

NEW DATA CONCERNING Mn BEARING MINERALS FROM ROŞIA MONTANĂ, METALIFERI MOUNTAINS, ROMANIA

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ABSTRACT. The paper gives new evidences on some mineral species from Romanian epithermal ore deposits. Microprobe analyses were used to identify the chemical composition of gangue and alteration minerals from Roşia Montană gold deposit. Special attention was given to rhodonite, rhodochrosite, and adularia.

Key words: rhodonite, rhodochrosite, Roşia Montană ore deposit, Romania.

INTRODUCTION

In the course of time the lack of pertinent analytical results gave rise to many controversies regarding Romanian mineralogical references. Many citations of minerals from Romania are based on empirical observations even only macroscopic examinations, sometimes intermingled with more accurate determinations (microscopy, XRD, etc.). As a general rule, the accurate quantitative data (e.g. microprobe results) of many mineral species is still lacking. Several exceptions can be noted: Cook and Damian (1997), Damian (1998), Har (1998), Nicolescu (1998), Damian and Costin (1999), Tămaş and Bailly (1999a). We join to these pioneering works giving new evidences about Mn-bearing minerals (rhodonite, rhodochrosite) and furthermore on K-feldspar (adularia) from Roşia Montană ore deposits.

GENERAL GEOLOGY

Roşia Montană area belongs to the Bucium Unit as separated by Bleahu et al. (1981) and reconsidered by Balintoni (1994, 1997). The crystalline basement of Baia de Arieş type (Balintoni, 1997) is covered by Cretaceous flysch. Within the so-called "Roşia Montană basin" two volcanic pulses are well developed, while another one is only inferred (Cioflica et al., 1973). First volcanic pulse is an explosive rhyolitic one of Lower Badenian - Middle Badenian age (Cioflica et al., 1973). Then follow the main dacite eruptions (upper badenian) - Cetate dacite - which was also followed by a

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pannonian andesitic phase - Rotunda type (Cioflica et al, 1973, Ianovici et al., 1976, Borcoș, 1994).

The high grade and large tonnage Roșia Montană low sulfidation epithermal ore deposit (Mârza et al., 1997, Tămaș and Bailly, 1999b) is related to the dacite activity. We may consign the complex brecciation - metallogenetic evolution within the Roșia Montană area as highlighted by Mârza et al. (1997), Tămaș (1998), Tămaș and Bailly (1999b). Consequently, several types of ore body morphologies are well developed: breccias (phreatomagmatic and phreatic types), vein systems (steeply and flatly dipping), stockworks (so-called "volburi"), impregnations as well as placers and paleoplacers (Petruțian, 1934, Ghițulescu and Socolescu, 1940, 1941). The Mn-bearing minerals occur as gangue minerals within breccias, veins and stockwork structures.

PREVIOUS DATA

Rhodochrosite and rhodonite are the most common minerals among the manganese bearing ones. The misunderstanding regarding the identification of manganese silicate and carbonate lasted for decades. Also, at present, there are a lot of misinterpretations regarding the type locality of these two minerals.

In this respect, according to Papp (1997), the first mention of rhodochrosite is usually attributed to Bergman in 1782 who used the term "*magnesium acido aereo mineralisatum*" without any description or locality data. Furthermore, Papp (1997) cited a series of authors from 17-th to 18-th centuries who gave evidence on Mn bearing minerals. We will underline below several informations available from Papp (1997). Bergman already described, in 1780, "*magnesium aeratum*" as the matrix of "*minera Nagyayensis*" (nagyagite). Rhodochrosite from Săcărâmb (former Nagyag) was described later in details by Fichtel in 1794. His and others' observations were published together with Ruprecht's analytical data on rhodonite from 1783 by Lenz in 1794. The modern term rhodochrosite was introduced by Hausmann in 1813 who made reference to the first accurate results of the quantitative analysis made by Lampadius in 1800 on a specimen from Kapnik (Cavnic, Romania). The above informations are in agreement with those of Rădulescu and Dimitrescu (1966), and Mureșan et al. (1990), but they do not agreed with those of Udubașa et al.(1992), Szakall and Gatter (1993) and Nicolescu (1996).

According to the principle of priority (Papp, 1997, p.70) the type locality for rhodochrosite should be Săcărâmb instead of Cavnic.

Referring to rhodonite, the first quantitative analysis was published by Ruprecht (1783, fide Papp, 1997). He analysed the "*reddish gangue or*

so-called feldspar" from Kapnik (Cavnic, Romania) known also as "*Kapniker Feldspath*". He regarded this mineral as a quartz (or jasper) "penetrated" with manganese. However, others like Karsten in 1800 regarded it as a distinct species. The term rhodonite was first used by Jasche in 1819 for a mineral from Elbingerode (Hartz Mts., Germany). According to the principle of priority, the type locality for rhodonite should be Cavnic (Papp, 1997, p.69).

The list of minerals from Roșia Montană Au-Ag epithermal ore deposit comprises about 40 mineral species as cited by Udubasa et al. (1992).

The rhodochrosite from Rosia Montana was mentioned by Cotta and Fellenberg (1862, fide Mike, 1882), Zepharovich (1872), Szabó (1875, fide Papp, 1997), Petruian (1934), Helke (1938), Ghițulescu and Socolescu (1941), Rădulescu and Dimitrescu (1966). All the available descriptions state that rhodochrosite occurs as globular or reniform masses, with a pink-yellowish colour, forming crusts or filling the veinlets. In most of the cases it is associated with rhodonite. Chalcopyrite, galena as well as gold as granular aggregates within quartz are to be noted.

The first mention of rhodonite at Roșia Montană was made by Helke (1938).

SAMPLING

The Mn gangue minerals are common within adularia-sericite (low sulfidation) epithermal deposits (Heald et al., 1987, Hedenquist, 1995). The abundance of these minerals within similar type of ore deposits from Romania (e.g. Cavnic) is well known (Marius, 1996). Various occurrences of Mn-bearing gangue minerals are observed in Roșia Montană ore deposits:

- infill of the open spaces among breccia fragments; it is visible in the open pit (Cetate Breccia) as well as in the underground workings (Racoși Breccia, +795 level);
- anastomosing veinlets within the stockworks;
- major component of the veins which cut off the dacite, the stockwork structures (Cârnic massif, +853 level), the breccias (Cetate breccia, open pit), as well as within those veins which cut off the Cretaceous flysch (Țarina, Igre mining fields).

In the underground workings, mostly abandoned for decades, the veins rich in Mn gangue minerals are easily visible even in the huge underground cavities ("coranda") from Cârnic mining field due to their continuity and dark colour. The exposed surface of the veins is black (covered by Mn oxides) and could be easily traced within the dacite rocks which was substantial whitened due to the widespread potassium silicate and phyllic alterations. At the surface, within the open pit (Cetate open pit), a vein system rich in Mn bearing gangue minerals occurred. This vein system consists of steeply dipping densely parallel vein swarm (sheeted veins) which cut off the so-called Glamm formation (Fig.1). The analysed Mn bearing minerals samples came from this area (open pit, level + 886)

from a vein with an average width of 15 cm. The veins cross over the open pit bench and could be traced on both sides of the access road.

Microscopic studies, both on thin and polished sections were performed. Preliminary ore micro-copy study carried on for several samples from this vein revealed the presence of common sulphides (chalcopyrite,

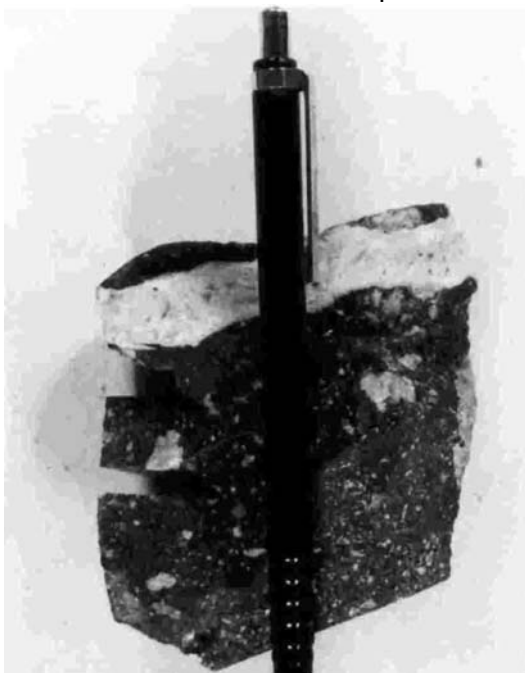


Fig. 1 – Rhodonite – rhodochrosite vein from Glamm formation, Cetate open pit, +886 m level.

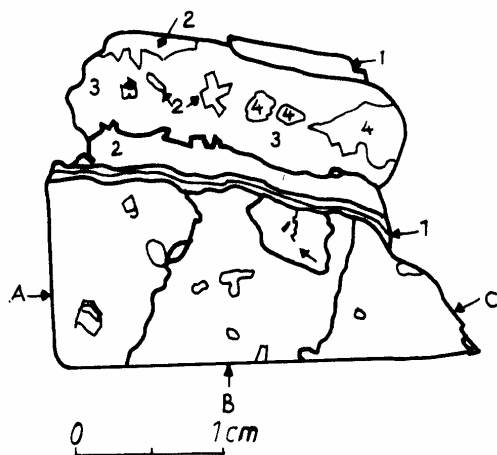
sphalerite, galena, pyrite) as well as native gold (Tămaș and Bailly, unpubl. data). In thin section, rhodochrosite appears usually as colorless grains, with a medium relief and a perfect rhombohedral cleavage. The other optical properties as birefringence (0,200-0,210) and the negative optic sign complete the observations. On the other side, in some thin sections, rhodonite presents a weak pleochroism, but usually it is also colorless, with a medium relief, good quality cleavage, an inclined extinction (~35°) and low birefringence (0.012-0.014). Rhodonite and rhodochrosite are almost always intimately mixed, rhodochrosite replacing rhodonite.

Fluid inclusion results (Tămaș and Bailly, 1999b) revealed the low salinity (0.7 to 4 wt% NaCl equiv.) and low homogenization temperatures (200-285°C) of the fluids. The fluid inclusion analyses were made also on different minerals (adularia, apatite, quartz) related to rhodonite-rhodochrosite deposition across the width of the vein.

ANALYTICAL TECHNIQUES

The microprobe analyses were performed on similar samples as those subjected for fluid inclusion investigations by Tămaș and Bailly (1999b) (vein fragments from Cetate open pit, level +886) (Fig. 2).

Fig. 2 – Sketch after a thin polished section on a vein fragment from Cetate open pit which was subjected to microprobe investigation.



A – fragment of hydrothermalised dacite;

B – gray glamm (breccia); the clasts are mainly subangular;

C – black glamm (breccia) poor in clasts;

1 – melange rhodonite – rhodochrosite finely rubanated;

2 – light pink, compact mixing of rhodonite – rhodochrosite;

3 – reddish pink mixing of rhodonite – rhodochrosite;

4 – final microcrystalline quartz.

Electron microprobe analyses for this study were performed on rhodonite, rhodochrosite, and adularia, using a SX 50 – CAMECA electron microprobe of B.R.G.M.³, Orléans.

A total of 10 elements were analysed: K, Si, Fe, Ca, Na, Ti, Al, Mn, Cr, Mg. For all the runs an accelerating voltage of 15 kV was used, with a beam current of 12 nA and a spot size of about 1 μm. Counting time was 6 s on standards and unknowns. A P.A.P. correction program was used for all the analyses.

RESULTS AND DISCUSSION

A number of 24 analyses on rhodonite, rhodochrosite, and adularia were performed. The selected electron microprobe analyses of these three minerals are listed below. The representative results for the rhodonite are given in Table 1A (% oxides) and Table 1B (% elements).

Table 1A

The chemical composition (% oxides) of rhodonite

Point no.	3	4	12	13	14	15	16	18	19
K ₂ O	0.018	0.034	0.033	0.024	0.118	0.018	0.010	0.031	0.069
SiO ₂	44.628	44.574	44.497	44.491	44.452	45.376	43.684	44.38	45.394
FeO	0.293	0.256	0.244	0.124	0.084	0.172	0.050	0.169	0.018
CaO	4.732	6.394	3.217	4.371	4.151	3.292	2.635	2.637	4.871
Na ₂ O	0.019	0.130	0.024	0.015	0.446	0.078	0.000	0.012	0.097
TiO ₂	0.000	0.060	0.010	0.088	0.058	0.000	0.055	0.000	0.000
Al ₂ O ₃	0.326	0.257	0.393	0.264	0.183	0.367	0.163	0.326	0.416
MnO	49.835	47.457	50.289	49.195	48.625	49.081	51.774	50.076	49.553
MgO	0.549	0.590	0.623	0.413	0.546	0.904	0.554	0.701	0.360
	100.400	99.752	99.330	98.985	98.663	99.288	98.925	98.332	100.778

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Point no.	20	22	23	29	33	34	35	37
K ₂ O	0.027	0.122	0.039	0.071	0.007	0.148	0.000	0.000
SiO ₂	45.926	56.644	61.466	56.407	45.212	67.999	45.582	46.908
FeO	0.121	0.105	0.087	0.162	0.071	0.018	0.005	0.144
CaO	3.936	2.902	2.742	3.075	4.332	3.908	4.500	9.041
Na ₂ O	0.000	0.120	0.082	0.171	0.034	0.148	0.175	0.051
TiO ₂	0.010	0.000	0.000	0.013	0.000	0.007	0.023	0.047
Al ₂ O ₃	0.308	0.326	0.326	0.347	0.612	0.465	0.565	0.238
MnO	49.540	37.790	33.193	38.814	50.081	28.285	50.017	43.787
MgO	0.657	0.532	0.376	0.509	0.466	0.229	0.400	0.257
	100.525	98.541	98.311	99.569	100.815	101.207	101.267	100.473

Table 1B

The chemical composition (% elements) of rhodonite

Point no.	3	4	12	13	14	15	16	18	19
K	0.001	0.001	0.001	0.001	0.003	0.001	0.000	0.001	0.002
Si	0.969	0.969	0.975	0.977	0.977	0.985	0.968	0.981	0.977
Fe	0.005	0.005	0.004	0.002	0.002	0.003	0.001	0.003	0.000
Ca	0.110	0.149	0.076	0.103	0.098	0.077	0.063	0.062	0.112
Na	0.001	0.006	0.001	0.001	0.019	0.003	0.000	0.001	0.004
Ti	0.000	0.001	0.000	0.002	0.001	0.000	0.001	0.000	0.000
Al	0.008	0.007	0.010	0.007	0.005	0.009	0.004	0.009	0.011
Mn	0.916	0.873	0.933	0.915	0.906	0.903	0.972	0.937	0.903
Mg	0.018	0.019	0.020	0.014	0.018	0.029	0.018	0.023	0.012
	2.028	2.029	2.021	2.019	2.028	2.010	2.027	2.016	2.021

Point no.	20	22	23	29	33	34	35	37
K	0.001	0.003	0.001	0.002	0.000	0.003	0.000	0.000
Si	0.986	1.132	1.187	1.123	0.973	1.232	0.975	0.994
Fe	0.002	0.002	0.001	0.003	0.001	0.000	0.000	0.003
Ca	0.091	0.062	0.057	0.066	0.100	0.076	0.103	0.205
Na	0.000	0.005	0.003	0.007	0.001	0.005	0.007	0.002
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001
Al	0.008	0.008	0.007	0.008	0.016	0.010	0.014	0.006
Mn	0.901	0.640	0.543	0.654	0.913	0.434	0.906	0.786
Mg	0.021	0.016	0.011	0.015	0.015	0.006	0.013	0.008
	2.010	1.868	1.811	1.877	2.020	1.767	2.018	2.004

The representative electron microprobe analyses for rhodochrosite (6 runs) are listed in Table 2A (% oxides) and in Table 2B (% elements).

Besides rhodonite, the thin section study revealed also the presence of plagioclase and adularia. The electron microprobe analysis of adularia (% oxides) is given in Table 3.

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Table 2 A

The chemical composition (% oxides) of rhodochrosite

Point no.	6	8	10	11	21	31
K ₂ O	0.027	0.000	0.000	0.000	0.019	0.000
SiO ₂	0.439	0.049	0.071	0.056	0.122	9.920
FeO	0.000	0.062	0.242	0.140	0.015	0.068
CaO	2.574	9.591	5.956	8.012	2.345	3.270
Na ₂ O	0.039	0.008	0.044	0.043	0.088	0.071
TiO ₂	0.008	0.038	0.013	0.000	0.020	0.035
Al ₂ O ₃	0.000	0.017	0.009	0.021	0.023	0.079
MnO	57.688	47.836	53.797	49.374	57.612	55.628
MgO	0.348	0.617	0.809	0.730	0.464	0.280
	61.123	58.218	60.941	58.376	60.708	69.351

Table 2B

The chemical composition (% elements) of rhodochrosite

Point no.	6	8	10	11	21	31
K	0.001	0.000	0.000	0.000	0.001	0.000
Si	0.017	0.002	0.003	0.002	0.005	0.310
Fe	0.000	0.002	0.008	0.005	0.001	0.002
Ca	0.104	0.396	0.238	0.332	0.096	0.110
Na	0.003	0.001	0.003	0.003	0.007	0.004
Ti	0.000	0.001	0.000	0.000	0.001	0.001
Al	0.000	0.001	0.000	0.001	0.001	0.003
Mn	1.847	1.561	1.702	1.615	1.863	1.474
Mg	0.020	0.035	0.045	0.042	0.026	0.013
	1.992	1.999	1.999	1.999	1.999	1.917

Table 3

The chemical composition of adularia and the resulted mineral % (O=8)

Point no.	5		5	Mineral % and calculated formula
K ₂ O	16.47	K	0.97	Adularia 97.36 %
SiO ₂	64.81	Si	3.00	Albite 1.63 %
FeO	0.13	Fe	0.01	Quartz 0.51 %
CaO	0.00	Ca	0.00	Pyroxmangite 0.37 %
Na ₂ O	0.19	Na	0.02	Rhodonite 0.06 %
TiO ₂	0.00	Ti	0.00	
Al ₂ O ₃	18.15	Al	0.99	K _{0,97} [Si _{3,00} Al _{0,99} O ₈] adularia
MnO	0.17	Mn	0.01	
MgO	0.00	Mg	0.00	
	99.93		5.00	

The mineralogical calculations made for the runs focused on rhodonite areas are listed in the table below (Table 4).

Table 4

The mineral % on the rhodonite areas and the calculated formula

Point no.	Mineral %				<i>Rhodonite</i>
	<i>Rhodonite</i>	<i>Adularia</i>	<i>Albite</i>	<i>Anorthite</i>	
3	99.69	0.11	0.16	0.44	(Mn _{0.916} , Ca _{0.110} , Fe _{0.005} , Mg _{0.018})[Si _{0.969} O ₃]
4	98.39	0.22	1.10	-	(Mn _{0.873} , Ca _{0.149} , Fe _{0.005} , Mg _{0.019})[Si _{0.969} O ₃]
12	98.40	0.22	0.20	0.49	(Mn _{0.933} , Ca _{0.075} , Fe _{0.004} , Mg _{0.020})[Si _{0.975} O ₃]
13	98.36	0.16	0.11	0.27	(Mn _{0.915} , Ca _{0.103} , Fe _{0.002} , Mg _{0.014})[Si _{0.977} O ₃]
14	97.21	0.66	0.32	-	(Mn _{0.906} , Ca _{0.098} , Fe _{0.002} , Mg _{0.018})[Si _{0.977} O ₃]
15	98.15	0.11	0.68	0.33	(Mn _{0.903} , Ca _{0.077} , Fe _{0.003} , Mg _{0.029})[Si _{0.985} O ₃]
16	98.57	0.06	-	0.24	(Mn _{0.972} , Ca _{0.063} , Fe _{0.001} , Mg _{0.018})[Si _{0.968} O ₃]
18	97.62	0.17	0.10	0.44	(Mn _{0.937} , Ca _{0.062} , Fe _{0.003} , Mg _{0.023})[Si _{0.981} O ₃]
19	99.26	0.39	0.84	0.28	(Mn _{0.903} , Ca _{0.112} , Mg _{0.012})[Si _{0.977} O ₃]
20	99.90	0.17	-	0.44	(Mn _{0.901} , Ca _{0.091} , Fe _{0.002} , Mg _{0.021})[Si _{0.986} O ₃]
22	96.82	0.72	1.00	-	(Mn _{0.640} , Ca _{0.062} , Fe _{0.002} , Mg _{0.016})[Si _{1.132} O ₃]
23	97.16	0.23	0.68	0.24	(Mn _{0.543} , Ca _{0.057} , Fe _{0.001} , Mg _{0.011})[Si _{1.187} O ₃]
29	97.74	0.40	1.42	-	(Mn _{0.654} , Ca _{0.066} , Fe _{0.003} , Mg _{0.015})[Si _{1.123} O ₃]
33	99.63	0.06	0.26	0.87	(Mn _{0.913} , Ca _{0.100} , Fe _{0.001} , Mg _{0.015})[Si _{0.973} O ₃]
34	98.97	0.89	1.26	0.09	(Mn _{0.434} , Ca _{0.076} , Mg _{0.006})[Si _{1.232} O ₃]
35	99.34	-	1.47	0.44	(Mn _{0.906} , Ca _{0.103} , Mg _{0.013})[Si _{0.975} O ₃]
37	99.76	-	0.42	0.24	(Mn _{0.786} , Ca _{0.205} , Fe _{0.003} , Mg _{0.008})[Si _{0.994} O ₃]

The final formula of the composition of rhodonite (Mn_{0.826}, Ca_{0.095}, Fe_{0.002}, Mg_{0.016})[Si_{1.022}O₃] was obtained as a mean value of the coefficients for each chemical element.

The results of mineralogical calculations made for rhodochrosite are given in table below (Table 5).

Table 5

The calculated formula for rhodochrosite

Point no.	Rhodochrosite
6	(Mn _{1.847} , Ca _{0.104} , Mg _{0.020})[C _{0.990} O ₃]
8	(Mn _{1.561} , Ca _{0.396} , Mg _{0.035})[C _{0.978} O ₃]
10	(Mn _{1.702} , Ca _{0.238} , Mg _{0.045})[C _{0.974} O ₃]
11	(Mn _{1.615} , Ca _{0.332} , Mg _{0.042})[C _{0.975} O ₃]
21	(Mn _{1.863} , Ca _{0.096} , Mg _{0.026})[C _{0.986} O ₃]
31	(Mn _{1.474} , Ca _{0.110} , Mg _{0.013})[C _{0.991} O ₃]

The final expression of the composition of rhodochrosite (Mn_{1.677}, Ca_{0.213}, Mg_{0.030})[Ca_{0.982}O₃] was obtained using the mean values of the coefficients for each element.

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