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MANGANOQUADRATITE AND Cd-MANGANOQUADRATITE FROM SĂCĂRÂMB Au-Ag-Te ORE DEPOSIT, METALIFERI MOUNTAINS, ROMANIA

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Abstract: New investigations using optical microscopy, scanning electron microscopy (SEM) and electron-probe micro-analysis (EPMA) have been performed on samples of alabandite rich veins from the Săcărâmb ore deposit, Metaliferi Mountains, in Romania. The second occurrence of manganoquadratite after Uchuccacua, Peru was discovered in Săcărâmb, in the rhodochrosite filled veins which crosscut the massive alabandite. The mineral usually occurs as euhedral and subhedral crystals in the secondary carbonate veins that fill the open spaces in the massive alabandite. The average chemical composition of manganoquadratite from Săcărâmb is $Ag_{0.98}Mn_{1.07}(As_{0.94}Sb_{0.08})_{1.02}S_{2.91.}$ A Cd-manganoquadratite variety with a mean composition of $Ag_{0.94}(Mn_{0.76}Cd_{0.36})_{1.12}(As_{0.94}Sb_{0.04})_{0.98}S_{2.94}$ was also identified in the investigated samples. The presence of Cd in manganoquadratite indicates Cd-Mn substitution which could confirm the existence of an isomorphic series between quadratite and manganoquadratite. Manganoquadratite crystals that have Cd in their composition appear only in association with pyrite. The presence of Cd can be related to the chemical characteristic of pyrite crystals to adsorb Cd^{2+} from aqueous solutions.

Keywords: Săcărâmb, sulfosalt, manganoquadratite, Cd-manganoquadratite, substitution, isomorphic series

1. INTRODUCTION

Săcărâmb Au-Ag-Te epithermal deposit is one of the most studied ore deposits in Romania and Europe. The presence of silver sulfosalts at Săcărâmb is rare, with only four documented mineral species: freieslebenite crystals associated on nagyagite (Groth 1878), unconfirmed; pearceite, proustite (Tokody 1930) and recently andorite, found in association with famatinite and tetrahedrite (Dinca & Popescu 2016). Manganoquadratite was identified as a new mineral species by Bonazzi et al., (2012) during studies of ore samples from the polymetallic Uchucchacua ore deposit, Peru. In that study, it was reported that manganoquadratite occurs as subhedral to anhedral grains up to grain size of 0.5 mm. It does not show any obvious twinning, and no inclusions of, or intergrowths with other minerals. The present study documents a new occurrence of manganoquadratite and cadmium manganoquadratite in epithermal Au-Ag-Te Săcărâmb deposit. The presence of cadmium in manganoquadratite from Săcărâmb could demonstrate the existence of an isomorphic series between quadratite and manganoquadratite.

2. GEOLOGICAL SETTING

Săcărâmb Au-Ag-Te ore deposit is located in the Metaliferi Mountains, which are part of the Apuseni Mountains, Romania. Săcărâmb ore deposit is the largest gold-silver-telluride mineral accumulation in Europe, it was exploited for gold and silver since the 18th century. In addition, Săcărâmb has an incredible mineral diversity, with over 100 mineral species identified and it is the type locality for alabandite, nagyágite, krennerite, petzite, stützite, muthmannite, krautite, and museumite (Ciobanu et al., 2004). This ore deposit belongs to the Brad-Săcărâmb metallogenic district which is part of the metallogenic subprovince associated with the Neogene volcanism of the Apuseni Mountains (Fig 1.). The ore mineralization in this subprovince has a Miocene-Pliocene age (14.7-7.4 Ma) and is related to the Neocene volcanic activity in the region, being part of the Alpine-Carpathian-Dinaride area (Udubaşa et al., 1992). Săcărâmb deposit is located in the eastern zone of the district. Although the mineralization has been exploited since the 18th century, at present there are no mining activities in the present day. Săcărâmb is classified as a low-sulphidation Au-Ag-Te epithermal deposit (Ciobanu et al., 2004), the ore mineralization having a hydrothermal origin. The host of the mineralization is an andesitic neck with about 230 veins in a 1000 m^2 area with a 600 m vertical extent. It is really an astonishing example of a high-grade epithermal mineralization (Udubaşa et al., 2002). A characteristic feature of this deposit it is the mineral deposition, which is shear assisted and syn-deformational (Ciobanu et al., 2004). The vein fields include four vein groups perpendicularly oriented, arranged as follows: Magdalena-Carolina and Nepomuc groups, having an NE-SW direction while Longhin-Antelonghin and Ertzbau groups have an NW-SE orientation (Udubaşa et al., 1992). The majority of the veins are rich in Au-Ag tellurides. However what makes it unique compared to other Au-Ag-Te deposits is the widespread presence of alabandite, a rare sulphide mineral. The most frequent disposition of this mineral assemblage type is found in the Magdalena-Carolina vein group (Fig. 1).

3. MATERIALS AND METHODS

During the research, samples were collected from Sector 3 waste dump. The material in the waste dump comes from the Carol mining gallery, which intersects Magdalena-Carolina vein group. Sixty polished sections were studied by optical microscopy with a Leitz Wetzlar reflected light microscope. The images were taken using a PANPHOT Leitz Wetzlar microscope equipped with a Nikon Eclipse E-400, 40W camera. The electron images were done with a Zeiss Merlin Gemini II column Scanning Electron Microscope (SEM). The operating conditions were: accelerating voltage of 15 kV, beam current ranging between 2 nA.

The chemical composition and back scattered electron images (BSE) were done by a JEOL JXA 8530F field-emission gun electron probe micro-analyser (EMPA), in the Central Laboratory at the Natural History Museum Vienna, Austria, employing JEOL and Probe for EMP analysis software (WDS mode, 25 kV, 20 nA, 2 µm beam diameter). Peak count time of 10 s and a background time of 5 s. Wavelength-dispersion data was collected using the following calibrant materials and emission lines: alabandite (MnKα), synthetic CdSe (CdKα), galena (PbMα), Ag metal (AgLα), stibnite (SbLα, SKα) and lorandite (AsLα).

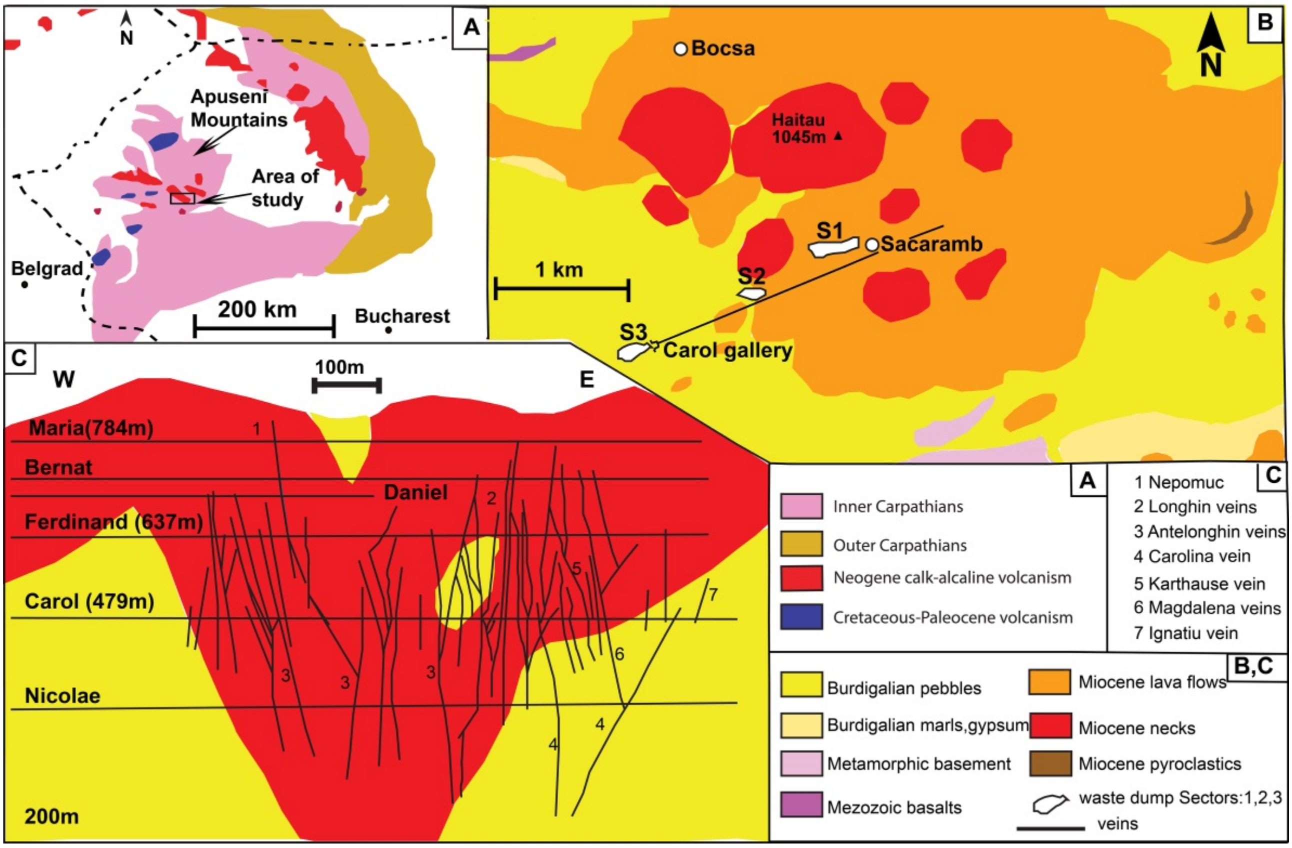

Figure 1 (A) Position of the Apuseni Mountains and Metaliferi Mountains in the Carpathians; (B) Simplified geological map of the Săcărâmb area, with the waste dumps; (C) Simplified geologic cross section through the Săcărâmb deposit, with the vein groups and mining galleries. Redrawn after Udubaşa et al. (1992) and Alderton and Fallick (2000)

The typical minimum detection limits for those analytical conditions were: Mn (117 ppm), Cd (700 ppm), Pb (650 ppm), Ag (450 ppm), As (370 ppm), Sb (300 ppm), S (120 ppm). The raw data were corrected for the matrix effects with the JEOL on-line ZAF procedure.

4. OPTICAL DATA AND SEM OBSERVATIONS

The main ore consists of the following minerals documented such as alabandite, Mn bearing sphalerite, galena, pyrite, and various contents of fahlores associated with a large diversity of sulfosalts, for example, bournonite, luzonite-famatinite, jordanite-geocronite, benavidesite, and andorite (Dinca & Popescu 2016). The gangue minerals are carbonates, quartz, and gypsum. Manganoquadratite from Săcărâmb was discovered in the alabandite rich veins, frequently associated with pyrite (Fig. 2). Cd-rich manganoquadratite crystals are forming rims after the pyrite crystals and in some cases, the pyrite crystals are completely enclosed by Cd-rich manganoquadratite (Fig. 3). In other samples, manganoquadratite usually occurs as euhedral and subhedral crystals in the secondary carbonate veins that fill the open spaces in massive alabandite (Figs. 2, 3). In some samples, the mineral forms directly on alabandite and in one sample it was found in an association with tennantite and famatinite. Optically, it has a grey colour in plane polarized light, in the crossed polarized light it has a low anisotropy with a light grey - dark grey colour. However, the mineral is frequently masqued by extensive red internal reflections.

5. CHEMICAL COMPOSITION

In comparison with manganoquadratite from Uchuccacua, the majority of the crystals from Săcărâmb have different contents of Cd, varying from 0.02 in manganoquadratite to 0.49 atoms per formula units (apfu) in Cd-rich manganoquadratite, while Mn varies between 0.66 to 1.08 apfu. Pb and Ag were constant in all analyzed crystals. Some of the representative chemical composition are reported in Table 1. On the basis of 6 atoms, the empirical formulas for manganoquadratite and Cd-manganoquadratite from Săcărâmb ore deposit are $Ag_{0.98}Mn_{1.07}(As_{0.9}4Sb_{0.08})_{1.02}S_{2.91}$ and $Ag_{0.94}(Mn_{0.76}Cd_{0.36})_{1.12}(As_{0.94}Sb_{0.04})_{0.98}S_{2.94}$.

6. DISCUSSION

The first time when it was discovered, manganoquadratite was named after the mineral quadratite $Ag(Cd, Pb)(As, Sb)S_3$ because of the strong

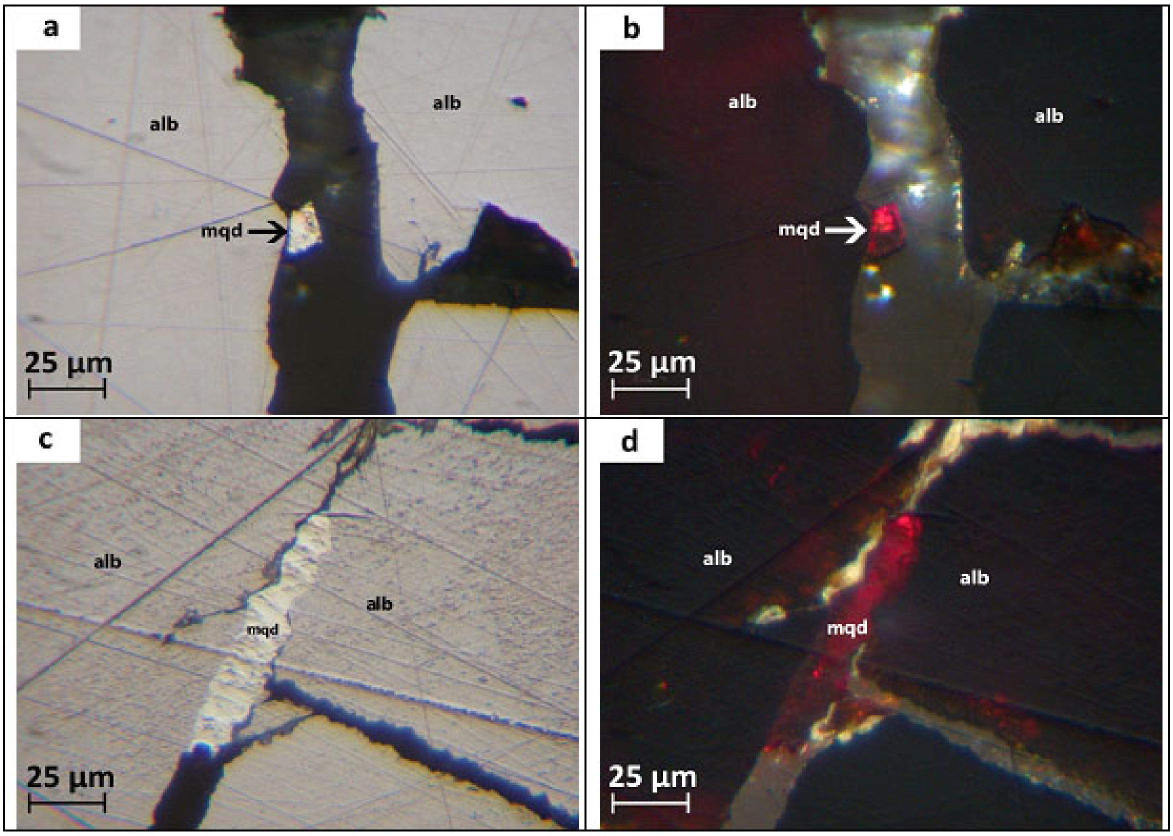

Fig. 2. Plane-polarized (a,c) and cross-polarized (b,d) photomicrographs in reflected light and oil immersion of manganoquadratite (mqd) in the carbonate veins which crosscut the massive alabandite (alb)

similarities between the two sulfosalts. Both minerals possess a galena-derivative framework with cations located in distorted octahedral coordination (Bonazzi et al., 2012). Furthermore, Bonazzi et al., (2012) hypothesized, that a substitution of Mn^{2+} in manganoquadratite by 0.80 Cd^{2+} + 0.20 Pb^{2+} in quadratite could be possible. Manganoquadratite from Săcărâmb ore deposit has a varied chemical composition, regarding Cd and Mn, with a clear substitution between them (Fig.4).

Considering the variation in respect to Cd+Pb and Mn, the samples from Săcărâmb in comparison with manganoquadratite from Uchucchacua and quadratite from Legenbach indicates a new intermediate phase (Fig. 4). Considering all the available data regarding the quadratite family and the recently discovered intermediate phase from Săcărâmb, the existence of an isomorphic series between manganoquadratite and quadratite is highly possible. Unfortunately, the crystals of Cd-manganoquadratite are only between 5-20 µm in size which is impossible to extract for single crystal diffraction. The compositional variation is strongly tied to the presence of pyrite. Cadmium variety of manganoquadratite occurs only in association with subhedral and euhedral pyrite crystals. Cd-manganoquadratite crystals are rimming the pyrite crystals and in some cases, the pyrite is enclosed completely by Cd-manganoquadratite (Fig. 3).

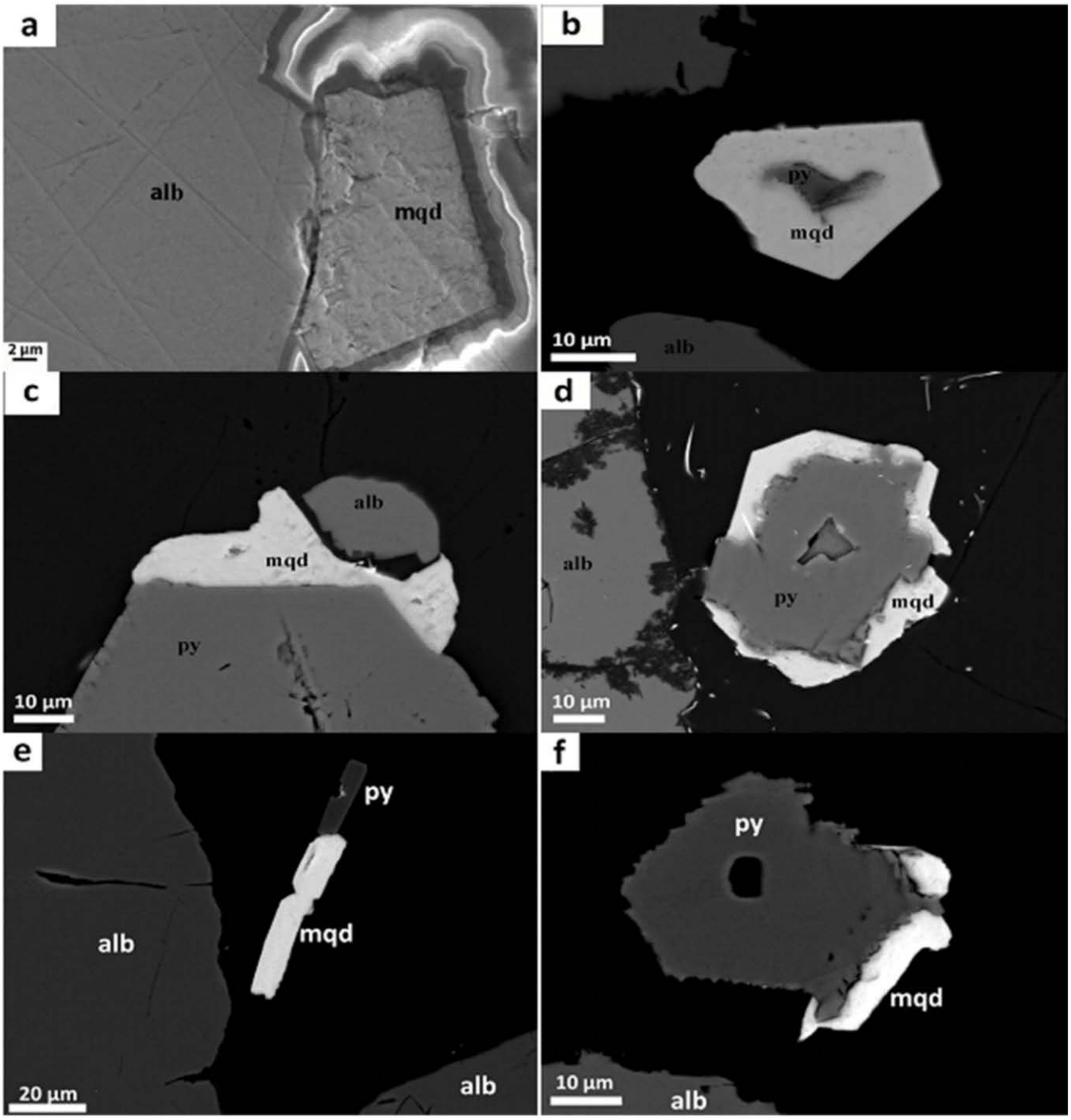

Figure 3. SE image of manganoquadratite with alabandite (a); BSE images illustrating the occurrence of manganoquadratite (mqd) in association with alabandite (alb) and pyrite (py) (b, c, d, e, f).

Table 1. Chemical composition of manganoquadratite and Cd-manganoquadratite from Săcărâmb

Sample Wt.%	SG8z7	SG8z10	S3I1	SG8z2	SG1	S6	SG1B	SG1B
	manganoquadratite		Cd-manganoquadratite					
Mn	16.33	17.27	12.18	13.51	13.74	12.19	10.22	10.29
Cd	2.76	0.54	10.83	7.66	7.51	10.73	15.14	14.69
Ag	30.35	31.03	27.98	29.73	29.60	29.04	28.44	28.58
Pb	0.32	0.07	0.18	0.21	0.29	0.11	0.08	0.03
As	20.89	20.92	19.89	20.89	20.21	20.43	19.8	20.23
Sb	2.21	2.34	1.35	1.06	2.25	0.93	1.17	1.6
S	27.21	26.83	27.54	26	26.21	26.18	25.88	27.03
Total	100.06	99.00	99.97	99.05	99.80	99.61	100.74	102.44
	Chemical formula based on 6 apfu							
Mn	1.02	1.08	0.78	0.87	0.88	0.80	0.67	0.66
Cd	0.08	0.02	0.34	0.24	0.24	0.34	0.49	0.46
Ag	0.96	0.99	0.91	0.98	0.97	0.96	0.95	0.93
Pb	0.005	0.001	0.003	0.004	0.005	0.002	0.001	0.001
As	0.96	0.96	0.93	0.99	0.95	0.97	0.95	0.95
Sb	0.06	0.07	0.04	0.03	0.06	0.03	0.04	0.05
S	2.91	2.88	3.01	2.88	2.89	2.91	2.91	2.96

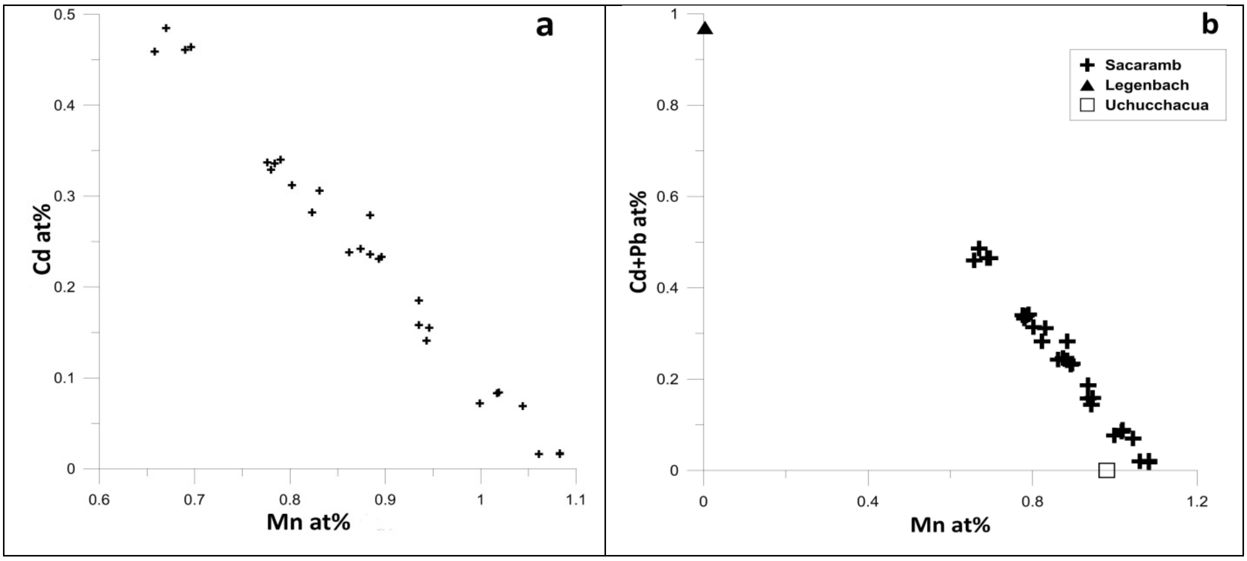

Figure 4. Compositional variation of manganoquadratite (apfu) from Săcărâmb in terms of Mn and Cd (a); Plot of Cd-manganoquadratite from Săcărâmb, in comparison with processed data of manganoquadratite from Uchucchaccua (Bonazzi et al., 2012) and quadratite from Legenbach (Bindi et al., 2013) expressed in terms of Mn and Cd+Pb (b)

This control of Cd by the presence of pyrite can be explained by the property of pyrite to adsorb Cd^{2+} from aqueous solution. This property was discovered experimentally at temperatures lower than one hundred degrees celsius and at a pH of 6 was achieved maximum adsorption (Borah & Senapati 2004). It was observed that the size of the pyrite crystals affects the adsorption capacity to a great extent and a decrease in crystal diameter enhances metal uptake (Borah & Senapati 2004). Furthermore, the adsorption process of Cd is endothermic with higher adsorption at higher temperatures (Özverdi & Erdem 2006). Regarding the hydrothermal fluid at Săcărâmb, it is known that the temperatures varied between 200°C and 300°C and the pH of the fluid was approximately 6 (Alderton & Fallick, 2000), which can explain the presence of Cd in manganoquadratite crystals associated with pyrite.

7. CONCLUSION

The discovery of manganoquadratite and Cd-manganoquadratite in Săcărâmb Au-Ag-Te deposit brings a new light on the variation of elements and diversity of minerals, in this hydrothermal vein type deposit. The relationship between Cd and Mn further confirms the hypothesis of an isomorphic series, between manganoquadratite and quadratite. Furthermore, the textural relationship between pyrite and Cd-rich manganoquadratite shows that small pyrite crystals acted as adsorbents of Cd from the hydrothermal fluid.

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