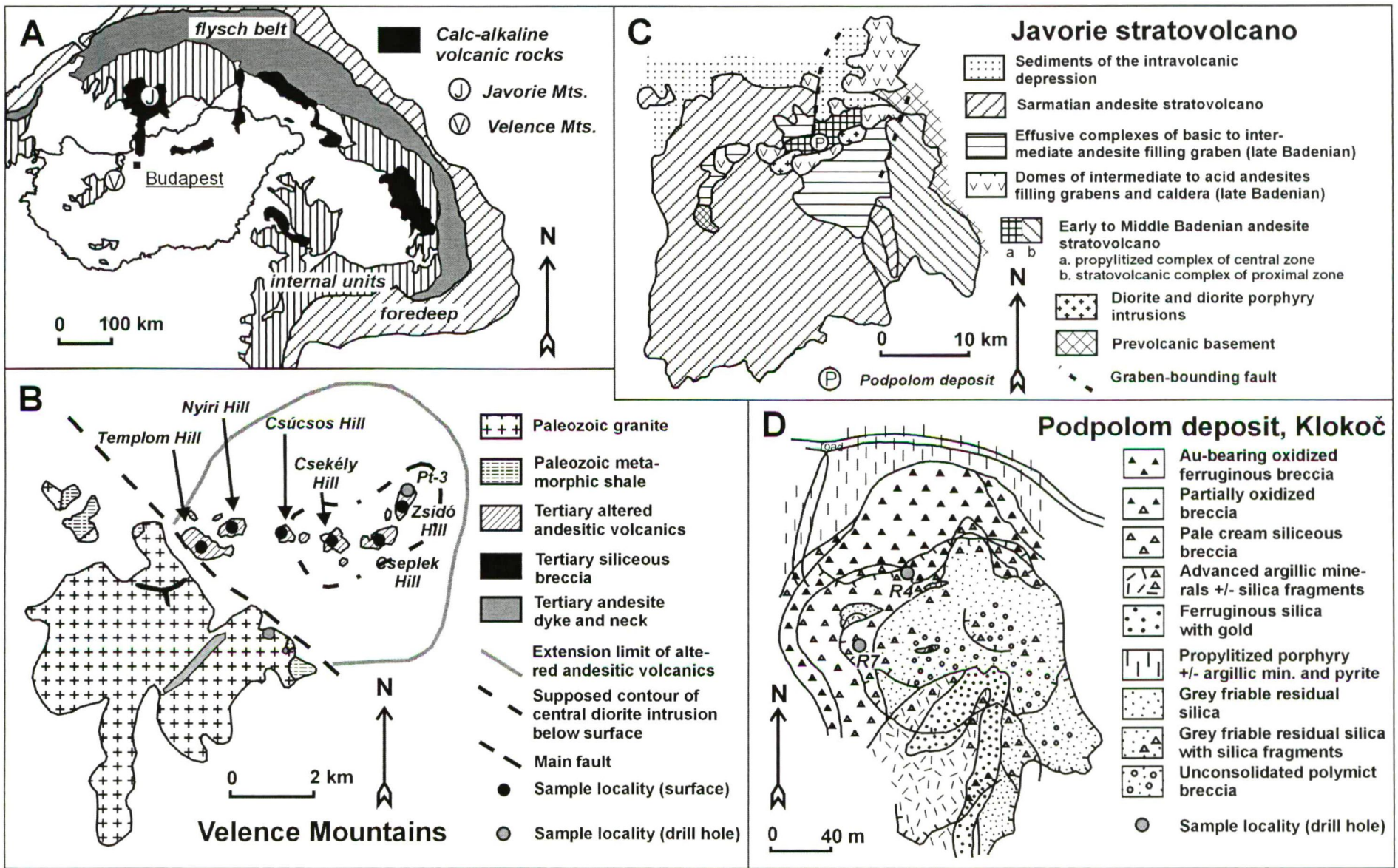
Fig. 1. Location and sketch of the studied high-sulphidation type epithermal deposits with indication of sample localities. *(A)* Position of the Velence and Javorie Mountains containing the studied high-sulphidation deposits in the Carpatho-Pannonian region. *(B)* Schematic geological map of the eastern part of the Velence Mountains (Hungary) (after Darida-Tichy, 1987). *(C)* Structural scheme of the Javorie stratovolcano with the position of the Podpolom deposit (after Konečny et al., 1995). *(D)* Distribution of rock types in the Podpolom deposit (Klokoč, Slovakia) (after Štohl et al, 1999).
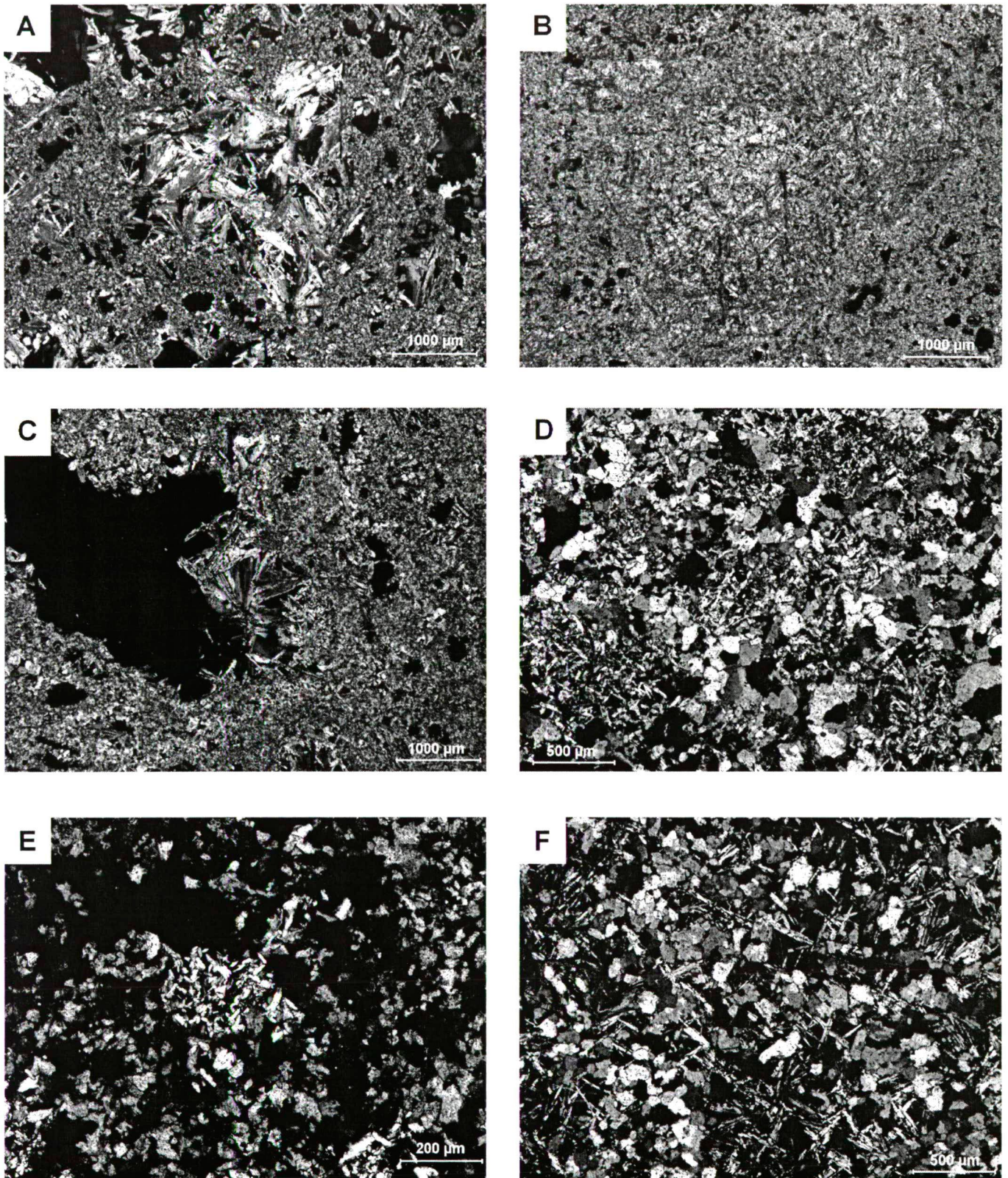
Fig. 2. Photomicrographs showing the texture of the studied hydrothermal rock samples. Transmitted light, crossed polars. *(A)* Tabular alunite crystals in a cavity after phenocryst of andesite and siliceous matrix. Andesite with advanced argillic alteration, Templom Hill, Velence Mountains. *(B)* Alunite infillings in a cavity after phenocryst of andesite and siliceous matrix. Andesite with advanced argillic alteration. Nyíri Hill, Velence Mountains. *(C)* Alunite in a cavity and siliceous matrix. Andesite with advanced argillic alteration, Csúcsos Hill, Velence Mountains. *(D)* Alunite (and some diaspore) in vugs of silicified rock. Weakly brecciated volcanic rock with advanced argillic alteration, Csekély Hill, Velence Mountains. *(E)* Alunite in a vug of silicified rock. Volcanic rock with advanced argillic alteration, Zsidó Hill (surface), Velence Mountains. *(F)* Alunite in vugs of silicified rock. Volcanic rock with advanced argillic alteration, Pt-3 drill hole 147.6-148.7 m, Zsidó Hill, Velence Mountains.
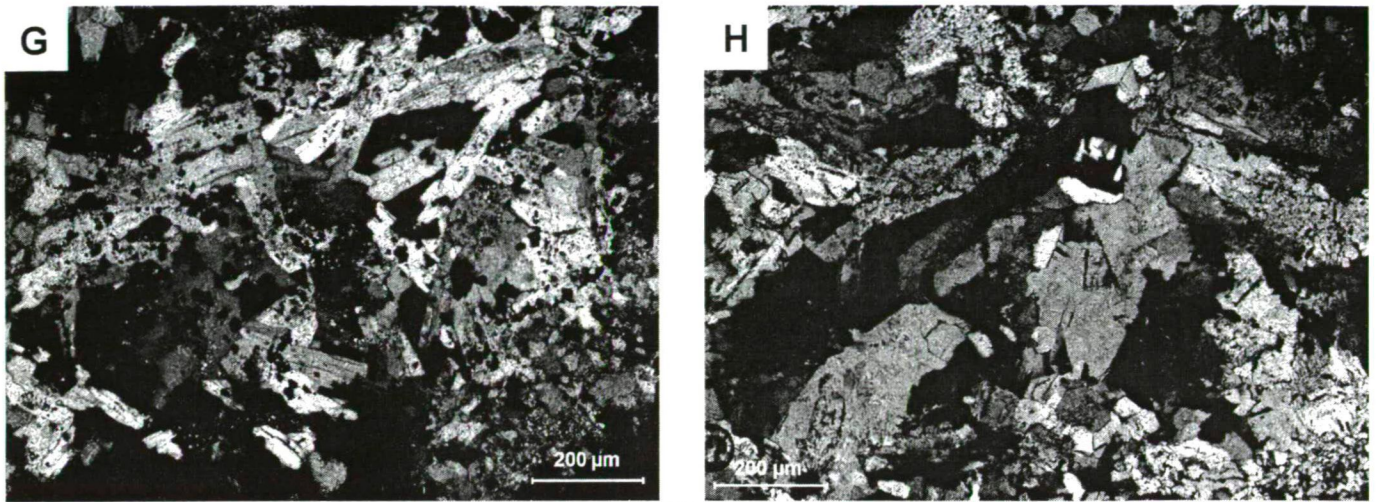
Fig. 2. Photomicrographs showing the texture of the studied hydrothermal rock samples. Transmitted light, crossed polars. *(G)* Tabular alunite and euhedral pyrite in siliceous matrix. Grey, argillic silica, R4 drill hole 79.5 m, Podpolom deposit. *(H)* Tabular crystals of augelite, filling the vugs of the silica matrix. Siliceous breccia, R7 drill hole 84.2 m, Podpolom deposit.

Samples from the Templom, Nyíri and Csúcsos Hills contain alunite, hematite (after pyrite), rutile and siliceous matrix. Tabular alunite crystals of up to 1 mm size occur in the cavities formed after leached phenocrysts of the porphyry andesite (Fig. 2A, B, C). In the Csekély Hill, vugs of weakly brecciated siliceous rock are filled with alunite, rutile and diaspore (Fig. 2D). Similar cavities in silicified rocks in the Cseplek and Zsidó Hills are filled with alunite and rutile, plus topaz in Zsidó Hill (Fig. 2E). Cavities in the sample from Pt-3 drill hole core contain 0.1 to 0.3 mm alunite crystals together with zunyite and abundant pyrite (Fig. 2F). Alunite in all of these hydrothermally altered samples usually displays compositional zoning due to variable Na content (Bajnóczi et al., 2002). The ^{34}S enriched sulphur isotope composition of alunite ($\delta^{34}S = 11.9–25.3‰$; Bajnóczi et al., 2002) is consistent with a high temperature magmatic-hydrothermal origin.

Podpolom deposit

The Podpolom deposit is situated in the central part of the Javorie andesite stratovolcanic sequence of Central Slovakia (Fig. 1). The Javorie stratovolcanic complex was formed between the Badenian and Pannonian and it is intruded by several stock-like diorite and monzodiorite intrusions. The Podpolom deposit is one mineralization centre, and appears at the surface as a silicic and advanced argillic alteration zone related to the intrusive units (Štohl et al., 1999).

At Podpolom, a high-sulphidation epithermal mineralised system developed in an oxidized, ferruginous breccia (Štohl et al., 1999) (Fig. 1D). The average gold grade in the deposit area is 1–2 ppm. Primary gold is associated with pyrite, but in the oxidized ferruginous rocks 1 to 2 μm in size gold grains occur in small cavities in goethite (Seres-Hartai, 2001). Hydrothermally altered rocks in the Podpolom deposit consist of vuggy silica, limonitic breccia, siliceous breccia and grey, argillic silica. Most of the rock types display extreme silicification and multiple episodes of brecciation. The alteration is characterised by the presence of quartz, topaz, corundum, rutile, and (in the more argillic lithologies) pyrophyllite, diaspore and alunite, with minor zunyite, kaolinite and illite.

The samples studied are from two drill holes (Fig. 1D). Abundant alunite was found in R4 drill hole core at 79.5 m depth. Alunite occurs as 0.02 to 0.2 mm elongated rhombohedra or lamellae. It forms clusters in the matrix or fills veins and cavities with second-generation quartz,
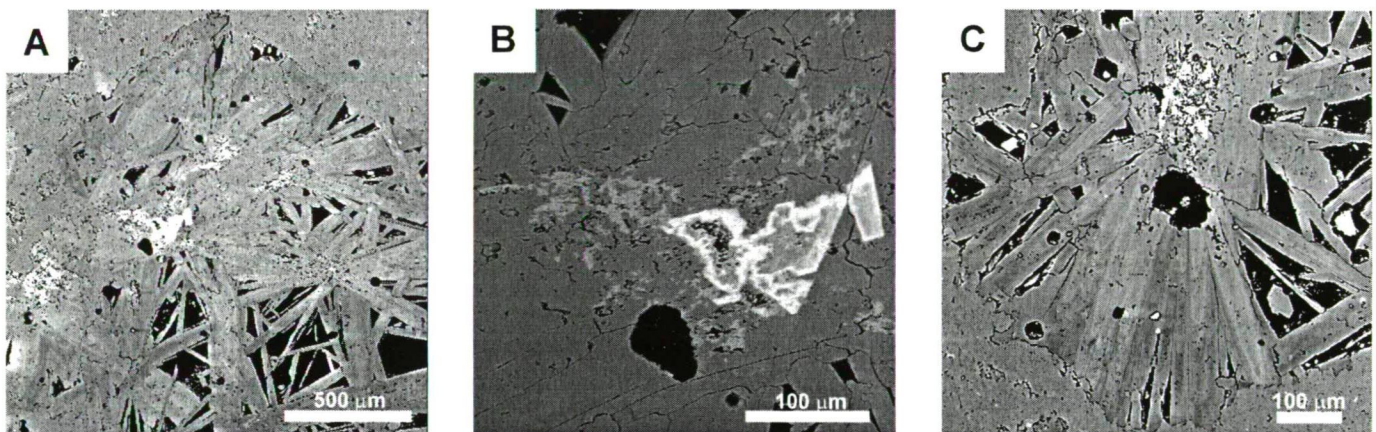

Fig. 3. BSE images of APS minerals in volcanic rocks with advanced argillic alteration from the Velence Mountains. *(A)* APS minerals (white) in bladed and zoned alunite (grey) in a vug, Templom Hill. *(B)* Enlarged portion of Fig. 3A, two types of APS minerals (light grey, xenomorphic and light grey hipidiomorphic with white rim, respectively) in alunite, Templom Hill. *(C)* APS minerals (white) in bladed and zoned alunite (grey) in a vug, Templom Hill.
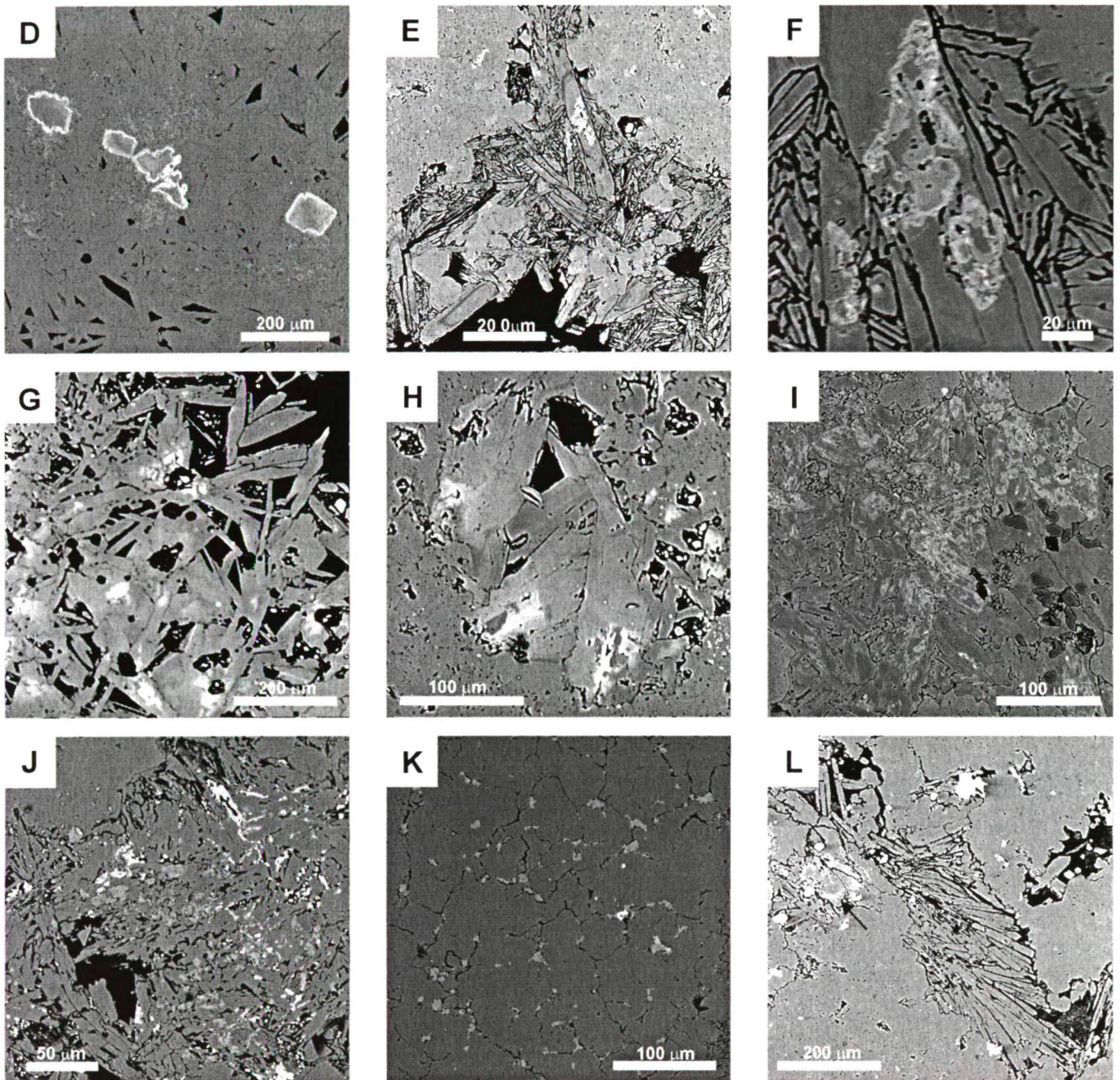
Fig. 3. BSE images of APS minerals in volcanic rocks with advanced argillic alteration from the Velence Mountains. *(D)* Two types of APS minerals in alunite: smaller, grey, xenomorphic grains and larger, hipidiomorphic crystals with white rims, Templom Hill. *(E)* APS minerals (white) in the core of zoned alunite (grey) in a vug, Nyíri Hill. *(F)* Enlarged portion of Fig. 3E, xenomorphic, slightly zoned APS minerals in alunite, Nyíri Hill. *(G)* APS minerals (white) with diffuse edge in alunite (grey) in a vug, Csúcsos Hill. *(H)* APS minerals (white-light grey) with diffuse edge in alunite in a vug, Csúcsos Hill. *(I)* Xenomorphic APS phases (white) in alunite (grey) with diaspore (dark grey) in a vug, Csekély Hill. *(J)* Xenomorphic APS phases (light grey) in alunite (grey) with rutile (white) in a vug, Cseplek Hill. *(K)* Xenomorphic APS grains in quartz matrix, Zsidó Hill. *(L)* Zoned APS grain (light grey-white, indicated by an arrow) in bladed alunite (grey) with pyrite (white) in a vug, Pt-3 drill hole 147.6–148.7 m.

zunyite and pyrite (Fig. 2G). The abundant pyrite shows close, interstitial association with alunite, an observation consistent with a hydrothermal origin for both minerals. In R7 drill hole core (84.2 m depth), augelite [$Al_2PO_4(OH)_3$] and topaz occur in vugs and small cavities of the silica matrix (Seres-Hartai et al., 2002). Augelite forms tabular crystals of 0.1 to 0.5 mm in size (Fig. 2H). Topaz is intergrown with augelite and also forms clusters of tabular crystals of about 10 μm in size, or encrusts rutile cores.

PHOSPHATE-BEARING (APS) MINERALS

Because of small sample amounts and the small grain sizes, the phosphate-bearing minerals observed in this study could only be identified and analysed chemically by scanning electron microscope (SEM) and electron microprobe analyser (EMPA). On backscattered electron images (BSE, Fig. 3 and Fig. 4), APS minerals appear as light-coloured, sometimes bright, mostly irregular, xenomorphic, rarely hipidiomorphic-idiomorphic grains of usually 20–50 (up to 150) μm in size.

In both areas examined, APS minerals occur in hydrothermal alunite or form cores of clusters of alunite crystals. In the samples from Zsidó Hill of the Velence Mountains and the Podpolom deposit, APS minerals also occur in the silica matrix, separate from alunite (Fig. 3K, and Fig. 4C). The rim of phosphate minerals is mostly discrete, but also can be diffuse (e.g. Fig. 3H, 4B, E).

In the Velence Mountains, APS minerals have different forms and sometimes also different generations. In the Templom Hill, two types of discrete APS minerals exist in alunite: smaller (up to 50 μm) xenomorphic APS minerals, and larger (80 to 120 μm) hipidiomorphic, sometimes almost idiomorphic (pseudocubic), oscillatory (occasionally sector-) zoned APS minerals with white rim on BSE images (Fig. 3B, D, enlarged in Fig. 6A). Slightly zoned APS can also be found in the samples from the Nyíri Hill and from the Pt-3 drill hole core (Fig. 3F, L). Alunite of the Csúcsos Hill has APS core with diffuse edges, which can suggest nearly continuous transition from phosphate-sulphate towards sulphate composition; alunite also contains 0.3% P_2O_5 on average (Bajnóczi et al., 2002).

In the Podpolom deposit, white rims or white zones in

APS minerals were observed in a sample of core from the R4 drill hole on BSE images (Fig. 4A, B, D, E). Minor amounts of APS minerals occur as light-coloured, irregular patches together with augelite in a sample of core from the R7 drill hole. The APS minerals usually appear in the peripheral zone of augelite, filling the cavities (Fig. 4F).

CHEMICAL COMPOSITION OF APS MINERALS

Quantitative EMPA measurements were performed at the Laboratory for Geochemical Research (Budapest, Hungary) using a JEOL JXA-733 microprobe equipped with an Oxford INCA 2000 energy dispersive spectrometer (EDS). Analytical conditions were 15 kV accelerating voltage, 4 nA electron beam defocused to 3–10 μm diameter, and 50 sec spectrum collection time. The following standards were used for calibration: albite (Na), corundum (Al), quartz (Si), apatite (P), pyrite (S), orthoclase (K), wollastonite (Ca), $SrBaNbO_{10}$ (Sr), BaF_2 (Ba) (Taylor Co., Stanford, California). The calibration supplied by the manufacturer was used for La, Ce and Nd. During analyses, a low amount of Na (and possibly K) may have been escaped detection, especially at small beam sizes.
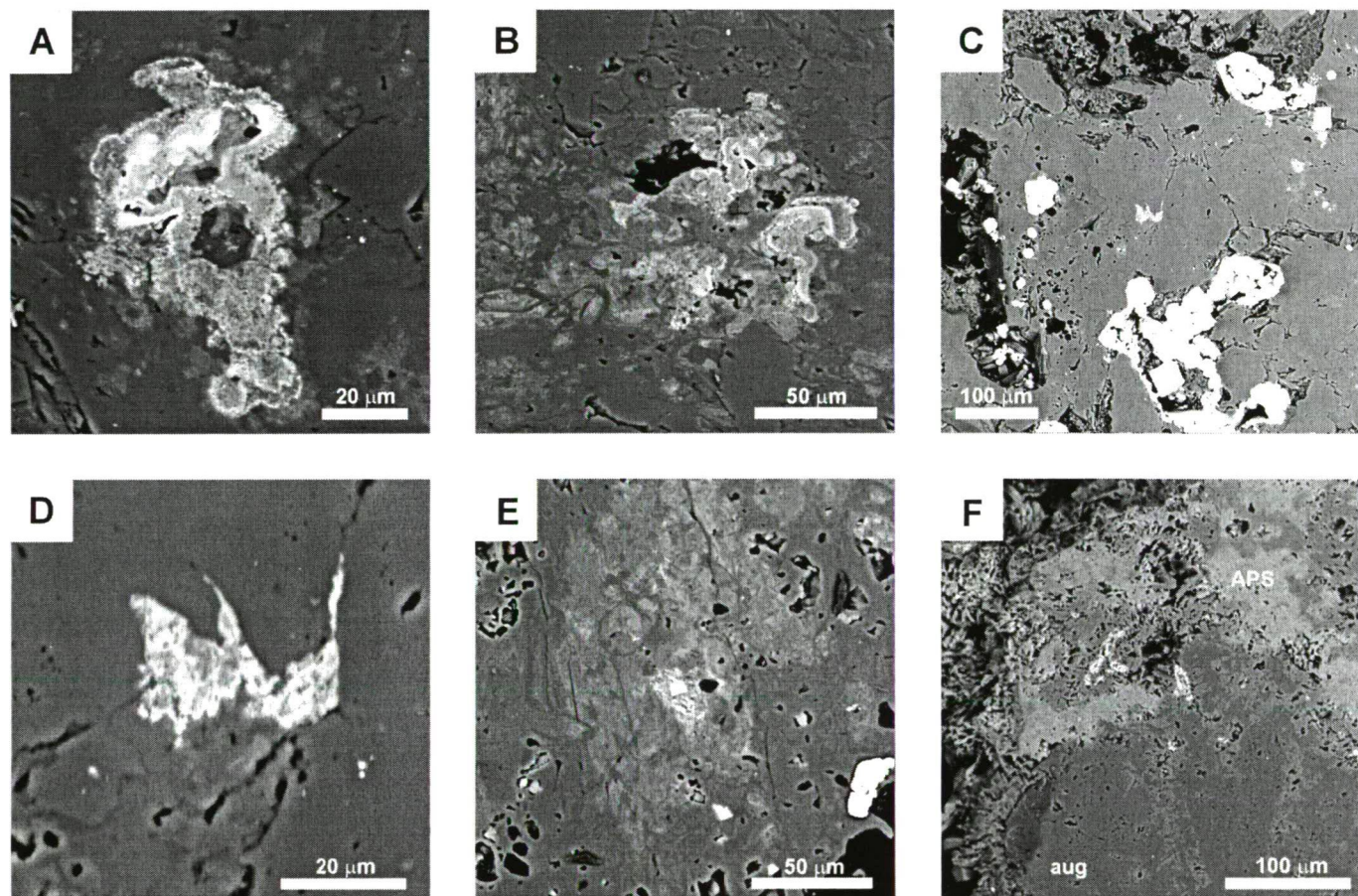

Fig. 4. BSE images of APS minerals from the Podpolom deposit. *(A)* Anhedral, zoned APS mineral (light grey) with white contour and discrete edge in alunite (dark grey). Grey argillic silica, R4 drill hole 79.5 m. *(B)* Irregular forms of APS minerals with white, discrete contour and diffuse contour, respectively, in alunite. Grey argillic silica, R4 drill hole 79.5 m. *(C)* Anhedral APS mineral (light grey in the middle) in quartz (grey) matrix. Vugs are filled by euhedral pyrite (white) and alunite. Grey argillic silica, R4 drill hole 79.5 m. *(D)* Enlarged portion of Fig. 4C, white-grey APS mineral at the edge of quartz (dark grey). Grey argillic silica, R4 drill hole 79.5 m. *(E)* Zoned APS minerals (light grey) with diffuse edge and white core in alunite. The white, euhedral crystal down right is pyrite. Grey argillic silica, R4 drill hole 79.5 m. *(F)* Augelite (dark grey) with topaz (lighter grey strips in augelite), rutile (white, elongated forms) and APS minerals (light grey, upper half) with diffuse edge in a cavity. Siliceous breccia, R7 drill hole 84.2 m.

Table 1 shows the average composition of APS minerals from the Velence Mountains and the Podpolom deposit. APS minerals from the Velence Mountains are Ca-dominant with variable amount of Sr, Ba, K, Na and REE (Fig. 5). In the sample from the Templom Hill hipidiomorphic-idiomorphic APS minerals have several zones with different chemical composition (Fig. 6A): the white rim and the last light zone of minerals contain REE elements, K and more S than inner parts of the same mineral.

At Podpolom, the APS minerals are also Ca-dominant with some Sr and Ba. Rare earth elements were detected in the sample from R4 drill hole core, and K and Na were detected in the sample from R7 drill hole core (Table 1 and Fig. 5). The REE elements are generally limited to the white rims of the APS minerals, but REE-bearing white parts can also occur in the central zone of the minerals (Fig. 6B).

Quantitative chemical analytical data indicate that the correlation between the concentration of S and that of other elements is variable (Fig. 7). Sulphur and P show a good negative correlation; REE elements and S also correlate negatively. The alkalies (A^+ = K + Na) display a weak positive correlation with S. The alkaline earths (A^{2+} = Ca + Sr + Ba) have wide range of ion numbers especially if the ion number of P is above 1. In case of P > 1, alkaline earths correlate negatively with REE elements, but if REE elements are absent A^{2+} ion numbers are near 1 (Fig. 7). The positive
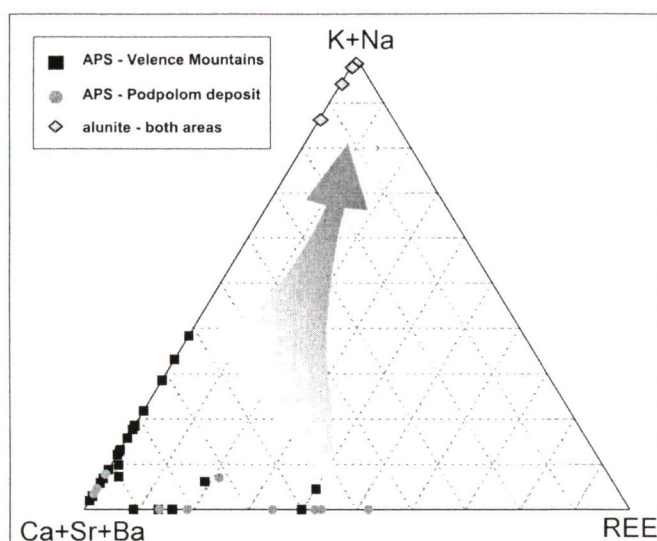

Fig. 5. Compositions of APS minerals from the Velence Mountains and the Podpolom deposit in the K+Na – Ca+Sr+Ba – REE ternary. Individual symbols represent individual analyses. Composition of alunite in both deposits is also shown (in case of the Velence Mountains data are from Bajnóczi et al., 2002). Arrow shows the evolution of chemical composition of parent fluids from early A^{2+}-dominant APS minerals towards late-stage K(-Na)-alunite in both hydrothermal systems.

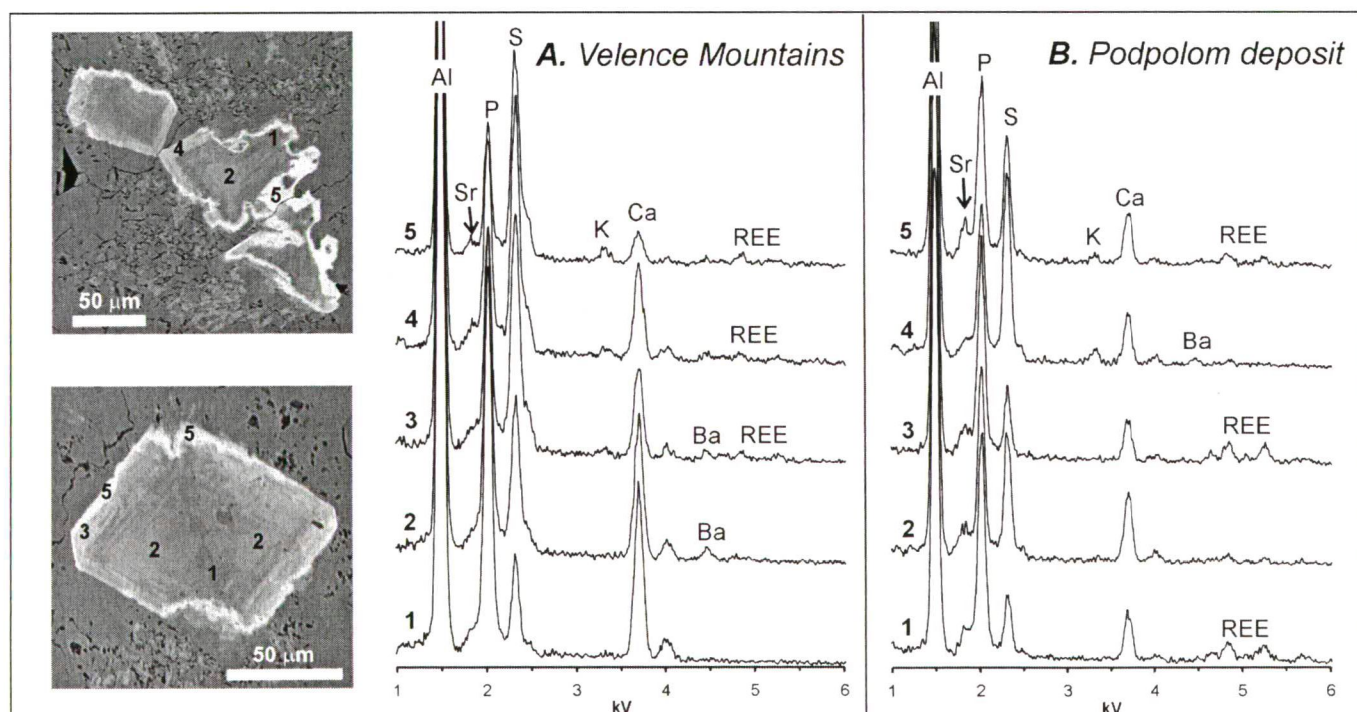**Fig. 6.** Zones with different chemical compositions (shown by EDS spectra) in APS minerals. *(A)* Hipidiomorphic-idiomorphic APS minerals with oscillatory and sector zoning in alunite, andesite with advanced argillic alteration, Templom Hill, Velence Mountains (BSE images, enlarged portions of Fig. 3d). *(B)* Xenomorphic APS minerals in alunite, grey argillic silica, Podpolom deposit, R4 drill hole 79.5 m (BSE images).

Table 1. Average chemical compositions of APS minerals from the Velence Mountains and the Podpolom deposit determined by electron microprobe analyses. Number of analyses, average (av.) and standard deviation (st. dev.) of analytical data are indicated. Names of minerals are determined according to Scott (1987). Names according to the newly proposed nomenclature of Jambor (1999) are also shown. *n. a.*: not analysed for.

	Velence Mountains															
	Templom Hill Not zoned APS		Nyíri Hill Inner part of APS		Csúcsos Hill	Csekély Hill		Cseplek Hill		Zsidó Hill		Pt-3 drill hole 147.6-148.7 m REE-bearing APS		Pt-3 drill hole 147.6-148.7 m APS without REE	
No. of	[2]		[4]		[1]	[5]		[3]		[5]		[3]		[3]	
analyses	Av.	St. dev.	Av.	St. dev.		Av.	St. dev.	Av.	St. dev.	Av.	St. dev.	Av.	St. dev.	Av.	St. dev.
Oxide wt%															
K_2O	1.85	1.03	0.00	0.00	0.00	1.15	0.37	1.34	0.47	0.25	0.13	0.33	0.30	1.05	0.35
Na_2O	0.77	0.35	0.00	0.00	0.52	0.00	0.00	1.01	0.11	0.11	0.07	0.00	0.00	0.26	0.29
CaO	5.34	1.39	8.45	0.80	7.38	8.25	1.03	6.67	0.78	7.36	0.39	5.66	1.78	9.18	0.69
BaO	2.75	0.52	0.00	0.00	4.84	2.13	0.62	2.80	0.08	1.19	0.37	0.00	0.00	0.61	1.05
SrO	4.76	0.24	3.11	0.75	1.05	1.27	0.54	2.33	0.25	7.34	0.80	2.09	0.79	0.16	0.28
La_2O3	0.00	0.00	1.10	0.45	0.00	0.28	0.42	*n. a.*	*n. a.*	*n. a.*	*n. a.*	5.46	1.40	0.00	0.00
Ce_2O_3	0.00	0.00	2.73	0.63	0.00	0.00	0.00	*n. a.*	*n. a.*	*n. a.*	*n. a.*	3.03	1.04	0.00	0.00
Nd_2O_3	0.00	0.00	0.91	0.29	0.00	0.00	0.00	*n. a.*	*n. a.*	*n. a.*	*n. a.*	1.72	1.19	0.00	0.00
Al_2O_3	34.03	0.53	32.51	0.58	34.83	36.42	0.62	32.26	0.77	32.03	0.63	33.16	1.38	35.58	0.82
SO_3	24.12	2.26	12.97	0.97	20.88	25.76	1.09	24.11	0.86	13.99	0.45	14.36	2.83	22.97	0.71
P_2O_5	12.30	2.39	21.58	0.73	14.66	12.93	0.91	10.64	0.57	19.54	0.70	20.50	0.90	15.06	0.41
Total	85.90	0.96	83.35	1.00	84.13	88.18	0.48	81.16	1.21	81.80	1.69	86.29	0.96	84.86	2.78
Cation numbers (recalculated on the basis of 11 oxygens)															
K	0.171	0.097	0.000	0.000	0.000	0.100	0.033	0.129	0.045	0.025	0.013	0.031	0.027	0.093	0.029
Na	0.108	0.050	0.000	0.000	0.074	0.000	0.000	0.148	0.016	0.016	0.011	0.000	0.000	0.035	0.040
Ca	0.413	0.104	0.682	0.057	0.578	0.604	0.076	0.541	0.060	0.609	0.026	0.449	0.121	0.687	0.066
Ba	0.078	0.014	0.000	0.000	0.138	0.057	0.016	0.083	0.002	0.036	0.012	0.000	0.000	0.016	0.028
Sr	0.200	0.012	0.136	0.035	0.044	0.050	0.021	0.102	0.010	0.329	0.033	0.091	0.037	0.006	0.011
La	0.000	0.000	0.031	0.012	0.000	0.007	0.010	*n. a.*	*n. a.*	*n. a.*	*n. a.*	0.150	0.044	0.000	0.000
Ce	0.000	0.000	0.075	0.018	0.000	0.000	0.000	*n. a.*	*n. a.*	*n. a.*	*n. a.*	0.084	0.031	0.000	0.000
Nd	0.000	0.000	0.025	0.008	0.000	0.000	0.000	*n. a.*	*n. a.*	*n. a.*	*n. a.*	0.047	0.033	0.000	0.000
Al	2.903	0.017	2.891	0.031	3.007	2.932	0.050	2.879	0.040	2.917	0.022	2.917	0.082	2.928	0.015
S	1.311	0.135	0.734	0.046	1.145	1.320	0.055	1.371	0.056	0.812	0.033	0.801	0.129	1.203	0.011
P	0.753	0.139	1.379	0.062	0.907	0.748	0.053	0.682	0.032	1.278	0.030	1.297	0.095	0.890	0.013
Sum cat.	5.937	0.020	5.953	0.008	5.949	5.818	0.023	5.935	0.024	6.021	0.020	5.868	0.038	5.859	0.041
Name according to Scott (1987)	Strontian woodhouseite		Strontian woodhouseite		Barian woodhouseite	Potassic woodhouseite		Sodic woodhouseite		Strontian woodhouseite		REE-bearing woodhouseite		Potassic woodhouseite	
Name according to Jambor (1999)	Strontian woodhouseite		Strontian crandallite		Barian woodhouseite	Potassic woodhouseite		Sodic woodhouseite		Strontian crandallite		REE-bearing crandallite		Potassic woodhouseite	

Table 1 continued

| No. of analyses	Podpolom deposit					
	R4 drill hole 79.4 m White APS [4]		R4 drill hole 79.4 m Grey APS [3]		R7 drill hole 84.2 m [3]	
	Av.	St. dev.	Av.	St. dev.	Av.	St. dev.
Oxide wt%						
K_2O	0.00	0.00	0.21	0.36	0.40	0.08
Na_2O	0.00	0.00	0.00	0.00	0.10	0.18
CaO	4.90	0.44	6.77	1.07	6.77	0.58
BaO	0.38	0.56	0.23	0.40	2.71	0.19
SrO	2.39	0.30	3.03	0.69	7.62	0.87
La_2O_3	3.45	0.79	0.87	0.49	n. a.	0.00
Ce_2O_3	7.25	1.81	3.30	1.22	n. a.	0.00
Nd_2O_3	3.54	0.89	1.47	0.31	n. a.	0.00
Al_2O_3	31.71	0.43	33.13	0.34	32.36	0.87
SO_3	8.64	1.03	13.69	2.61	10.48	0.36
P_2O_5	21.66	1.29	20.59	2.29	22.95	0.50
Total	83.91	2.13	83.29	1.37	83.41	1.54
Cation numbers (recalculated on the basis of 11 oxygens)						
K	0.000	0.000	0.020	0.035	0.040	0.008
Na	0.000	0.000	0.000	0.000	0.016	0.027
Ca	0.425	0.040	0.549	0.086	0.560	0.035
Ba	0.012	0.018	0.007	0.012	0.082	0.004
Sr	0.112	0.014	0.133	0.032	0.342	0.046
La	0.103	0.023	0.024	0.013	n. a.	n. a.
Ce	0.215	0.052	0.091	0.033	n. a.	n. a.
Nd	0.102	0.025	0.040	0.009	n. a.	n. a.
Al	3.025	0.035	2.957	0.050	2.945	0.011
S	0.525	0.068	0.777	0.140	0.607	0.014
P	1.484	0.075	1.321	0.161	1.500	0.005
Sum cat.	6.003	0.013	5.919	0.047	6.091	0.013
Name according to Scott (1987)	REE-bearing woodhouseite		Strontian woodhouseite		Strontian woodhouseite/ crandallite	
Name according to Jambor (1999)	REE-bearing crandallite		Strontian woodhouseite		Strontian crandallite	
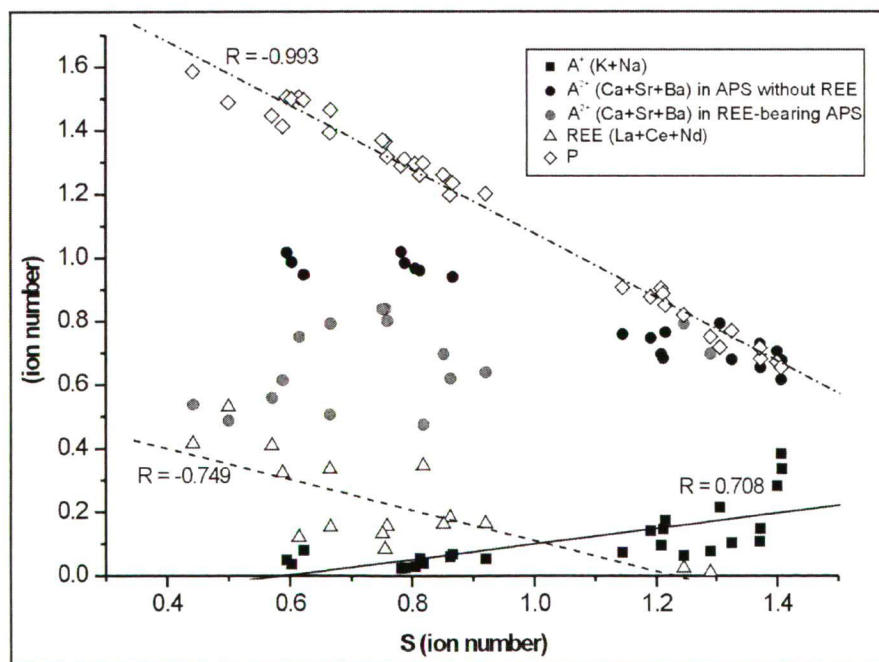
Fig. 7. A^+ (K+Na), A^{2+}(Ca+Sr+Ba), REE (La+Ce+Nd) and P vs. S expressed in ion numbers recalculated on basis of 11 oxygens in the studied samples. Individual symbols represent individual analyses. Fitted linear regression curves and correlation coefficient are also indicated for A^+, REE and P, respectively.

correlation between A^+ and S is the result of coupled substitution of phosphate and divalent cation for sulphate and monovalent cation: (K^+, Na^+) + SO_4^{2-} = (Ca^{2+}, Sr^{2+}, Ba^{2+}) + PO_4^{3-} (Stoffregen and Alpers, 1987). Trivalent REE elements can substitute A^{2+} when the phosphate exceeds 1 mol per formula unit (S ion number < 1) because of further compensation of charges (Fig. 7). In the case of P > 1, and no REE present, the charge balance is presumably maintained by protonation of the phosphate (Scott, 1987).

Fig. 5 shows that there is no continuous transition between A^{2+}-dominant and A^+-dominant alunite-type minerals in the studied samples. Even in the sample from Csúcsos Hill, where continuous transition between APS minerals and alunite seem to appear on the BSE images (Fig. 3G, H), there is a compositional gap between the monovalent and divalent cations. Results from various other deposits also suggest a limited degree of the coupled substitution in samples of magmatic-related, hypogene alunite formed at temperatures below about 300 °C (Stoffregen and Alpers, 1987). Stoffregen et al. (2000) assume that the availability of phosphate may be a limiting factor in determining the extent of solid solution by the exchange reaction.

APS MINERALOGY

The studied phosphate-bearing minerals are solid solutions of Ca-, Sr-, Ba-, REE-, K- and Na-bearing APS minerals of the woodhouseite-beudantite [$(A^{2+})Al_3((P,S)O_4)_2(OH, H_2O)_6$], crandallite [$(A^{2+}, A^{3+})Al_3(PO_4)_2 (OH, H_2O)_6$] and alunite [$(A^+)Al_3(SO_4)_2 (OH)_6$] mineral groups. 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 and Alpers, 1987).

For naming the studied APS minerals, the current classification of alunite supergroup minerals proposed by Scott (1987) was used. It is based on the molar proportion of XO_4^{3-} anion in the formula unit and type of the dominant cation in A-site. If Ca is the dominant cation and molar proportion

of phosphate is between 0.5 and 1.5, the mineral is woodhouseite; if PO_4^{3-} >1.5 mol, then the mineral is crandallite. To indicate the most abundant minor cation in the A-site (A>0.05 mol) an adjectival modifier can be added to the mineral name. According to Scott (1987), the APS minerals of the Velence Mountains are strontian, barian, potassic, sodic or REE-bearing woodhouseite, the APS minerals of Podpolom are REE-bearing or strontian woodhouseite (Table 1). Recently Jambor (1999) proposed a new classification for alunite supergroup and he defined the boundary between woodhouseite and crandallite at PO_4^{3-} = 1 mol. If we consider this new proposal, some of the analysed minerals may become crandallite instead of woodhouseite (Table 1).

Woodhouseite in the Velence Mountains has sulphate-dominant (1.15 to 1.37 mol SO_4^{2-} in formula unit) and phosphate-dominant varieties (0.73 to 0.81 mol SO_4^{2-} in formula unit), with 35 to 67% SO_4^{2-} in the X site. Al-phosphate-sulphate minerals in the Podpolom deposit are phosphate-dominant (0.53 to 0.78 mol SO_4^{2-} in formula unit), with 26 to 37% SO_4^{2-} in the X site.

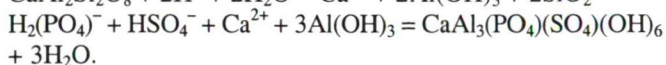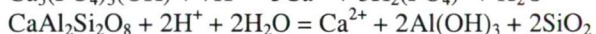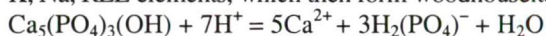## GENESIS OF THE PHOSPHATE-BEARING MINERALS

The presence of phosphate-bearing minerals in close connection with, mostly in, hydrothermal alunite or other hydrothermal mineral indicates a hypogene origin for these phases, and suggests that their formation usually occurred prior to alunite precipitation.

In high-sulphidation epithermal systems, primary alunite is formed by acidic magmatic-hydrothermal fluids. Magmatic HCl, SO_2 and HF gas-rich vapours released by a cooling subvolcanic magma ascend to the surface along volcanic conduits, and at levels closer to the surface they mix and condensate into groundwater (Hedenquist and Arribas ,1999). The resulting high temperature (< 300 to 350 °C) magmatic-hydrothermal fluids are very acidic (pH = 1 to 2) because of the dissociation of HCl and H_2SO_4, the latter produced at slightly deeper levels by the disproportionation of magmatic SO_2 (Hedenquist and Arribas, 1999):
$$4SO_2 + 4H_2O = 3H_2SO_4 + H_2S$$
$$H_2SO_4 = H^+ + HSO_4^-$$
$$HCl = H^+ + Cl^-.$$
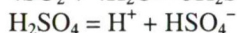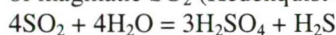
This acidic fluid is capable of dissolving rock-forming minerals, even Al_2O_3 completely, leaving a porous silica residue (typically termed "vuggy silica"). Vuggy silica is typically surrounded by an alunite-kaolinite-pyrophyllite-bearing advanced argillic alteration zone, where sulphate precipitates with Al as alunite, and coexisting H_2S precipitates as pyrite.

Dissolution of magmatic apatite by these acidic fluids at high temperatures can induce and contribute to the precipitation of APS minerals (Stoffregen and Alpers, 1987). During the initial stage of leaching, dissolution of apatite and magmatic feldspar (plagioclase) results in release of Ca, P, Al and minor K, Na, REE elements, which then form woodhouseite:
$$Ca_5(PO_4)_3(OH) + 7H^+ = 5Ca^{2+} + 3H_2(PO_4)^- + H_2O$$
$$CaAl_2Si_2O_8 + 2H^+ + 2H_2O = Ca^{2+} + 2Al(OH)_3 + 2SiO_2$$
$$H_2(PO_4)^- + HSO_4^- + Ca^{2+} + 3Al(OH)_3 = CaAl_3(PO_4)(SO_4)(OH)_6 + 3H_2O.$$

The precipitating Ca-dominant Al-phosphate-sulphates can be zoned (e.g. APS from Templom Hill). APS minerals from Zsidó Hill (Fig. 3K), and rarely in the sample from drill hole R4 at Podpolom (Fig. 4C), seem to have precipitated in equilibrium with quartz.

The usually irregular, xenomorphic-hipidiomorphic shape of APS minerals suggests that the early formation of phosphate-bearing minerals was followed by dissolution (the prominent examples are APS minerals on Fig. 6A showing the start of dissolution). The dissociation of HCl and H_2SO_4 with time results in fluids of lower pH and the dissolution of early APS minerals (Watanabe and Hedenquist, 2001).

Periodic pulses of hydrothermal fluid flow of varying composition is indicated by the precipitation of a new generations of APS as REE-bearing white rims observed on dissolved minerals in the Velence Mountains and Podpolom deposit samples (Fig. 6). Rare earth element enrichments in the margins of the APS minerals have been interpreted to be the product of supergene alteration processes caused by meteoric fluids (Dill et al., 1997, 2000; Dill, 2001). This is probably not the case for the APS analysed in this study. A new generation of APS minerals with REE enrichment may indicate falling temperatures of the hydrothermal fluids, since the stability field is enlarged with decreasing temperatures and its structure is stabilised with the incorporation of trivalent cations such as REE (Dill, 2001).

After complete dissolution of apatite and because of continuous sulphate supply, the subsequent hydrothermal fluid was sulphate-dominant and alunite precipitated around APS minerals. Late-stage sodic alunite from the Velence Mountains also shows a zoned character with Na- and K-enriched zones and a 1.14 to 2.35 wt% average Na_2O content (Bajnóczi et al., 2002). Alunite in the sample from R4 drill hole at Podpolom is K-dominant with a minor Na-content. However, in the sample from R7 drill hole (84.2 m), where instead of other alunite(-type) mineral, pure Al-phosphate (augelite) was observed, APS minerals were probably altered to augelite due to latter high-temperature hydrothermal processes (Seres-Hartai et al., 2002).

Stoffregen and Alpers (1987) demonstrated that chemical differences in the composition of APS minerals might exist between the lower and the higher temperature alteration assemblages. They pointed out in the Summitville deposit, Colorado, that a higher Ca content, Ba and K was characteristic of APS minerals, which occurred together with pyrophyllite at deeper levels and higher formation temperatures. On the other hand, APS minerals formed at shallower levels had a higher Sr content and were accompanied by alunite and kaolinite. In the Velence Mountains, we could not determine the compositional difference between APS minerals in the likely lower temperature assemblage at Templom, Nyíri and Csúcsos Hills and the higher temperature alteration assemblage of Cseplek and Zsidó Hills.

Similar APS minerals of woodhouseite, svanbergite, florencite or crandallite compositions were also found in the core of or close connection to magmatic-hydrothermal alunite from advanced argillic zones of other high-sulphidation or Cu-porphyry deposits, e. g. Summitville, Colorado, USA, La Granja, Peru, La Escondia, Chile (Stoffregen and Alpers, 1987); Baguio district, Philippines (Aoki et al., 1993); Nansatsu, Japan (Hedenquist et al., 1994); Rodalquilar, Spain (Arribas et al., 1995); Lepanto,

Philippines (Hedenquist et al., 1998) and El Salvador, Chile (Watanabe and Hedenquist, 2001). In Bulgaria, APS minerals with similar genesis were described from the alunite- and/or pyrophyllite-quartz alteration zones of the Asarel porphyry copper deposit (svanbergite, woodhouseite, Velinov et al., 1991) and the quartz-sericite, advanced argillic and vuggy silica alteration zones of the Chelopech Cu-Au deposit (svanbergite-woodhouseite, Simova et al., 2001). The presence of phosphate-bearing minerals in the core of alunite is not typically found in alunite formed in the steam-heated or supergene environments (Aoki et al., 1993; Rye et al., 1992); although small amounts of APS minerals have been observed in these two types of alunite (e. g. Arribas et al., 1995; Dill, 2001; Watanabe and Hedenquist ,2001).

CONCLUSIONS

During this study, evidence was collected from the Velence Mountains (Hungary) and the Podpolom deposit (Klokoč, Slovakia) to support that, in addition to magmatic-hydrothermal alunite, other primary (hypogene) alunite-type, phosphate-bearing minerals can exist in the advanced argillic alteration zones of high-sulphidation type epithermal systems. In the Velence Mountains and the Podpolom deposit these are Ca-dominant Al-phosphate-sulphate (APS) minerals, mineralogically woodhouseite with minor Ba, Sr, K and REE elements. The form of these minerals is variable and sometimes they grew during more than one generation. Our evidence indicates that these minerals formed prior to alunite. Then, they represent one of the first alteration minerals formed during leaching by strong acidic magmatic-hydrothermal fluids. The presence of several generations of alunite-type minerals indicate varying physicochemical characteristics of hydrothermal fluids such as a decrease of in pH and probably the temperature of the fluids, followed by a decrease in phosphate concentration.

This study represents the first detailed documentation of hydrothermal woodhouseite in alteration systems of the Carpatho-Pannonian region and the appearance of this mineral mostly in the core of magmatic-hydrothermal alunite in the above-mentioned deposits is in accordance with observations in advanced argillic zones of high-sulphidation or Cu-porphyry deposits in other regions.

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