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Mn-bearing sulfosalts from Roveňské pásmo Lode of Kutná Hora ore district, Czech Republic: benavidesite, Mn-rich jamesonite, Mn-rich Ag-excess fizélyite and Mn-rich senandorite

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Abstact

A rare and interesting occurrence of Mn-bearing sulfosalts has been found in samples from medieval mine dumps of Roveňské pásmo Lode of Kutná Hora ore district, Czech Republic. The following suite of manganese-containing sulfosalts was identified: Mn-rich Ag-excess fizélyite, Mn-rich senandorite, benavidesite and Mn-rich jamesonite. Chemical analyses are presented and discussed. The empirical chemical formula of Mn-rich Ag-excess fizélyite is $Ag_{6.10}Cu_{0.06}(Pb_{12.69}Mn_{0.70}Fe_{0.26})_{\Sigma 13.65}Sb_{20.98}S_{48}$, that of Mn-bearing senandorite is $(Ag_{0.94}Cu_{0.05})_{\Sigma 0.99}(Pb_{0.99}Mn_{0.03})_{\Sigma 1.02}Sb_{3.00}S_{5.98}$. The mean chemical composition of benavidesite is $Pb_{3.92}(Mn_{0.50}Fe_{0.45})_{\Sigma 0.95}Sb_{6.18}S_{13.95}$ and that of Mn-rich jamesonite is $Pb_{3.92}(Fe_{0.57}Mn_{0.37})_{\Sigma 0.94}Sb_{6.13}S_{14.02}$. An overview of Mn-containing sulfosalts is given.

***Key words**: Mn-bearing sulfosalts, benavidesite, Mn-rich jamesonite, Mn-rich Ag-excess fizélyite, Mn-rich senandorite, chemical composition, Kutná Hora ore district, Czech Republic*

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Introduction

Mn-containing sulfosalts are a fairly scant group of sulfosalts, comprising until 2008 according to the sulfosalt systematics (Moëlo et al. 2008) of only four mineral species. Two of them are Mn-analogues of much more frequently occurring Fe-containing sulfosalts: benavidesite, $MnPb_4Sb_6S_{14}$ (Oudin et al. 1982), which is an Mn-analogue of jamesonite, and clerite $MnSb_2S_4$, which can be viewed upon as a Mn analogue of berthierite (Murzin et al. 1996). Uchucchacuaite, $MnAgPb_3Sb_5S_{12}$ is a Mn sulfosalt belonging to andorite series (Moëlo et al. 1984; Yang et al. 2011), and one is a specific mineral having no counterpart in the mineralogical system: samsonite $MnAg_4Sb_2S_6$ (Edenharter, Nowacki 1974).

Between 2008 and 2023, new Mn-containing sulfosalts have been described: manganoquadratite, $AgMnAsS_3$ (Bonazzi et al. 2012), menchettiite, $Pb_5Mn_3Ag_2Sb_6As_4S_{24}$ (Bindi et al. 2012) and graţianite, $MnBi_2S_4$ (Ciobanu et al. 2014): followed several years later by oyonite, $Ag_3Mn_2Pb_4Sb_7As_4S_{24}$ (Bindi et al. 2018), tsygankoite, $Mn_8Tl_8Hg_2(Sb_{21}Pb_2Tl)_{\Sigma 24}S_{48}$ (Kasatkin et al. 2018), agmantinite, Ag_2MnSnS_4 (Keutsch et al. 2019), gladkovskyite, $MnTlAs_3S_6$ (Kasatkin et al. 2019), luboržákite, Mn_2AsSbS_5 (Kasatkin et al. 2020), ramosite, $Pb_{25.7}Sn_{8.3}Mn_{3.4}Sb_{6.4}S_{56.2}$ (Keutsch et al. 2020), auerbakhite, $MnTl_2As_2S_5$ (Kasatkin et al. 2021) and lasmanisite, $Ag_{12}Pb_{13}Mn_{11}Sb_{44}S_{96}$ (Topa et al. 2023).

Apart from these minerals, manganese appears in limited amounts in some sulfosalts of the andorite series, concretely in ramdohrite, $(Cd,Mn,Fe)Ag_{5.5}Pb_{12}Sb_{21.5}S_{48}$ ($And_{68.75}$) (Moëlo et al. 1989).

The Kutná Hora Ag-Pb-Zn ore district (located 60 km east of Prague, Central Bohemia, Czech Republic) contains a hydrothermal vein type mineralization of Variscan age (Holub et al. 1982). Geologically and mineralogically, two mineral assemblages are present in this ore district, one „silver-rich“ in the southern part of the ore district and one „pyrite-rich“ in the northern part (Malec, Pauliš 1997).

In Kutná Hora ore district the sulfide mineralization is rich in sulfosalts of Ag-Sb, Ag-Pb-Sb and Pb-Sb (Pažout et al. 2019) in the southern part of the ore district, as well as sulfosalts of Ag-Pb-Bi, Ag-Pb-Bi-Sb and Pb-Bi-Sb in the northern part (Pažout 2017, Pažout et al. 2017).

As mentioned above, the sulfosalt minerals of the andorite series tend to concentrate divalent metals such as Fe, Cd, Mn in minor amounts. The chemistry of andorite series is an interesting feature of the mineralogy of the Kutná Hora ore district. Cadmium and Fe were determined in ramdohrite, fizélyite, Ag-excess fizélyite from lodes of both parts of the ore district. Manganese has not been detected in andorite minerals and other sulfosalts in Kutná Hora until samples from the Roveňské pásmo Lode were analysed and three finds with Mn-bearing sulfosalts were found. The description of these finds is the subject of this paper.

Samples and occurrence

The samples with Mn-bearing sulfosalts were found in the material collected by the first author of the article on the medieval mine dumps of the southern part of the Roveňské pásmo Lode of the Kutná Hora ore district (49°56'38.14"N, 15°16'12.00"E). This lode is about 2 km long and several hundred meters wide and was extensively mined since the beginning of the 14th century soon after the discovery of the deposit. The lode is formed by two principal veins, the main Hlavní Roveňská žíla vein and the Petrská klufta vein, reaching maximum depths around 200 m (Holub 2018). Typical of this lode are lower amounts of base-metal sulfides in the extracted ore on the one hand and richer accumulations of silver minerals on the other hand.

The samples with Mn-bearing sulfosalts were discovered in three different finds (RO 1, RO 203, RO 205). All three samples type of the ore are characterized by the same stockwork

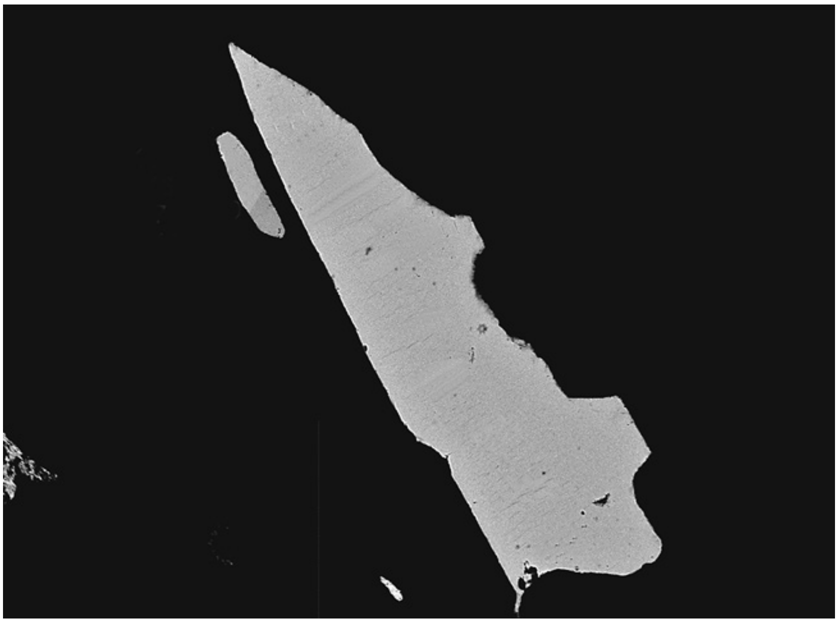

Fig. 1 *The large grain is Mn-rich Ag-excess fizélyite with 0.41 - 0.59 wt. % of Mn; lower (darker) part of the small grain is Mn-rich senandorite with 0.17 - 0.25 wt. % of Mn; upper (lighter) part of the small grain) corresponds to a mineral of the andorite group. Field of view 600 μm. BSE photo of sample RO 1 R2.*

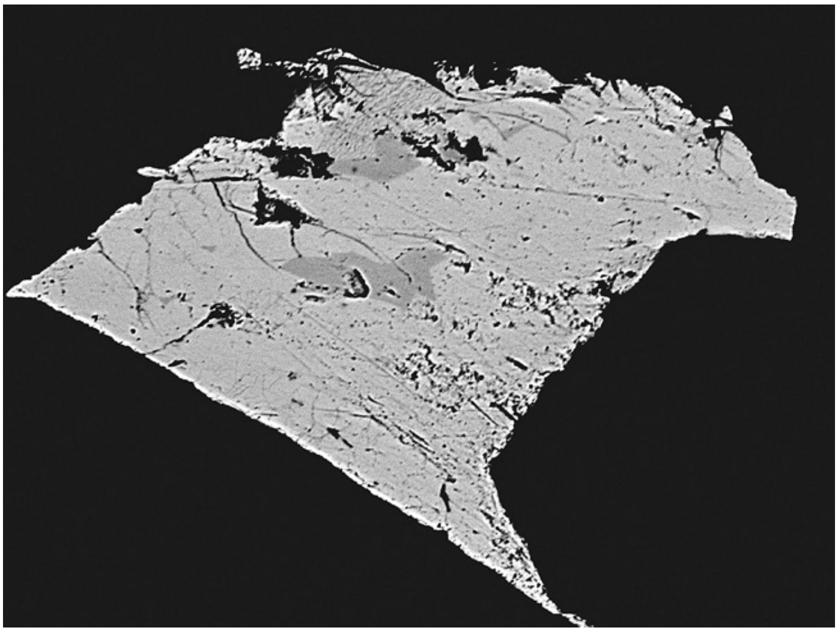

Fig. 2 *A grain with minerals of benavidesite - jamesonite series (medium grey). The central part of the grain between the two darker grains (minerals of the andorite group) is formed by benavidesite with Mn > Fe, while the remaining part of the grain is Mn-rich jamesonite (slightly lighter than the central part due to Fe > Mn). Field of view 400 μm. BSE photo of sample RO 203 A.*

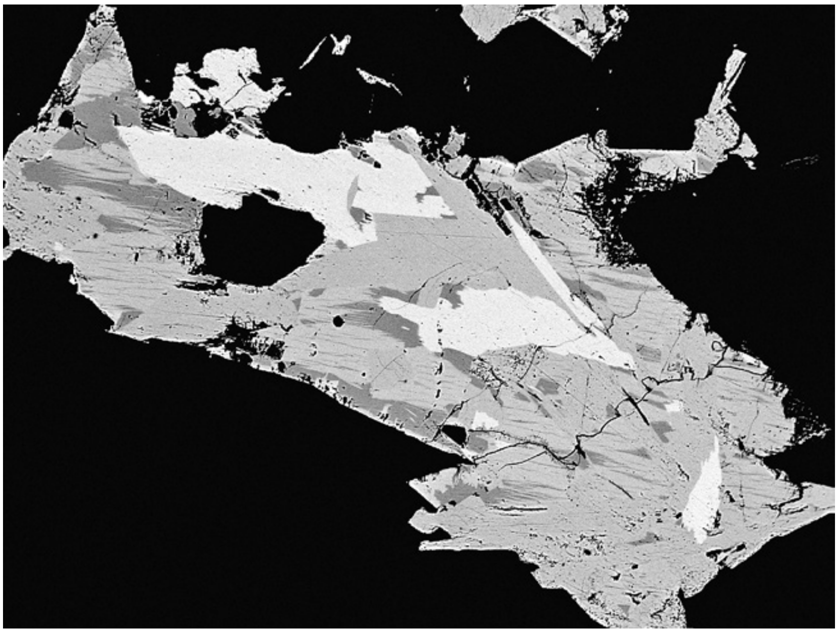

Fig. 3 *A grain of Mn-rich jamesonite (medium grey) with darker and lighter tints reflecting the Mn - Fe substitution, replaced by Mn-free quatrandorite (dark grey) which is subsequently replaced by Mn-free owyheeite (white). The grain is in quartz - kutnohorite gangue (black). Field of view 860 μm. BSE photo of sample RO 203 A.*

mineralization. The sample RO 1 is formed by a block (50 × 30 × 20 cm) of gneiss hosting stockwork-type mineralization with drusy quartz veinlets with the thickness from 5 to 10 mm, in which crystals up to 2 mm and grains of diaphorite, pyrargyrite, owyheeite, boulangerite, freieslebenite, *freibergite* and a suite of andorite minerals (Ag-exces fizélyite, ramdohrite, quatrandorite, some with Mn, some without) occur. Interesting is the discovery of Cd-rich sphalerite with Cd > Fe with up to 10.73 wt.% of Cd, 4.68 % Fe and 3.39 % Mn. Galena has minor amounts of Ag (up to 0.93 wt.%) and Sb (up to 1.38 wt.%) in the sample. The sample RO 203 is formed by up to 5 mm thick quartz veinlets in gneiss with plentiful disseminated silvery grains (up to 2 mm) of benavidesite, Mn-rich jamesonite, Mn-rich fizélyite, Mn-free quatrandorite, owyheeite, *freibergite* and brown sphalerite with 3.9 - 5.3 wt.% Fe and 2.2 - 3.5 wt.% Mn. The sample RO 205 is again a piece of gneiss with thin veinlets of quartz up to the thickness of 4 mm with disseminated silvery grains of benavidesite, Mn-jamesonite, freieslebenite, diaphorite, owyheeite, Ag excess fizélyite and Mn,Fe-rich sphalerite. Of the present sulfosalts, only benavidesite and jamesonite contain Mn in amounts above its detection limits. Maximum size of individual grains is 3 mm.

Methods of identification

Quantitative chemical analyses were performed with two electron microprobes (EPMA) in the wave-length dispersive mode (WDS). Two polished sections (RO 203 A and RO 205 A) were measured on CAMECA SX100 electron probe microanalyser at the National Museum, Prague in 2015. The analytical conditions were as follows: accelerating voltage of 25 kV, beam current of 20 nA, electron-beam diameter of 2 μm and standards: chalcopyrite (S*K*α), Bi_2Se_3 (Bi*M*β), PbS (Pb*M*α), Ag (Ag*L*α), halite (Cl*K*α), Sb_2S_3 (Sb*L*α), CdTe (Cd*L*α), HgTe (Hg*M*α), pyrite (Fe*K*α), Cu (Cu*K*α), ZnS (Zn*K*α), NiAs (As*L*α) and PbSe (Se*L*β). Measured data were corrected using PAP algorithm (Pouchou and Pichoir 1985).

The analysis of the sample RO1 R2 was obtained using Cameca SX100 electron probe microanalyzer at the Institute of Geology of the Czech Academy of Sciences, Prague, the correction procedure X-φ was applied (Merlet 1994). The operating conditions were: the accelerating voltage 20 kV, beam current 4 nA and focused beam (diameter ~0.8 μm). The following standards and X-ray lines were used: marcasite (S*K*α, Fe*K*α), tugtupite (Cl*K*α), sphalerite (Zn*K*α), stibnite (Sb*L*α), CdS (Cd*L*α), galena (Pb*M*α), Bi_2Se_3 (Se*L*β), GaAs (As*L*β), Mn (Mn*K*α), Cu (Cu*K*α) and Ag (Ag*L*α).

Results

Manganese contents in sulfosalts were detected in three samples (polished sections) from the Roveňské pásmo Lode. Four minerals have been detected, two belonging to the andorite branch of the lillianite homologous series (Ag-excess fizélyite and senandorite, Fig. 1, Table 1), two to the benavidesite - jamesonite series (Fig. 2, Table 2).

Ag-excess fizélyite forms a subhedral grain 450 × 100 μm in size in quartz matrix in a close vicinity to further subhedral grains of other andorite-group minerals (Fig. 1). The chemical composition of Ag-excess fizélyite (mean of five point analyses) corresponds to the empirical formula $Ag_{6.10}Cu_{0.06}(Pb_{12.69}Mn_{0.70}Fe_{0.26})_{\Sigma 13.65}Sb_{20.98}S_{48}$. Manganese contents vary between 0.41 and 0.59 wt. % (0.57 and 0.80 *apfu* Mn, respectively). Silver is well increased above the value of „normal" fizélyite due to almost one excess Ag atom in the structure of Ag-excess fizélyite. Silver contents vary in the Mn-rich member between 8.56 and 8.85 wt.% (5.97 and 6.17 *apfu* Ag). Yang et al. (2009) described ideal content 8.42 wt. % Ag (5.95 *apfu*) in the structure while „normal" (Ag-poorer) fizélyite contains ideally 7.16 wt. % of Ag (5.0 *apfu*). The order of the lillianite homologue *N* (Makovicky, Karup-Møller 1977), which should ideally be 4, is increased to 4.57, in agreement with the structure refinement result of 4.42 (Yang et al. 2009) and in line with observations from other oc-

Table 1 *Chemical composition of Mn-rich Ag-excess fizélyite (AEF) and Mn-bearing senadorite (AndVI) from Roveňské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu, N and L% for lillianite homologues)*

point	309	310	315	316	317	329	330	331	332	333
sample	RO 1R2	RO 1R2	RO 1R2	RO 1R2	RO 1R2	RO 1R2	RO 1R2	RO 1R2	RO 1R2	RO 1R2
mineral	AEF	AEF	AEF	AEF	AEF	AndVI	AndVI	AndVI	AndVI	AndVI
Ag	8.85	8.56	8.77	8.80	8.78	11.54	11.57	11.28	11.49	11.31
Cu	0.00	0.00	0.00	0.23	0.00	0.37	0.40	0.41	0.31	0.40
Pb	35.26	34.34	35.48	35.46	34.37	22.72	23.47	23.21	22.80	23.49
Fe	0.15	0.26	0.15	0.22	0.19	0.00	0.00	0.00	0.00	0.00
Mn	0.49	0.54	0.41	0.52	0.59	0.17	0.25	0.21	0.25	0.19
Sb	34.45	33.86	34.06	33.37	34.20	41.59	41.04	40.89	40.76	40.87
S	20.43	20.47	20.48	20.50	20.52	21.64	21.43	21.57	21.27	21.78
total	99.68	98.05	99.42	99.14	98.76	98.01	98.15	97.59	96.94	98.03
Ag	6.18	5.97	6.11	6.12	6.10	0.95	0.95	0.93	0.96	0.93
Cu	0.00	0.00	0.00	0.28	0.00	0.05	0.06	0.06	0.04	0.06
Pb	12.82	12.46	12.87	12.85	12.44	0.97	1.01	1.00	0.99	1.00
Fe	0.20	0.36	0.20	0.29	0.26	0.00	0.00	0.00	0.00	0.00
Mn	0.68	0.74	0.57	0.71	0.80	0.00	0.00	0.00	0.00	0.00
Sb	21.32	20.91	21.03	20.58	21.07	3.03	3.00	2.99	3.01	2.97
S	47.90	48.00	47.96	47.98	47.82	5.98	5.94	5.99	5.96	6.01
N	4.55	4.48	4.57	4.76	4.49	3.97	4.09	4.01	4.02	4.02
L%	67.19	66.48	66.78	65.45	67.17	99.96	97.00	98.23	98.67	98.03

Chemical formulas are based on 48 S for Ag-excess fizélyite and on 11 *apfu* for senandorite.

currences. The substitution percentage L% of the andorite substitution Ag + Sb = 2 Pb (Makovicky, Karup-Møller 1977) is 66.62, again in agreement with the structure refinement result of 65.55 (Yang et al. 2009) and in line with observations from other occurrences. Pažout et al. (2019) published analyses of Ag-excess fizélyite from Anthony of Padua Mine of the Oselské pásmo Lode in the southern part of the Kutná Hora ore district, where the *N* value of the sixteen analyses varies between 4.29 and 4.83, the substitution percentage L% is between 60.53 and 67.05.

Senandorite was found as subhedral grain 50 × 20 μm in size in quartz gangue associated with subhedral grains of other andorite group minerals (Fig. 1). The chemical composition of senandorite (mean of five point analyses) corresponds to the empirical formula $(Ag_{0.94}Cu_{0.05})_{\Sigma 0.99}(Pb_{0.99}Mn_{0.03})_{\Sigma 1.02}Sb_{3.00}S_{5.98}$. The Mn contents are between 0.17 and 0.25 wt. % (0.03 - 0.04 *apfu*). The average value of *N* is 4.02, L% is 98.4, which is below the ideal value of 100 %. The copper contents ranging from 0.31 to 0.41 wt. % (0.04 - 0.06 *apfu*) are interesting. This element usually does not appear in the crystal structure of Ag-Pb-Sb lillianite homologues. An exception is the senandorite variety „*nakaseite*". Moëlo et al. (1989) confirmed that *nakaseite* is an oversubstituted, Cu-rich (app. 1 wt. %) variety of senandorite, with a formula close to $(Ag_{0.93}Cu_{0.13})_{\Sigma 1.06}Pb_{0.88}Sb_{3.06}S_{6}$.

The minerals of the **benavidesite - jamesonite series** occur as individual anhedral to subhedral grains up to 400 × 300 μm in quartz gangue (Fig. 2) or as anhedral grains, occasionally as subhedral or column-like aggregates up to 1000 μm, associated with owyheeite, quatrandorite and sphalerite in quartz - kutnohorite gangue (Fig. 3). The minerals of this series are represented by thirteen analytical points, of which five display Mn > Fe and therefore correspond to mineral benavidesite. The chemical composition of benavidesite (mean of five point analyses) corresponds to the empirical formula $Pb_{3.92}(Mn_{0.50}Fe_{0.45})_{\Sigma 0.95}Sb_{6.18}S_{13.95}$, with Mn contents ranging from 1.25 to 1.37 wt. % (0.49 - 0.52 *apfu*). The remaining eight analytical points display a surplus of Fe over Mn, thus representing Mn-rich jamesonite with the chemical composition expressed as $Pb_{3.92}(Fe_{0.57}Mn_{0.37})_{\Sigma 0.94}Sb_{6.13}S_{14.02}$. The Mn contents are between 0.68 and 1.21 wt. % (0.26 - 0.44 *apfu*). In cases of both minerals we deal with a continuous Fe^{2+} - Mn^{2+} solid solution, the end members were not found in this particular association (Fig. 4).

Table 2 *Representative analyses of Fe-rich benavidesite (Bnvd) and Mn-rich jamesonite (Jam) from Roveňské pásmo Lode of Kutná Hora ore district, Czech Republic (wt. %, apfu)*

point	1072	1073	1074	1057	1058	1050	1051	1075	1076	1096	1124	1126	1138
sample	RO 203A	RO 203A	RO 203A	RO 203A	RO 203A	RO 203A	RO 203A	RO 203A	RO 203A	RO 203A	RO 205A	RO 205A	RO 205A
mineral	Bnvd	Bnvd	Bnvd	Bnvd	Bnvd	Jam	Jam	Jam	Jam	Jam	Jam	Jam	Jam
Pb	38.80	39.20	38.61	39.95	39.68	39.16	38.57	38.65	38.61	39.07	39.26	39.10	39.12
Fe	1.21	1.19	1.14	1.23	1.24	1.84	1.55	1.35	1.37	1.52	1.51	1.58	1.61
Mn	1.29	1.34	1.37	1.25	1.28	0.68	0.98	1.21	1.16	1.01	1.04	0.92	0.92
Sb	36.09	36.26	35.69	36.76	36.75	36.22	36.09	35.73	35.75	35.95	36.39	36.31	36.04
S	21.65	21.66	21.57	21.55	21.56	21.76	21.53	21.75	21.73	21.67	21.74	21.70	21.77
total	99.04	99.65	98.38	100.74	100.51	99.66	98.72	98.69	98.62	99.22	100.01	99.66	99.50
Pb	3.89	3.91	3.89	3.98	3.95	3.90	3.88	3.87	3.87	3.91	3.90	3.90	3.90
Fe	0.45	0.44	0.43	0.45	0.46	0.68	0.58	0.50	0.51	0.56	0.56	0.58	0.60
Mn	0.49	0.50	0.52	0.47	0.48	0.26	0.37	0.46	0.44	0.38	0.39	0.35	0.35
Sb	6.15	6.16	6.12	6.23	6.23	6.14	6.18	6.09	6.10	6.12	6.16	6.16	6.12
S	14.02	13.97	14.04	13.87	13.87	14.02	13.99	14.08	14.08	14.01	13.97	13.99	14.03

Chemical formulas are based on 25 *apfu.*

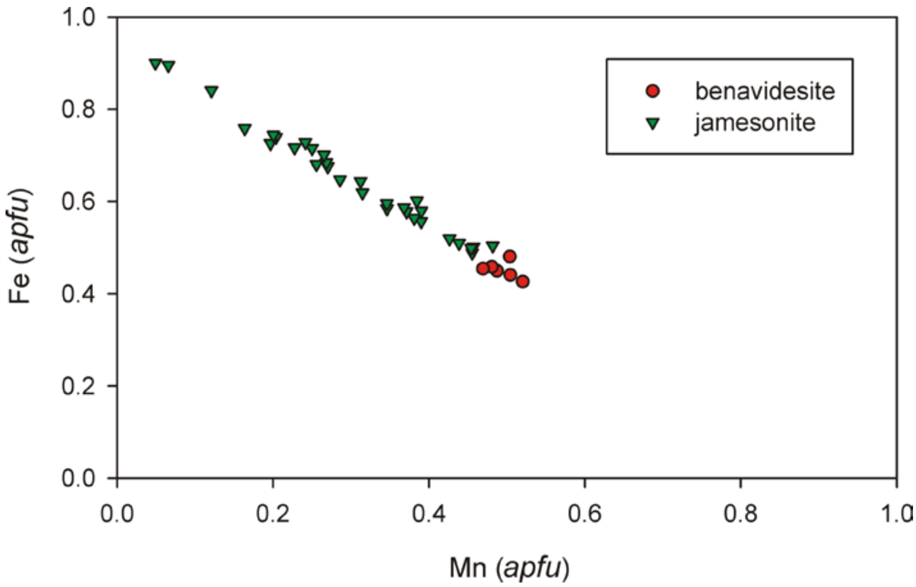

Fig. 4 *The variation of Fe vs. Mn contents (apfu) in minerals of the jamesonite - benavidesite series from the Roveňské pásmo Lode of the Kutná Hora ore district (samples RO 203, RO 205).*

It should be noted that until now only Cd and Fe have been found among minor divalent elements in the minerals of andorite series at southern silver-rich lodes of the Kutná Hora ore district. So the observed contents of Mn in sulfosalts are still considered rare. Also, no manganese contents have so far been determined in sulfosalts of the Oselské pásmo Lode, the second of the two main silver-rich lodes in the southern part of this ore district, although Mn-carbonates (kutnohorite, rhodochrosite) are as plentiful here as they are at the Roveňské pásmo Lode.

Geochemistry of manganese is an interesting feature of Kutná Hora ore district. There are two sources and concentrators of manganese: sphalerite and Mn-carbonates, each belonging to a different mineralization stages. Manganese is present in sphalerite of all lodes of the ore district, both in „silver-rich" in the southern part as well as in „pyrite rich" in the northern part (up to 4 wt.%). At the southern „silver-rich" lodes, there is abundant Mn-carbonate kutnonohorite and occasionally also rhodochrosite, belonging to the of the first mineralization stage (Hoffman, Trdlička 1976; Pažout et al. 2019) while the (Ag-)Pb-Sb sulfosalts belong to the second mineralization stage and the Ag-Sb mineralization to the third mineralization stage.

The character and type of gangue, the stockwork, is common for all three finds. It can be assumed that manganese comes from Mn-carbonates of the earlier mineralization stage which underwent a later alteration. It appears that the remobilization of Mn and the ensuing interaction with Ag-Pb-Sb fluids and subsequent crystallization took place more favourably or more preferentially in stockwork type of mineralization. A profound hydrothermal alteration of rock silicates is observable in the studied samples.

Conclusions

The first three occurrences of four species of Mn-rich (Ag)-Pb-Sb sulfosalts in Kutná Hora ore district were found, determined and described. The Mn-rich Ag-excess fizélyite, Mn-rich senandorite, benavidesite and Mn-rich jamesonite were identified. The source of Mn can be in earlier-stage carbonate period rich in Mn carbonates (kutnohorite and rhodochrosite). The remobilization of Mn from the gangue due to interaction of later Ag-Pb-Sb fluids with the gangue seems to be probable.

Acknowledgements

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