SECONDARY SULFATES FOUND IN AN OLD ADIT FROM ROȘIA MONTANĂ, ROMANIA¹

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ABSTRACT. Recent investigation on several secondary minerals formed in old mining galleries in the Cămic district (Roșia Montană, Romania) enabled us to characterize ten minerals. Out of these ten identified minerals, the discovery of jokokuite is the first reported occurrence in the Carpathians. A second mineral identified as apjohnite represents a new occurrence in Romania. Along with these two rare minerals, some other species of the halotrichite group (pickeringite, halotrichite, apjohnite, and dietrichite), iron sulfates, and K-Al sulfates were identified. Minerals were identified using light microscopy, X-ray diffraction, infrared, and scanning electron microscopy with energy dispersive spectroscopy. The chemical composition of some samples was determined with inductively coupled plasma atomic emission spectrometry. The precipitation of these sulfates is largely controlled by cations substitutions and changes in the temperature, relative humidity, and evaporation along the sampled gallery. The general sequence of sulfate deposition at the investigated site includes the following main steps: (1) oxidation of pyrite by meteoric water seepage through dacites to create ferrous sulfate and sulfuric acid solutions; (2) chemical reaction between dacites and sulfuric acid from which other cations (Al^{3+} , Zn^{2+} , Mn^{2+} , K^{+}) are released into solution; and (3) precipitation of various hydrated sulfates as a result of a combination of dehydration/hydration, oxidation, and neutralization reactions that take place under different microclimatic settings.

Keywords: secondary minerals, efflorescent sulfates, supergene alteration, Roșia Montană, Romania.

GENERAL DATA

The Roșia Montană metallogenic district is part of the “Gold Quadrangle”, located in the Metaliferi Mountains, the core of the South Apuseni Mountains (Fig. 1). The Roșia Montană low sulfidation epithermal ore deposit (Mârza et al., 1997; Tămaș & Bailly, 1999) hosts important economic concentrations of gold and silver. These ore bodies were intensively mined (both in adits and in open pits) since pre-Roman times (Cauuet et al., 2003). The mineralization is hosted within Neogene dacites and occurs disseminated in various types of breccia pipe bodies or is concentrated along veins and stockworks known as “volburi” (Petrulian, 1934; Ghițulescu & Socolescu, 1941; Tămaș, 2002).

¹ Paper presented at the 2nd *Mineral Sciences in the Carpathians* Conference in Miskolc, Hungary (March, 2003).

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Fig. 1. Location of the Roșia Montană mining region (Courtesy of Gabriel Resources Ltd.).

This paper focuses on the initial description of eight secondary sulfate minerals formed in a restricted area of the Cârnic (Roșia Montană) mining district due to supergene alteration. In addition, the study documents the paragenesis and environmental condition under which these minerals were precipitated.

The bedrock geology of the Roșia Montană consists of a complex tectonic setting that brings into contact the Cretaceous flysch formation (Bucium Unit) and the sedimentary rocks of Badenian and Sarmatian age. All these formations including the crystalline basement have been penetrated by Neogene dacites of Cetate type and andesites of Rotunda type (Cioflica et al., 1973; Ianovici et al., 1976; Borcoș, 1994; Balintoni, 1997).

Various geological, mineralogical, and ore-related aspects concerning this deposit were the subject of many detailed studies (Petrușian, 1934; Ghițulescu & Socolescu, 1941; Borcoș, 1967; Giușcă et al., 1969; Mârza & Ghergari, 1992; Mârza et al., 1995, 1997; Benea et al., 2000; Tămaș, 1998, 2002).

SAMPLING SITE: GEOLOGY & TOPOCLIMATE

Seventeen samples were collected from an old prospecting adit (horizon 958) located in the Cârnic mining district (Fig. 2). The mining gallery traverses a body of weathered dacites. When fresh, this rock is light grey in color and shows a porphyritic structure and massive texture. Bipyramidal phenocrysts of quartz (2-3 cm) are set in an aphanitic groundmass along with plagioclases, K-feldspars, brown hornblende, biotite, and accessories minerals (apatite, zircon) (Tămaș, 2002; Leach, pers. comm.). Pyrite, chalcopyrite, marcasite, and sphalerite impregnations are common in the dacites that outcrop at Cârnic. Rhodochrosite

and rhodonite are the chief Mn-bearing minerals to appear in the gangue association of this hydrothermal ore deposit (Rădulescu & Dimitrescu, 1966). The Mn concentration in the dacites around the sampling site was found to be greater than 1100 ppm (Leach & Hawke, pers. comm.).

Fig. 2. Location of the sampling site in the Cârnic mining district (arrows and numbers: temperature and relative humidity stations).

The hypogene alteration heavily affected all the primary minerals. Both plagioclases and K-feldspars in the dacites were transformed into adularia and/or clay minerals. The groundmass was altered into an intermediate potassic and argillic along with silicification. The supergene alteration recorded along the sampled gallery was caused by meteoric waters percolating through a dense network of fissures (averaging 5 fissures/m²) and reacting with previously mineralized ground (Leach & Hawke, pers. comm.).

One particular aspect observed when walking along the sampled gallery was the change in temperature. As the gallery was entered, the temperature was suddenly much higher than in the previous galleries. A temperature/relative humidity survey showed that both of these parameters varied when compared to the values recorded outside the mine, in the main gallery, or close to the sampling site (Table 1).

Table 1

Mean temperature and relative humidity values along the horizon +958 m during the sampling period (6 readings).

Location		T (°C)	Relative humidity (%)
Entrance		-5.4	53
Main gallery		3.2	98
Piller's Room		6.7	97
Sampled Gallery	1	8.9	95
	2	12.6	92
	3	13.2	87

METHODS OF INVESTIGATION

The secondary minerals described herein occur as crusts, efflorescences, needle-like crystals, and botryoidal, granular, rosette-like, and fibrous aggregates. Their mineralogical and chemical characterization relies on macroscopic description (including optical binocular), routine X-ray powder diffraction (XRD) analyses performed on a Scintag Pad V (30mA/35kV no filter, Cu- $K\alpha$ radiation) and a DRON 3 diffractometer (40 mA/45 kV, Ni-filtered, Cu- $K\alpha$ radiation), infrared (IR) analyses, and scanning electron microscope (SEM) observations on a Hitachi 3500N model. Chemical data was collected on the samples using an energy-dispersive spectrometer (EDS) fitted to the SEM and a Jobin Yvon Sequential Spectrometer (JY 24) inductively coupled plasma - atomic emission spectrometer (ICP-AES). Calculation of the unit-cell parameters was accomplished using the UnitCell program prepared by Holland & Redfern (1997).

The specimens investigated and presented in this paper are deposited in the Mineralogical Museum of the „Babeș-Bolyai” University in Cluj-Napoca, Romania.

MINERAL DESCRIPTION

Iron and manganese-rich sulfates

Melanterite - $\text{Fe}^{2+}\text{SO}_4 \cdot 7\text{H}_2\text{O}$ forms colorless to translucent, sometimes slightly green (with increasing substitution of Cu for Fe), beard-like, hanging-fibrous aggregates (up to 4 cm in length) having a vitreous luster (Pl. I, Fig. 1). Upon exposure to dry air the crystals become white-yellowish and opaque.

Melanterite was identified by XRD and SEM-EDS analyses. The strongest six diffraction lines observed for melanterite are located at 4.90 Å (100), 4.869 Å (70), 3.782 Å (40), 3.739 Å (18), 4.031 Å (14), and 2.757 Å (10).

Rozenite - $\text{Fe}^{2+}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ represents the main component of the rosette-like aggregates found on the ceiling of abandoned adits of the gold deposit at Roșia Montană (Pl. I, Fig. 2 and Pl. IV, Fig. 2). The white or colorless anthodite-like aggregates of rozenite form directly on highly weathered dacites and can reach 3 to 5 cm in length. XRD analyses confirmed that the anthodites are composed of rozenite and the less common sulfate, jokokuite. The values for the X-ray reflections of rozenite are listed in Table 2 (see supplementary information).

Other occurrences of rozenite in Romania are known from the Iacobeni manganiferous deposit (Bălan, 1976) and from abandoned adits of the Borzaș gold deposit (Tatu, 1989).

Copiapite – $\text{Fe}^{2+}\text{Fe}_4^{3+}(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$. In Romania, copiapite was usually found associated with oxidation of pyrite in the coalfields within the Petroșani basin (Udubașa, pers. comm.) or as a Zn-rich variety at Băișoara in the oxidation zone of a quartz and sulfate vein (Tatu, 1989). At our study site, copiapite occurs in a rather moist section of the gallery as yellowish-orange, pasty-like botryoidal crust (up to 3 mm in thickness) (Pl. II, Fig. 1) covered by mammillary aggregates of halotrichite. Copiapite has been identified using XRD method (Table 3; see supplementary information).

Jokokuite – $\text{Mn}^{2+}\text{SO}_4 \cdot 5\text{H}_2\text{O}$ (chalcantite group) forms pale pink, rosette-like aggregates up to 2-3 cm in length on the gallery walls (Pl. I, Fig. 2). Jokokuite is intimately associated with rozenite. The jokokuite crystals have a vitreous luster, no cleavage, and are very soluble in water. The energy-dispersive analyses of the pink anthodite (*anthos* = flower, in Greek) crystals revealed Mn, S, and O to be the major elements, whereas Fe appears to be a minor element. The ICP-AES analyses (wt.%; MnO, 31.9%; SO_3 , 34.99%; FeO, 1.08%; H_2O , 31.68%) confirmed the chemical composition of jokokuite. The average cell parameters obtained on the basis of 24 powder reflections are $a = 6.36(5) \text{ \AA}$, $b = 10.75(9) \text{ \AA}$, $c = 6.12(2) \text{ \AA}$, $\alpha = 98.934(1)^\circ$, $\beta = 109.966(5)^\circ$, $\gamma = 75.11(9)^\circ$, $V = 379.81(1) \text{ \AA}^3$. These values are nearly identical to those from ICDD file 31-836 (Table 4) accounting for a pure compound. This is the first reported occurrence of jokokuite in the Carpathian Range.

Table 4

Comparison between the powder diffraction pattern of Roșia Montană jokokuite and the standard reference pattern from ICDD file 31-836.

Jokokuite (this study)		Jokokuite (ICDD card 31-836)	
$d(\text{\AA})$	I	$d(\text{\AA})$	I
10.369	3	10.4	4
5.840	100	5.84	100
5.187	7	5.19	13
4.975	85	4.98	60
4.383	15	4.39	25
3.717	15	3.72	20
3.447	5	3.46	3
3.289	17	3.28	25
3.014	10	3.015	3
2.914	14	2.916	18
2.818	15	2.821	19
2.721	65	2.727	70

Jokokuite (this study)		Jokokuite (ICDD card 31-836)	
2.521	6	2.523	11
2.487	8	2.487	4
2.431	8	2.440	13
2.392	7	2.395	8
2.312	6	2.322	8
2.297	23	2.290	25
2.190	11	2.196	11
2.062	14	2.067	17
1.995	6	1.994	8
1.970	11	1.969	20
1.690	14	1.692	13
1.621	15	1.622	30

Aluminum-rich sulfates

Pickeringite - $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ & **Halotrichite** - $\text{Fe}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$. Pickeringite was first identified in Romania from Miocene sandstones and claystones along the Sub-Carpathians (Petrescu, 1948). Other reported occurrences of pickeringite and halotrichite have been reported in the oxidation zone of the base-metal deposit at Borzaș, Gutâi Mountains (Tatu, 1989), and in Diana Cave, Băile Herculane (Diaconu & Medeșan, 1973).

In our investigated occurrences, the mineral forms shiny white to silky thin crystals (3-5 mm in length) covering apjohnite crusts. The identification of this mineral relies on IR spectrometry, XRD (Table 5; see supplementary information), and SEM-EDS analyses (Pl. III, Fig. 1). The IR spectrum shows 4 distinctive absorption bands (very strong at 1123 and 1083 cm^{-1} ; medium at 960 and 1650 cm^{-1}) superimposed on a rather broad background.

Samples composed of yellowish-brown mammillary aggregates with a vitreous luster occurred in the near vicinity of the pickeringite. XRD analyses revealed these samples to be composed of halotrichite. Except for a few lines assigned to pickeringite, the strongest reflections on the X-ray spectrum belong to halotrichite (Table 6; see supplementary information). Furthermore, the IR spectrum is slightly different from that of the pickeringite. The spectrum shows a strong, but broad absorption band at 625 cm^{-1} and a very strong one at 1119 cm^{-1} along with two inflections at 1068 and 1149 cm^{-1} that are not present on the pickeringite spectrum. In another location along the gallery, halotrichite appears as hair-like efflorescences. The size of the crystals never exceeds 3 mm in length and 0.5 mm in width. In one of the samples, (#1541) botryoidal halotrichite crust was found overlying copiapite.

Apjohnite - $\text{Mn}^{2+}\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$ was found in several samples collected from either the floor or the walls of old adits. Apjohnite forms white to yellowish-brown or greenish crusts or fibrous and needle-like crystals up to few centimeters in length (Pl. II, Fig. 2). The XRD pattern of sample # 1538 (considered representative) contains well-resolved diffraction lines corresponding to the reference patterns of apjohnite (Table 7).

Table 7

Powder pattern of apjohnite compared with its diagnostic reflections from the ICDD 29-886 reference.

Apjohnite (Roșia Montană)		Apjohnite ICDD 29-886	
<i>d</i> (Å)	I	<i>d</i> (Å)	I
9.665	10	9.65	10
7.971	10	7.96	10
6.088	24	6.07	20
5.848	4	5.85	5
5.309	8	5.29	8
4.969	21	4.97	18
4.822	90	4.82	90
4.681	7	4.69	5
4.604	6	4.61	6
4.409	10	4.41	6
4.385	20	4.38	6

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Apjohnite (Roșia Montană)		Apjohnite ICDD 29-886	
<i>d</i> (Å)	I	<i>d</i> (Å)	I
4.336	32	4.34	30
4.181	15	4.18	12
4.137	29	4.13	20
4.013	15	4.01	10
3.972	17	3.97	25
3.792	35	3.79	35
3.67	4	3.67	4
3.526	100	3.52	100
3.46	10	3.45	11
3.361	9	3.36	8
3.308	6	3.31	4
3.208	6	3.21	3
3.191	12	3.18	10
3.053	12	3.06	9
2.97	15	2.974	15
2.908	13	2.901	11
2.842	10	2.84	12
2.798	8	2.793	11
2.729	4	2.726	5
2.69	17	2.689	19
2.623	11	2.617	10
2.582	3	2.583	1
2.569	14	2.563	12
2.529	5	2.524	4
2.471	8	2.465	8
2.408	12	2.408	9
2.292	6	2.288	4
2.248	5	-	-
2.238	4	2.239	6
2.206	3	2.199	3
2.169	3	2.168	2
2.141	2	-	-
2.087	3	2.087	5
2.068	3	2.064	3
2.053	3	2.051	3
2.023	21	2.020	13
1.977	4	1.977	4
1.96	6	1.96	6
1.899	8	1.896	5
1.879	12	1.879	12
1.839	1	1.84	2
1.829	2	1.827	3
1.786	4	1.784	4
1.717	4	1.715	4
1.678	6	-	-
1.612	5	-	-
1.577	7	-	-
1.55	4	-	-
1.517	4	-	-
1.497	3	-	-
1.474	5	-	-

Refinement of the powder diffraction data (53 reflections) gave a monoclinic cell that is slightly different when compared to the reference material (Table 8). As observed in Table 8, all cell parameters for Roșia Montană apjohnite (except for the β value) are constantly higher than the one recorded in the ICDD file 29-886, a fact that was ascribed to Fe-for-Al substitution. In sample #1541 apjohnite appears associated with pickeringite.

Table 8

Comparative lattice parameters data for apjohnite.

<i>Lattice parameters</i>	<i>This study</i>	<i>ICDD 29-886</i>
<i>a</i> (Å)	6.259	6.198
<i>b</i> (Å)	24.425	24.347
<i>c</i> (Å)	21.303	21.266
β (°)	99.466	100.28

Apjohnite crystals examined with a SEM show composite fibers having prismatic habitus. The fibers are parallel aligned and cemented together; some are gently curved along their length (Pl. III, Fig. 2). Most of the crystals are euhedral, showing flat and smooth surfaces that lack dissolution features.

This is the first identification of apjohnite in Romania. The only other occurrence of this mineral in the Carpathian Range is from Smolník, Slovakia (Szakáll, 2002).

Dietrichite - $(\text{Zn,Fe}^{2+},\text{Mn}^{2+})\text{Al}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$. The type locality for dietrichite is Baia Sprie, Romania (Udubașa, 1999; Szakáll, 2002). Roșia Montană represents its second occurrence in Romania. At this particular site, dietrichite forms millimeter-tufted aggregates of acicular crystals that efflorescences along the ceiling of the galleries. The color of the crystals is dirty yellow or greenish. SEM images revealed, slightly curved micron-sized prismatic crystals (Pl. IV, Fig. 1).

Powder XRD data matched very closely with the dietrichite patterns (Table 9; see supplementary information). ICP-AES analyses confirmed the presence of this rare mineral. However, when comparing the chemical composition of the samples from Baia Sprie to that from Roșia Montană, one can observe a significant variation in the amount of Mn, Zn, and Fe in the latter specimen (Table 10).

Table 10

Chemical analyses of dietrichite.

<i>Oxide wt. %</i>	<i>MnO</i>	<i>Al₂O₃</i>	<i>ZnO</i>	<i>FeO</i>	<i>SO₃</i>	<i>MgO</i>	<i>H₂O</i>	<i>Total</i>
Roșia Montană	0.52	1.74	4.55	2.43	35.49	0.17	45.27	99.73
Baia Sprie*	11.30	10.92	3.70	3.11	35.94	0.33	44.38	100.12

* Data from Rădulescu & Dimitrescu (1966).

Kalinite - $\text{KAl}(\text{SO}_4)_2 \cdot 11\text{H}_2\text{O}$ is abundant in the investigated gallery and appears as delicate, tiny fibers overlying halotrichite aggregates (Pl. II, Fig. 3). Crystals are translucent and if removed from the gallery environment will decompose within minutes into a white milky powder. Until now, this rare mineral was solely identified from Miocene sandstones and claystones along the Sub-Carpathians (Petrescu, 1948). Our description is based on XRD analyses. The X-ray powder diffraction patterns are listed in Table 11 (see supplementary information).

Alunogen - $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$. After 75 years since its most recent citation in the Romanian mineralogical literature, alunogen was “re-discovered”. Alunogen was associated with pickeringite occurring as efflorescence on dietrichite botryoidal aggregates. The prismatic crystals of alunogen have a length of to 3 mm and are extremely thin (<0.5 mm). In the present occurrence, alunogen crystals are colorless or white and show a silky luster. The mineral was identified by means of XRD (Table 12; see supplementary information) and EDS (Fig. 3) investigations. Alunogen was cited in Romania as early as the mid-XIXth century (Herbich, 1853), but all the other available references end in 1928 (Rădulescu & Dimi-trescu, 1966).

Fig. 3. EDS spectra of alunogen.

GENETIC CONSIDERATIONS & CONCLUSIONS

The stability and formation mechanism of most efflorescent sulfate minerals is largely unknown (Jambor et al., 2000; Buckby et al. 2003). As shown in Table 1, temperature, relative humidity and paragenesis vary along the sampled gallery. Temperature, relative humidity, and airflow are the prime variables that control evaporation, which in turn is responsible for concentrating chemically different solutions. Field observations and mineralogical identifications suggest that the sulfates from our site evolved in the manner illustrated in Fig. 4.

Meteoric waters and oxygen react with the pyrite inside the fractured dacites to form ferrous sulfate and sulfuric acid solutions. As these solutions evaporate (when coming in contact with the adit atmosphere), the sulfuric acid concentration increases. Some of this acid reacts with surrounding dacites or other primary/secondary minerals to release other cations (Al^{3+} , Zn^{2+} , Mn^{2+}) into solution (Jambor et al., 2000).

At relative humidities less than 92%, melanterite will be extruded from the capillary pores and small fissures forming beard-like efflorescences. Depending on relative humidity of the environment, melanterite will undergo further oxidation and dehydration to form other sulfate minerals. Under dryer conditions, melanterite dehydrates to rozenite. Since the two minerals occur at different locations along the investigated gallery, we believe rozenite would have been directly precipitated from ferrous sulfate solutions when the relative humidity in the gallery atmosphere was such to allow its deposition. Due to Fe - Mn substitution, rozenite (regardless of how it formed) may subsequently transform into jokokuite. Under moist conditions, some ferrous iron oxidizes to ferric iron and the $(\text{Fe}^{2+}\text{-Fe}^{3+})$ - acid rich solution migrates until evaporating conditions will lead to the deposition of copiapite in the form of yellowish-orange efflorescent blooms.

Fig. 4. Depositional summary of the sulfates and their relationship to evaporation, relative humidity, and cation substitutions.

Since the Al activity becomes high relative to Fe as the dissolved iron is removed by the precipitation of iron sulfate minerals, halotrichite may precipitate when the relative humidity exceed 92%. The presence of three other minerals of the halotrichite group (pickeringite, apjohnite, and dietrichite) is not surprising, since they form a complete solid-solution series (Gaines et al., 1997). The precipitation of one or more of these minerals is controlled solely by cation substitution.

The importance of local geochemical conditions in determining the type of mineral precipitated in a specific efflorescence is emphasized by the presence of kalinite in a potassic alteration zone. An acid-sulfate solution is essential to sustain leaching of Al and K at a low pH from dacites and their subsequent co-precipitation in the form of translucent needle-like kalinite crystals upon halotrichite.

When the activity of additional ions (iron, manganese, magnesium, or potassium) remains very low, but the aluminum and sulfate are readily supplied, alunogen is precipitated along or upon other minerals of the halotrichite group.

The optimal microclimatic conditions required for kalinite and alunogen to form and persist are mainly controlled by local (micro)-ventilation conditions, which are indirectly related to fluctuations in relative humidity and temperature.

Changes in the discharge of the percolating water due to seasonally climate conditions will cause large excursions in pH and cation content of the seepage water and also in the relative humidity of the underground atmosphere. This situation might be responsible for local variations in the mineral paragenesis, (such as heavy rain events) and may cause dissolution of the highly soluble sulfate minerals presented herein.

The secondary efflorescent sulfate minerals associated with the weathered dacites along an abandoned adit from the Cărnic mining district are spectacular. Apart from jokokuite and apjohnite, the first reported occurrence in Romania within this study (not to be found in Udubașa, 1999), several other rare sulfates (dietrichite, kalinite, alunogen etc.) have formed under particular underground climatic settings. In particular, it is interesting to note that the precipitation of all these sulfates is controlled not only by cation substitution, also by variations in ionic activity, temperature, relative humidity, and evaporation. All the last three variables relate to seasonally episodic fluctuations in water discharge along the fissures and capillary pores and to water drainage chemistry. However, due to the limited amount of data available, more geochemical and mineralogical work is needed to detail information on these aspects and to assess if there are any relation between efflorescent sulfates deposition and the annual hydrologic cycle.

Acknowledgements. Permission for entering and sampling the old adits at Cărnic mining district was granted by the S. C. Roșia Montană Gold Corporation. Part of this research was supported by MEC-CNCSIS grants 38/41 and 1696 to B. P. Onac.

Supplementary information for this paper are to be found on *Studia's* website (<http://bioge.ubbcluj.ro/~bonac/studia/rosia>)

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SECONDARY SULFATES FOUND IN AN OLD ADIT FROM ROȘIA MONTANĂ, ROMANIA

Pl. I.

Fig. 1. *Efflorescences of melanterite.*

Fig. 2. *Rozenite/jokokuite anthodites.*

Pl. II

Fig. 1. *Botryoidal crusts of copiapite.*

Fig. 2. *Fibrous crystals of apjohnite.*

Pl. III

Fig. 1. SEM image of *pickeringite*.

Fig. 2. SEM image showing composite fibers of *apjohnite*.

Pl. IV

Fig. 1. SEM image of curved prismatic crystals of dietrichite.

Fig. 2. SEM image showing aggregates of rozenite.