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Geology, mineralogy and geochemistry of manganese mineralization in Gumushane, Turkey

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Abstract
In the scope of this study, geochemical and genetic characteristics of manganese mineralization of the Gümüşhane were investigated. The mineralizations area is located in near Gümüşhane city, the Eastern Black Sea Tectonic Unit. Different from other manganese occurrences in the Black Sea region, this mineralization occurred in massif limestone of Late Jurassic–Early Cretaceous Berdiga formation. The ore mineralization exhibits mainly lens shaped stacks and stockwork-form structures and is characterized with late filling of open cavities and replacement of limestone by manganese oxides. Manganese oxides are in relation with the nortwest-southeast oriented feeder cracks and fault zones and often associated with jasper and iron oxide minerals like hematite and goethite. The ore mineralization exhibits mainly lens shaped stacks and stockwork-form structures and is characterized with late filling of open cavities and replacement of limestone by manganese oxides. Element analysis such as major, minor and trace elements, and XRD and ore microscopy studies were carried out to investigate the geochemical and genetic properties and mineralogical association of manganese mineralizations. As a result of mineralogical studies, pyrolusite, braunite, manganite, psilomelane and stiplomelane are defined as manganese minerals, and also quartz, calcite, dolomite and smectite are found as gangue minerals. According to geochemical data such as, major oxides, trace and rare earth elements, the mineralizations are determined as hydrothermal in origin, supported with hydrogenic contributions.

Keywords: manganese mineralizations, ore deposits, geochemistry, XRD analysis, Gümüşhane.

1. Introduction

Depending on the model used for crustal composition, manganese (Mn) is the ninth, sometimes tenth most abundant element in the Earth's crust. It is used in making steel, or a much lesser amount in the production of batteries. Mn is commonly found in +2 and +3, rarely +4 valances. Mn is generally found to be substituted in small amounts in iron minerals. Mn is generally found as oxide minerals; sulfides are quite rare. Most Mn deposits, because of their redox sensitivity, form seawater. Mn mineralizations can be classified in to sedimentary rock-hosted, volcanic rock-hosted and karst-hosted. On the other hand, the sediment-and volcanic-hosted deposits have supergene versions of them. They are distinguished according to dominant mineral contents. In supergene versions, dominant minerals are cryptomelane, manganite, nsutite, psilomelane, or todorokite. Tonnages of the karst-hosted deposits are comparatively in minor tonnages, 0.5 percent in all total reserves while volcanic and sedimantary hosted-rocks are about 93 percent of total reserves. Most of the oxides Mn mineralizations are generally supergene origin, so they are younger their host rocks.

The Old Gümüşhane manganese mineralization which is karst-hosted and fault-controlled, is situated to 3 km West of Gümüşhane City Center, NE Turkey (Fig. 1), covers an area of approximately 0,65 km^2. This area which contains the mineralization is located in south part of Eastern Black Sea Mounts, in Alpine-Himalayan belt which hosts a lot of ore mineralizations. The region has attracted the attention of many researchers and exploration companies due to its geology, tectonic activity and potential of ore/mineral deposits (e.g. [1-15]).

As operated and/or ready to run or abandoned, many precious and base metals (Pb, Zn, Cu, Au, Ag) ore deposits are available in the region. Apart from this mineralization, it is also observed manganese mineralization at different locations in the region, especially in Gümüşhane Province. Manganese mineralization in the region was generally abandoned after operated the economic part of the mineralizations. The most remarkable and big sized mineralization in the field is Old Gümüşhane

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Manganese Mineralization which is located at about 300-400 m north-West of Old Gümüşhane (in the ancient period called as Argyropolis) neighborhood. Apart from this, there are also some small scaled manganese occurrences and its tailings in different locations in the site. The objectives of this paper are to reveal the geologic setting, geochemical properties and origin of Old Gümüşhane manganese mineralization using geological, mineralogical, geochemical characteristics of the area.

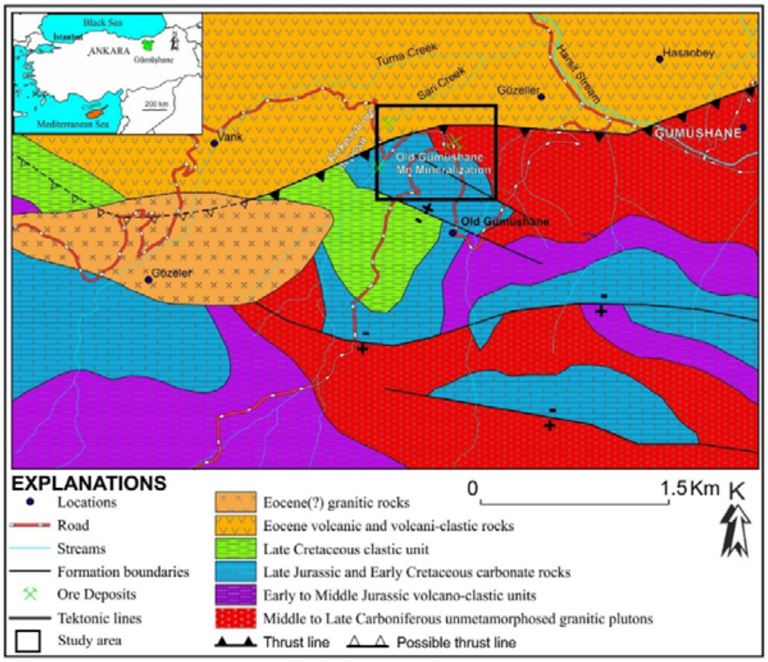

Figure 1. Geology and location map of the study are [8,15].

1.1. Geological setting of the study area and surrounding

The study area is located at the southern zone of the Black Sea Tectonic Unit (BSTU, called as Eastern Pontides by some researchers, [16–18]). The basement rocks in the region, consists of Early Carboniferous metamorphic rocks [19] and crosscutting unmetamorphic granitic plutons of Middle to Late Carboniferous age [3, 20-23]. These granitic plutons outcrop also in the study area and mainly consists of granodiorite, quartz-microdiorite, granite and dacite porphyry, called Gümüşhane Pluton [3, 20, 24]. The Permian and Triassic events are poorly recorded in the region. So, Gümüşhane Pluton is unconformably overlain by an Early to Middle Jurassic volcano-clastic unit (Şenköy formation, [25]), which pass upward conformably to the Late Jurassic and Early Cretaceous carbonate rocks (Berdiga formation, [26]. The Late Cretaceous clastic unit called Kermutdere formation, [2], which conformably covers the Berdiga formation, consist of sandy limestone at the bottom and then grades upward to reddish pelagic limestone.

The unit continues with turbiditic series towards the upper levels, consisting of sandstone, siltstone, marl, and limestone. All these units were crosscut by Late Cretaceous [14,27] intrusive rocks in the NW of the study area and Early Eocene adakitic intrusive rocks [28-31], in the NE of the area. The Eocene volcanic and volcano-clastic rocks also overlie all these pre-Middle Eocene rocks with an angular unconformity [13, 32] and were intruded by similar aged calc-alkaline granitoids [33] in the vicinity of the area (Fig. 1).

2. Materials and method

In this study, field studies for geological purposes were carried out and revised 1/25 000 scaled geological map of the area. Samples were collected to investigate the petrographic-mineralogical and ore mineralization characteristic of the area. For mineralogical- petrographic studies, thin sections for lithological features of the area and polished samples for ore microscopy samples were prepared and mineralogical and petrographic determinations were conducted in Gümüşhane University, Department of Geological Engineering.

X-ray Diffraction (XRD) measurements were also performed at Department of Mineral Analysis and Technology of The Directorate of Mineral Research and Exploration (MTA) and the Physics Laboratory of Karadeniz Technical University for mineral types of ore mineralization. X-ray diffraction (XRD) measurements were performed using a Rigaku-Geigerflex model diffractometer with monochromatic Cu Kα radiation operated at 40 kV and 30 mA, scanning from 2 to 70° 2 theta with a step size of 0.02° and a counting time of 1 s/step. The diffraction patterns were compared with a set of standard patterns compiled by the Joint Committee on Powder Diffraction Standards (JCPDS) and mineralogical determinations were carried out using MDI/JADE6 software. Samples collected from area were initially crushed by hand using hammer to reduce the samples to cm-sized fragments. Finally, the material has been ground with a tungsten disc mill to approximately 600-μm grain size.

In the scope of geochemical studies, 25 samples (11 ore samples and 14 rock samples) of whole-rock analysis of the major, trace, and rare earth elements by inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) were performed by Acme Analytical Laboratories, Vancouver, British Columbia (Canada). Whole-rock analysis of the major, trace, and rare earth elements were performed using ICP-AES and ICPMS.

The rock samples were shattered by jaw crusher and milled by using a tungsten carbide shatter box. Elements are expressed as common oxides for each element (i.e. Al_2O_3, CaO, Cr_2O_3, Fe_2O_3, K_2O, MgO, MnO, Na_2O, P_2O_5, TiO_2) in wt.% and other element concentrations are in ppm. Total abundances of the major oxides and several minor elements are based on a 0.2 g sample analyzed by ICP-AES and MS following a lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition has been determined by weight difference after ignition at 1000°C.

3. Result and discussion

Obtained results of mineralogy-petrography studies conducting for general geological purposes are outside the scope of this paper, so they were not given in detailed. The details of geochemical analysis results of ore samples were given in Table 1. The results of the analysis were used to determine the geochemical characterization of the manganese mineralization.

3.1. Ore mineralogy and XRD analysis

Ore microscopy studies and XRD analysis were performed on samples collected from manganese mineralization. The most abundant non-metallic minerals in the ores are quartz which is production of silicification, clay, with minor amounts of calcite.

The most abundant metallic minerals after Mn-minerals are pyrite as scattered, then less commonly chalcopyrite, covellite, ilmenite, magnetite, hematite, goethite and rarely galena. Pyrite grains are commonly under 0.2 micron. Though they were often seen as a euhedral, were commonly observed as a semi-euhedral and anhedral (Fig. 2). The dominant Mn-minerals are commonly pyrolusite, psilomelane and less commonly alabandite and rhodochrosite (Fig. 2). In XRD studies, braunit, pyrolusite, psilomelane, stilpnomelane, manganite, ramsdellite, goethite, hematite and magnetite minerals were identified as ore minerals, and quartz, calcite and dolomites as gangue minerals (Fig. 3). Pyrolusite and braunite are the main mineral of oxic- assemblages. Manganese oxide minerals which made up assemblage, such as braunite, pyrolusite, ramsdellite and minor hematite and magnetite implies oxidic environment.

Both these minerals were common the Old Gümüşhane Manganese Mineralization. Pyrolusite were observed as fine-grained crystals and it was also seen with ramsdellite while replacing of braunite minerals. Ramsdellite was more or less replaced by pyrolusite. It can be considered that braunite occurred in the result of hydrothermal or biogenic silica reaction after sedimentation. This kind of reactions occur during diagenesis or low temperature/high pressure metamorphism [34] references therein. The absence or less of Mn carbonate minerals in assemblages indicate that the mineralization is not associated with supergene origin [35]. Rhodochrosite is not common mineral in the area, therefore, it was concluded that the effects of supergene process remained limited on mineralization.

Table 1. Major oxides, trace elements and proportional values for some elements of ore samples (major oxides in wt.%, trace elements in ppm).

	OA2	OA3	OA5	OA6	OA10	OA17	OA21	OA22	OA23
SiO_2	1.56	20.27	56.85	0.03	14.32	6.51	1.66	5.15	8.62
TiO_2	0.01	0.41	0.01	50.5	0.04	0.02	0.02	<0.01	<0.01
Al_2O_3	0.36	27.63	1.01	1.57	1.25	0.35	0.27	0.39	0.4
FeOt	37.46	10.92	23.9	7.96	5.31	18.34	34.08	38.21	32.48
MnO	40.11	3.97	0.52	0.39	0.37	23.69	45.33	25.45	39.93
MgO	0.28	0.96	1.76	0.68	15.68	9.62	0.15	2	0.58
CaO	0.48	4.96	5.8	0.1	23.47	13.63	0.45	2.08	1.16
Na_2O	<0.01	0.02	0.03	0.22	<0.01	0.02	<0.01	<0.01	0.05
K_2O	0.14	0.94	0.15	0.06	<0.01	0.09	0.1	0.04	0.34
P_2O_5	<0.01	0.12	0.04	0.22	0.01	0.02	0.02	1.56	0.12
LOI	15	26.4	9.7	29.81	33.5	25.3	14.8	24.8	15.2
Total	95.41	96.65	99.81	0.024	93.94	97.59	96.91	99.67	98.86
Ni	8.7	71.9	105.2	6	14.9	10.3	6.7	3.9	6.8
Co	5.5	10.4	22	8.3	5.7	4.6	4.3	1.5	5
Cu	97.8	2715.6	60.6	82	490.2	52.3	736.1	25.6	983.9
Zn	10001	10001	194	<1	7034	9028	9735	1163	5971
Rb	3.9	27.7	5.3	0.7	0.6	3	3.2	2.5	5.1
Pb	10001	3598.5	126.7	7.6	7586	5374.4	10001	644.4	1084.9
Ni/Co	0.1207	0.209	1.2483	0.3826	0.1311	0.4466	0.6418	0.3846	0.7353
Fe/Mn	0.84	2.48	41.53	0.24	12.96	0.69	0.67	1.35	0.73
Co/Zn	0,0005	0,001	0,1134	-	0,00081	0.00051	0,0004	0,00129	0.00084
Ba	3	159	103	82	7	129	9	198	21
Co	5.5	10.4	22.0	72.9	5.7	4.6	4.3	1.5	5.0
Ga	46.3	13.2	4.2	24.9	7.0	20.3	51.7	38.7	30.8
Sr	341.7	106.6	14.4	74.5	35.6	453.3	172.8	575.9	506.5
Ta	0.1	0.2	<0.1	0.2	<0.1	<0.1	<0.1	<0.1	<0.1
V	94	117	118	159	26	103	42	49	37
W	1.7	2.0	1.1	2.8	0.9	3.6	1.3	1.9	1.3
Zr	18.0	61.0	7.8	24.9	9.9	12.6	8.6	7.5	6.2
Y	8.0	16.8	17.5	3.9	2.5	6.4	4.4	20.3	8.3
La	9.7	9.3	8.5	5.2	2.8	6.4	2.2	7.3	1.9
Ce	21.9	21.0	3.6	27.1	4.9	12.9	6.0	14.8	4.5
Gd	2.09	5.43	3.17	0.96	0.48	2.01	1.32	8.65	1.74
Lu	0.08	0.36	0.24	0.08	0.03	0.06	0.03	0.12	0.04
Mo	2.1	1.2	4.9	97.1	1.4	2.8	1.0	3.1	1.2
As	649.0	169.9	19.4	20.9	115.4	248.4	276.4	186.6	234.5
Cd	78.6	88.9	0.3	0.2	36.2	59.3	59.8	19.0	71.9
Sb	9.2	2.5	0.7	3.8	22.3	3.1	9.4	2.3	1.6
Bi	0.7	0.1	<0.1	<0.1	42.0	1.1	1.3	0.3	0.4

3.2. Trace Element Geochemistry

Main components of the Old Gümüşhane mineralization are Mn, Fe and Si. Secondary importance components of are Al, Mg and Ca. Fe/Mn ratio of the mineralization is below 0.1 or close to 0.1, while Fe/Mn ratio in hydrogenetic deposits which slowly precipitate from sea water is approximately 1, in hydrothermal deposit settling under sea, it is below 0.1 (rich in Mn) or above 10 (rich in Fe) [36-37]. Based on Fe/Mn ratio, it was concluded that the mineralization in the area is dominantly hydrothermal originated. To determine the origin and geochemical properties of the manganese mineralization, it was used major and trace element concentration of the samples collected from the ore mineralization. In the literature, there are many ternary and binary plots used to investigate the geochemical properties and origin of manganese mineralizations. The most commonly used plots were used in this study. By some researchers using the cation-adsorption capacity of the manganese oxide, were proposed discrimination plots, based on the presence of certain trace elements in the manganese oxide. These plots were used to discriminate hydrothermal (continental or marine) or hydrogenetic originated deposits [38-39]. Ba, Cu, Ni, Co, Pb, Cr, V vs. Zn as the elements often are found in systems in rich of hydrothermal manganese. In order to distinguish exhalative deposits from terrestrial deposits, Fe / Ti-Al / (Al + Fe + Mn) plot is used [34].

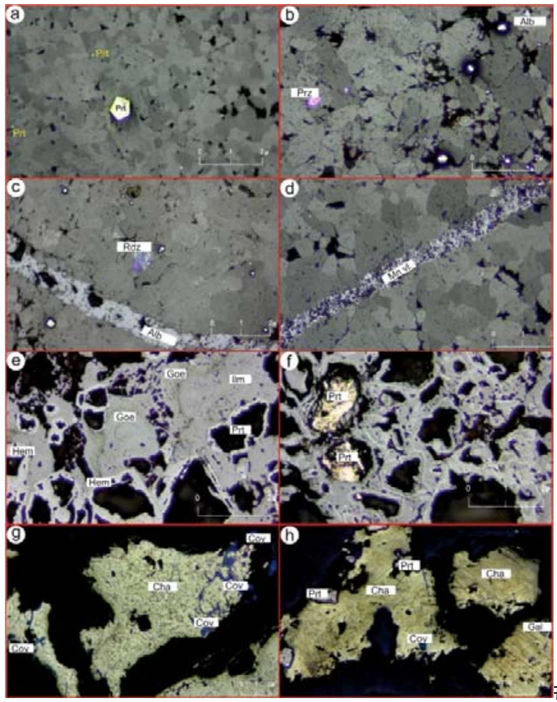

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Figure 2. Photomicrographs in reflected light showing representative ore minerals, Old Gümüşhane Manganese Mineralization. a) euhedral pyrites (Prt), b) piroluzite (Prz) and alabandite (Alb), c) rhodochrosite (Rdz) and alabandite veinlet, d) Mn-veinlet (Mn vl.), e) oxidized pyrites were surrounded by hematites (Hem), reniform-goethite minerals (Goe) and scattered ilmenites (Ilm), f) oxidized pyrites were surrounded by hematites, g) covellites occurred as veinlet at the edge of chalcopyrite (Cha), h) covellite (Cov), galena (Gal) and pyrite occurrences in chalcopyrite minerals.

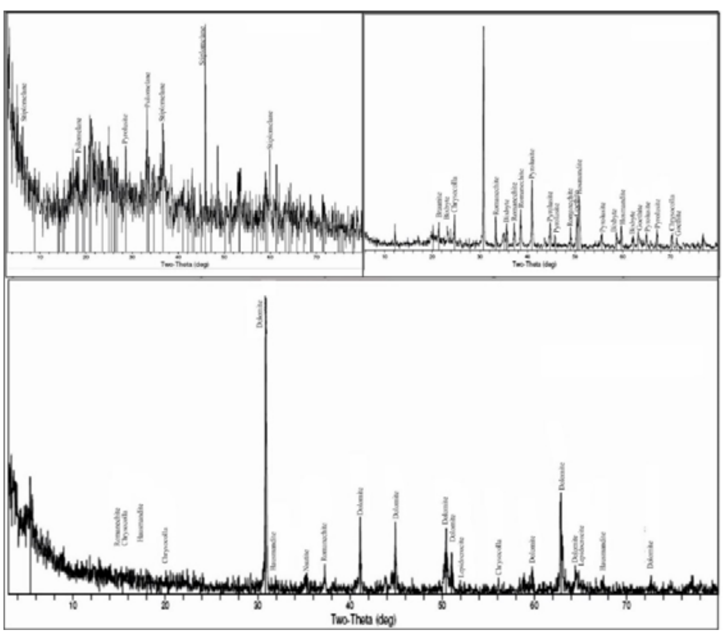

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Figure 3. Diffractograms of XRD analyses for ore samples

The mineralization in the area is in hydrothermal-sedimentary region according to Fe/Ti ratio (Fig. 4a). Two type of Mn-oxide deposit can be easily distinguished each other using Co, Ni, Cu and Zn concentrations. Co amount is quite high in hydrogenetic deposit. In contrast, Ni and Zn concentrations are pretty much in hydrothermal deposits. When we used these parameters, the ore deposit occurred as a hydrothermal origin (Fig. 4b, c). Low Fe/Mn and high Ni and Zn against Co show great similarities with today's submarine hydrothermal Mn-Oxides [40]. The Mn values of the mineralization are concentrated in the hydrothermal area in Mn-Fe-(Ni+Co+Cu)*10 triangle diagram [34], Fig. 4c).

High Si content indicates that Mn precipitates in environments which occur in volcanic activity and hydrothermal process [34, 38]. According to plot Si wt.% vs Al wt.%, Old Gümüşhane Manganese Mineralization is generally in hydrothermal area (Fig. 4d). Ba content also increase due to hydrothermal activity in manganese mineralization [41]. Old Gümüşhane manganese mineralization has generally high Ba and low Al content so it implies that the mineralization is partly of hydrothermal origin and partly of terrestrial character (Fig. 4e). Al and Ti elements in sedimentary formations are more than hydrothermal occurrences. These two elements have low amount and behave together, so they also point to hydrothermal occurrences for the mineralizations (Fig 4f, Table 1). Co/Zn ratio can be also used pathfinder for determination of origin of manganese mineralizations. Ratio Co/Zn is 0.15 in hydrothermal deposits, 2.5 in hydrogenetic deposits. Trace elements such as Co, Ni and Zn, and rare earth elements (REE) in manganese occurrences are absorbed by Mn-oxides. Trace elements (Co, Ni and Zn) are provided by hydrothermal solutions since seawater has how Co, Ni and Zn contents. REE contents have low value in hydrothermal solutions, so high REE contents are provided sea water [42-44]. According to these parameters, studied mineralization implies dominantly hydrothermal characterization (Table 1, Fig. 4g). Variable quantities of trace elements, indicating that mineralization may have different sources. Mn-As is well observed in association with hydrothermal deposits. In addition, high values of As, Zn and Sb reflect the hydrothermal activity in manganese mineralizations [40,45]. When evaluated the diagram (Fig.4h) which were drawn utilizing these parameters, manganese mineralization fell to hydrothermal area and partly hydrogenetic one. Aluminum in environment comes from clay mineral depending on deposition. Therefore, very low Al and high Fe contents in environment imply an indication of hydrothermal activity during mineralization [46]. When the study area was evaluated in light of all these parameters, it was concluded that mineralization formed dominantly by hydrothermal activity (Fig. 4 a-h, Table 1).

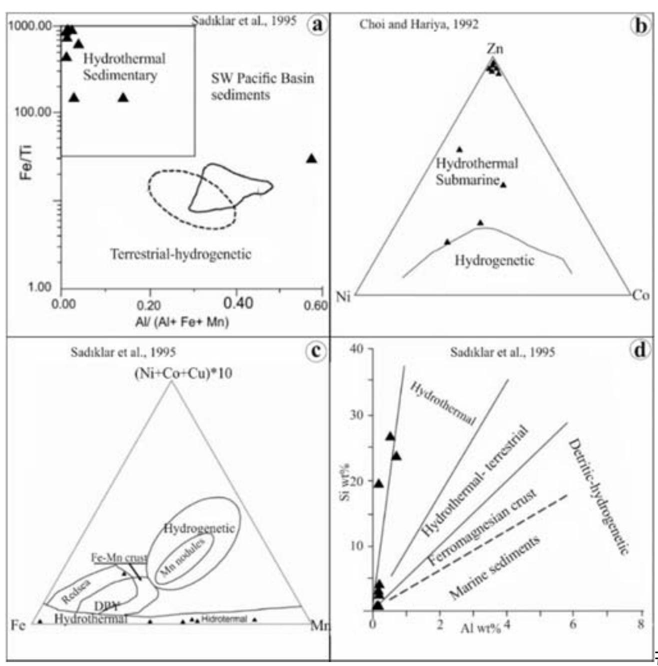

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Figure 4. Genetic and geochemical evaluation plots of the manganese mineralization

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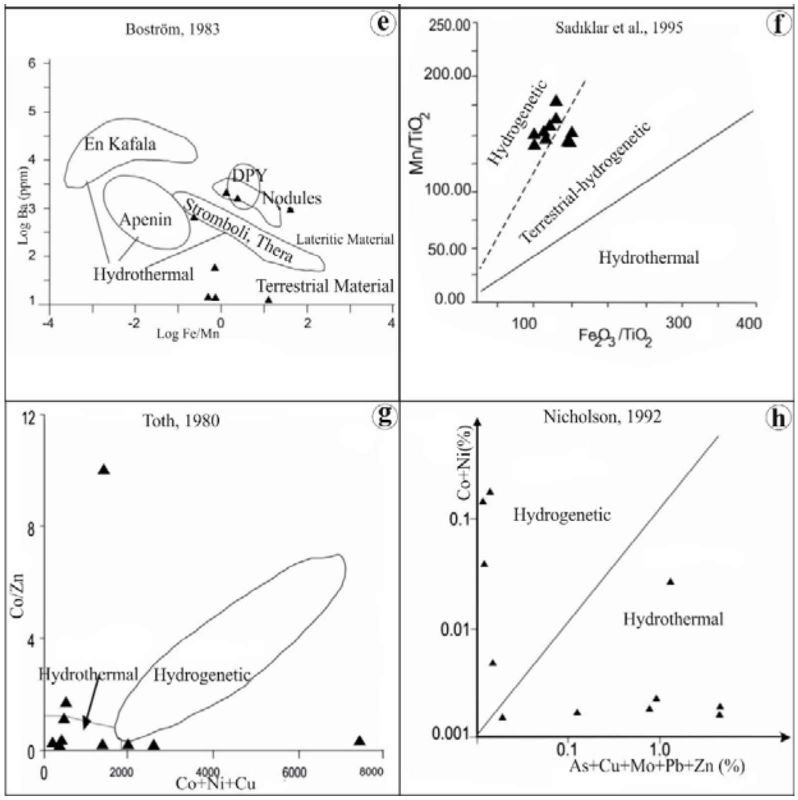

Figure 4. (continue)

4. Conclusions

It was concluded from field and laboratory studies that Old Gümüşhane Manganese mineralization occurred in tectonic lines which were developed in the Late Jurassic-Early Cretaceous massive limestones as called Berdiga formation. From ore microscopy and XRD studies; as main manganese mineral, braunite, pyrolusite, manganese, bixbyite hausmanite minerals have been identified. This mineral assemblage is generally indicator for hydrothermal occurrences in oxidized environments. Geochemical studies benefiting from major oxides and trace elements in the field, manganese mineralization is of hydrothermal origin and it was observed that hydrogenetic effect contributed the mineralization.

When all the data are evaluated together, the mineralization occurred in veins, fractures and cracks of limestone of Berdiga formation via settlement of hydrothermal fluids originated from magmatic activity in the region. It occurred in form of veins, stock-work veinlets, gap filling, and disseminated in limestone. In addition to hydrothermal mineralization, during circulation of meteoric solution of environment in the limestone's fractures and cracks, hydrogenetic mineralization also developed

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