

Article

New Ag-Rich Mn-Zn±Pb Vein Mineralization at the Mavro Xylo Manganese Oxide Deposit, Drama, Greece

George Soulamidis ^{1,*}, Christina Stouraiti ¹, Panagiotis Voudouris ^{1,*} and Harilaos Tsikos ²

¹ Department of Geology and Geoenvironment, National and Kapodistrian University of Athens, Panepistimiopolis, 15784 Athens, Greece; chstouraiti@geol.uoa.gr

² Department of Geology, University of Patras, Rio Campus, 26504 Patra, Greece; htsikos@upatras.gr

* Correspondence: gsoulamidis@geol.uoa.gr (G.S.); voudouris@geol.uoa.gr (P.V.)

Abstract: The manganese deposits at the Kato Nevrokopi area are located in the Drama Basin (Northern Greece) and belong to the Rhodope Metamorphic Province. The deposits were previously exploited for several supergene Mn-oxide ore bodies of massive, battery-grade nsutite, spatially associated with fault zones in the vicinity of Oligocene granitic intrusions. We conducted detailed geological, mineralogical, and geochemical investigations at the Mavro Xylo deposit, which led to the identification of Ag-rich Mn-Zn±Pb vein-type mineralization. The studied paragenesis appears to have developed during two hydrothermal stages: stage I, characterized by the mineral assemblage rhodonite–quartz–rhodochrosite–pyrophanite–pyrite–galena–Te bearing argentite–sphalerite–wurtzite–alabandite, and stage II, dominated by Ag-rich, Mn-Zn±Pb oxides in the form of fracture-fills along a high-angle NE-SW fault zone in brecciated marbles. Bulk analyses of the stage-II oxide assemblage yielded concentrations of Ag up to 0.57 wt.%. In the veins, wurtzite is present in bands, succeeded by manganese oxides, while calcite and quartz are the main gangue minerals. We placed particular emphasis on the occurrence of Ag in high concentrations within distinct manganese oxides. Major silver carriers include Zn-bearing todorokite, chalcophanite, and hydrous Pb-Mn oxide. The vein-type mineralization at Mavro Xylo shares many characteristics with other intermediate-sulfidation epithermal precious metal-rich deposits associated with high Mn concentrations. The evolution of the mineral paragenesis indicates a change in the physicochemical attributes of the ore-forming fluids, from initially reducing (stage I) to oxidizing (stage II). Although the origin of the initial ore-forming fluid remains to be constrained, the above redox change is tentatively attributed to the increasing incursion of meteoric waters over time.

Keywords: manganese; Mavro Xylo deposit; Ag-bearing chalcophanite; Ag-bearing todorokite; rhodonite; epithermal IS Mn-Zn-Ag mineralization; Greece



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1. Introduction

Manganese oxy/hydroxides exhibit remarkable adsorption properties and act as scavengers in geological environments for base metals, aiding in the discovery of new base metal deposits [1–3]. With the increasing demand for base and critical metals, identifying new deposits in Europe has become crucial [4]. Moreover, manganese has been assigned to the list of critical and strategic metals for the EU as a vital component in green energy applications, particularly in lithium-ion batteries as a cathode material [5,6].

Manganese–silver ores occur in different parts of the world and have been a focus of geochemical exploration due to their importance as a mineral resource for both manganese and silver [7–9]. Silver exists either encapsulated or in the crystal lattice of manganese oxides [10]. A variety of up to fifteen types of manganese oxides have been identified in Mn-Ag deposits worldwide [8,9,11,12]. Among these, three manganese oxides play a fundamental role in silver deportment within manganese–silver ores, namely cryptomelane, todorokite, and chalcophanite [11,13,14].

The Kato Nevrokopi manganese deposit (Northern Greece) is the largest manganese deposit exploited in Greece [15]. Kato Nevrokopi is located approximately 60 km northwest of Drama in northern Greece and represented the primary mining center for battery-grade manganese oxide ore from 1950 to 1994. Nimfopoulos et al. (1991, 1997) [15,16] characterized Mn mineralization at Kato Nevrokopi to be a result of progressive oxidation of rhodochrosite-sulfide veins, leading to a paragenetic sequence of MnO gel–todorokite–nsutite–chalcophanite–birnessite–cryptomelane–pyrolusite. Manganese ore deposits are structurally controlled and developed along E–W and NW–SE fault zones [15–17]. Apart from a few mineral-chemical analyses conducted on manganese ore bodies in the Kato Nevrokopi area [16,17], many genetic aspects of the deposits remain poorly constrained. Notably, the origin of these deposits remains unclear, and understanding is limited due to previous research primarily focusing on the geochemical properties of the battery-grade supergene manganese oxide ore driven by the region’s mining activities.

This study provides a more detailed investigation of the manganese deposits in the Kato Nevrokopi area, particularly at Mavro Xylo, and presents a new hypogene argentiferous manganese ore assemblage in the Mavro Xylo mine. It investigates the mineralogy and mineral chemistry of the argentiferous mineral assemblage at Mavro Xylo and provides new paragenetic constraints for the origin of Ag-rich Mn–Zn±Pb mineralization. Our results also offer new insights into hydrothermal manganese metallogenesis through comparisons with similar Ag- and base metal-bearing Mn mineralization elsewhere.

2. Regional Geology

2.1. Rhodope Metamorphic Core Complex

The Kato Nevrokopi area, as well as the whole Drama district, is part of the Rhodope massif, which represents a metamorphic core complex in the internal Hellenides (Figure 1). The structure, magmatic, and tectono-metamorphic characteristics of the Massif have been the center of attention for many researchers [18–20].

The Rhodope Metamorphic Core Complex, located in the northeastern Hellenides region, forms the core of the arc-type Hellenic orogenic belt. This core complex comprises intricate alpine nappe stacks of various metamorphic continental and oceanic units [21,22]. These nappes were sequentially emplaced through intense compressional tectonics and thrusting from the Jurassic to the Tertiary, driven by multiple subduction processes, high to ultra-high pressure metamorphism, and the closure of oceanic basins [19]. Extensional Tertiary tectonic activity has reworked the compressional structures between the nappes into low-angle normal detachment faults. The extensional phase was also marked by high-grade metamorphism, emplacement of syn- to post-tectonic granitoid intrusions (i.e., Vrontou, Panorama, Granitic, and Kavala, Figures 1–3), and extensive migmatite formation [23,24].

The structural configuration of the Rhodope Province in the study area is relatively straightforward and comprises several distinct units. These include the Falakron marble series, a thick and highly strained carbonate platform of undetermined age situated between the Strymon and Nestos Rivers. On its southwestern edge, the series is bordered by a brittle, low-angle, southwest-dipping shear zone, which is overlain by the “Kerdylion Unit” and a cover of intensely deformed, unmetamorphosed Neogene sediments (Figure 1). Initially, this shear zone was thought to be a northeast-vergent Neogene thrust. However, Dinter and Royden (1993) [25] reinterpreted this tectonic contact as a southwest-vergent, low-angle normal fault, known as the Strymon Valley detachment. They demonstrated that this structure played a crucial role in the exhumation of the Falakron marble series during the Neogene period.

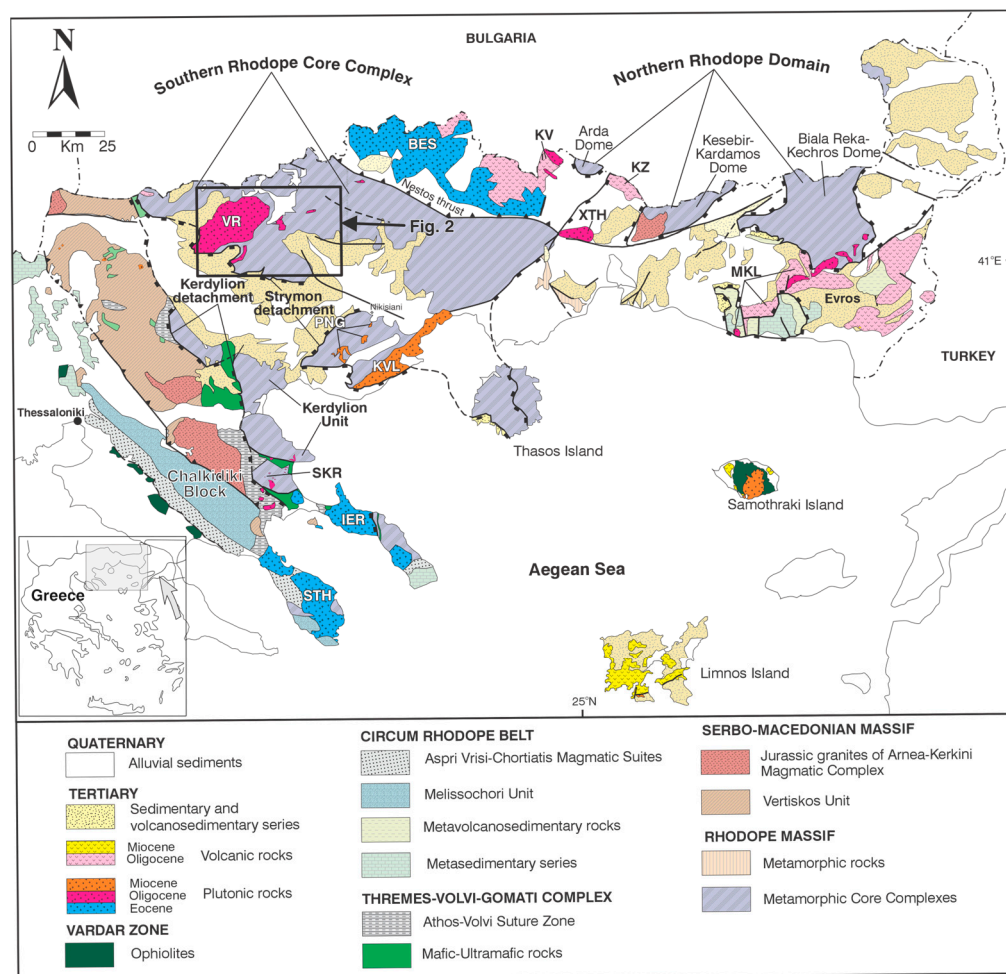


Figure 1. Simplified geological map of the Greek Rhodope Massif in northern Greece showing the main tectonic units referred to in the text (modified from Voudouris et al. 2016 [26] and Melfos and Voudouris, 2017 [27]).

2.2. Geology and Mineralization of the Falakro Mt

The Falakron marble series in the broad area corresponds to the “lower tectonic unit” of the Greek Rhodope Province, as defined by Papanikolaou and Panagopoulos (1981) [28] and Dinter and Royden (1993) [25]. This series is exposed between the Strymon and Nestos Rivers [29–31]. The structural thickness of the marble increases northeastwards within the Rhodope core complex, ranging from less than 200 m in southwestern Mount Pangeon and the Menikion Mountains to over 5000 m in the central Falakron and Lekanis Mountains [32,33]. The primary lithology is a massive marble that is highly sheared and recrystallized (Figure 2). Micaceous gneiss, two-mica schist, and actinolite schist appear as local intercalations in the form of lenses and layers (from less than 1 m to over 400 m thick). The age of the Falakron series is poorly constrained [34].

The mineral compositions and assemblages found in mica schists and impure marbles across the mainland exposure of the Falakron series are characteristic of greenschist facies regional metamorphism, specifically the quartz–albite–epidote–biotite subfacies [35]. The major structural features of the Falakron marble include upright, kilometer-scale, gently northeast-plunging, open anticlines, and synclines. These ductile deformational elements are all attributed to a single, early Tertiary Alpine compressional event [36].

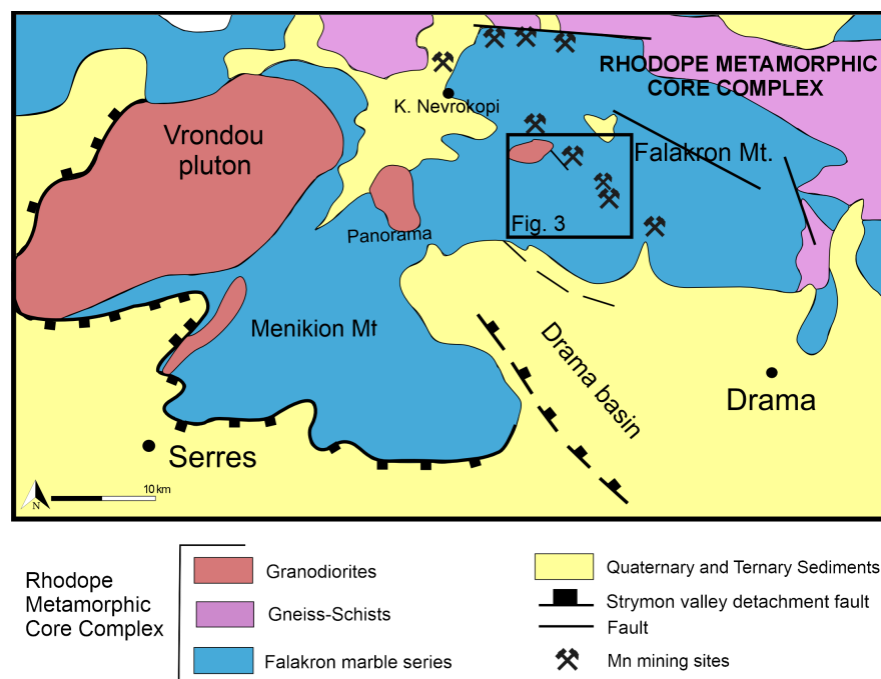


Figure 2. Generalized geological map of the Drama basin area, northeastern Greece, showing the granodiorite intrusions and the manganese mining sites (redrawn from [16,25]).

Previous studies report the Mn mineralization at Kato Nevrokopi as epigenetic, hosted by a thick sequence of marbles (i.e., Falakron upper marbles) and an alternating sequence of gneisses, mica schists, and marble located beneath them (Figures 2 and 3) [17,29]. Mineralization mainly occurs within faults and veins, cross-cutting marbles and extending into host rocks [15–17]. Based on Mn mineralization and its geological setting, Nimfopoulos and Patrick [15] described three ore zones: (i) the deeper, mineralized sulfide-carbonate-rich zone, which can be found as a deeply eroded relic in the southernmost mine of Pyrgi. (ii) The upper mineralized Mn-oxide-rich zones, reported close to the surface at Mavro Xylo and other mines, such as the 25th Km mine situated NW of Mavro Xylo (Figure 3) and the Karposluk and Tartana mines, both occurring along the E–W fault zone (Figure 2). Lastly, (iii) secondary manganese oxides found in formations described as karstic cavity fills originating from zone (ii). In the upper zones of Mn mines, manganese is reported to be concentrated in ‘black calcite’, which consists of coarsely crystalline calcite intergrown with, and replaced by, todorokite along cleavages [16,17,36,37].

The age of hydrothermal mineralization was determined by K/Ar dating using separates of hydrothermal muscovite [36]. The results yielded an age of 32.5–33.0 Ma, contemporaneous with magmatism in the Drama area. Mavro Xylo was the primary manganese mine in the area, located 5 km SE from the Granitis intrusion (Figure 3).

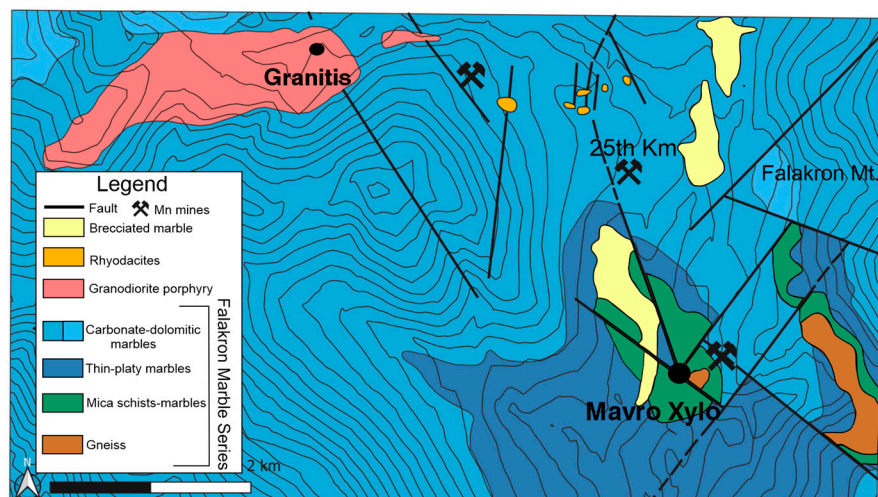


Figure 3. Geological map of granitis intrusion and Mavro Xylo (modified from Papapetros [38], a geological map of IGME, Kato Nevrokopo Sheet).

3. Methods

Seven samples were collected from a major vein exposed at the surface and within an abandoned gallery at the Mavro Xylo mine (Figure 4). All samples were processed for mineralogical and geochemical analyses. The bulk mineralogical composition of the samples was examined by X-ray diffraction using a Siemens D-5005 diffractometer (SIEMENS, Munich, Germany) at the Faculty of Geology & Geoenvironment, National and Kapodistrian University of Athens. The device has a Cu anode and was operated at a generator voltage of 40 kV and a current of 55 mA. The goniometer 2θ values ranged from 2° to 70° , with a scan rate of 0.02 s per step. Mineral phases were identified using the Joint Committee for Powder Diffraction Standards (JCPDS) file and DIFFRAC software EVA (V.6, Bruker Corporation, Billerica, MA, USA) provided by Bruker. Analysis of major and selected trace elements was conducted on bulk ore powdered samples using an X-ray Fluorescence spectrometer equipped with a wavelength dispersive system, specifically the ZSX Primus IV device from Rigaku instruments (Rigaku, Tokyo, Japan) at the Laboratory of Metallurgy, National and Technical University of Athens, Greece. Samples were prepared as pressed tablets of 32 mm by mixing 4 g of sample powder and 1 g of binding material (HWC).

Five polished-thin sections and 11 polished blocks were studied by optical microscopy at the Faculty of Geology and Geoenvironment, National and Kapodistrian University of Athens and by scanning electron microscopy (SEM) with a Jeol JSM-IT500 instrument (Jeol USA, Inc., Peabody, MA, USA), equipped with an OXFORD Ultim Max 100 analytical device (Oxford Inc., Oxford, UK), at the Hellenic Survey for Geology and Mineral Exploration, Athens, Greece. The operating conditions were 20 kV accelerating voltage and 1.5 nA beam current with a 4 μ m diameter beam. Precise chemical compositions of sulfides, oxides/hydroxides, silicates, and carbonates were further determined using a JEOL JXA 8530F field emission gun electron microprobe microanalyzer (Jeol USA, Inc., Peabody, MA, USA) at Utrecht University. Operating conditions were 20 kV and 20 nA, with a beam diameter of <1 mm. The following X-ray lines were used: SiKa, FeKa, MgKa, AlKa, SKa, KKa, CaKa, MnKa, ZnKa, CuKa, AsLa, AgLa, and PbMa. Diopside (for Si and Ca), chalcopyrite (for Fe, S, and Cu), forsterite (for Mg), jadeite (for Al), tephroite (for Mn), sphalerite (for Zn), indium arsenide (for As), pure silver (for Ag), and galena (for Pb) were used as standards.

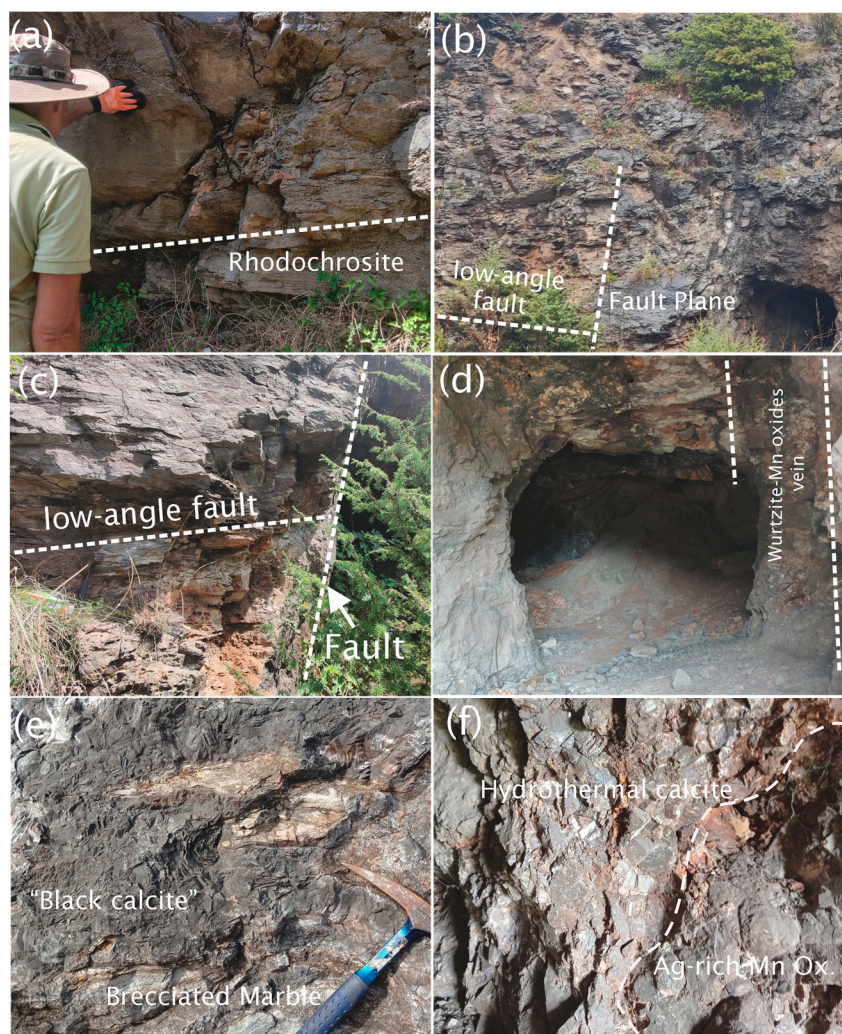


Figure 4. Field photos demonstrating various mineralization styles at the Mavro Xylo mine. (a–c) Manganese mineralized marbles are cross-cut by both low-angle and high-angle faults; (d) vein mineralization with wurtzite and Ag-bearing Mn oxides; (e,f) brecciated marble cemented by coarse-grained black calcite containing silver-rich manganese oxides.

4. Results

4.1. Mineralization at Mavro Xylo

Based on field observations and ore textures of this study, we distinguished two types of mineralization at Mavro Xylo (Figures 4 and 5): (1) vein-type and (2) breccia-type. Two major fault systems are present in the Mavro Xylo deposit, controlling hydrothermal fluid flow and ore deposition (Figures 3 and 4): a low-angle SW–NE trending fault (probably part of a detachment system in the area) and a high-angle NW–SE normal fault, which cross-cuts the previous one (Figure 4a–c). Rhodochrosite associated with disseminated pyrite is developed in veins alongside the low-angle SW–NE fault at higher topographic levels of the deposit (Figure 4a). A hydrothermal rhodonite–quartz–rhodochrosite-bearing vein was located at deeper topographic levels and was described from the Mavro Xylo area for the first time (Figure 5a). Sulfide–manganese oxide veins are developed along strike the high-angle normal faults at deeper levels of the deposit (Figure 4d). These veins are banded and characterized by the early deposition of sulfides at the margins of the vein (i.e., wurtzite, the polymorph of ZnS), followed by the deposition of a mixture of manganese oxide minerals in the inner part within a carbonate–quartz gangue assemblage (Figure 5b,c). Breccia-type mineralization is characterized by fragments of marbles cemented by Ag-

bearing manganese oxides and calcite, occasionally dark colored due the inclusion of Mn oxides (Figure 4e,f).

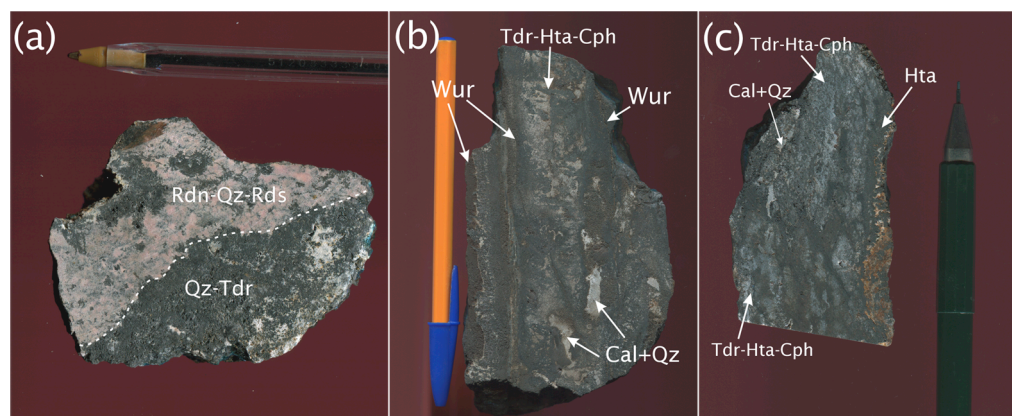


Figure 5. Hand specimens demonstrating vein-type assemblage of the Mavro Xylo area: (a) rhodonite (Rdn)–quartz (Qz)–rhodochrosite (Rds) followed by later quartz (Qz) and todorokite; (b) early wurtzite (Wur) followed by todorokite (Tdr)–hetaerolite (Hta)–chalcophanite (Cph), grey in color with quartz and calcite as gangue minerals; (c) hetaerolite (hta) and silver-rich manganese oxides. Abbreviations were obtained from Warr (2021) [39].

4.2. Mineralogy

4.2.1. Sulfides

Sulfides at Mavro Xylo (i.e., galena, sphalerite, pyrite, and alabandite) occur either as inclusions in hydrohetaerolite and silver-rich manganese oxides, or inclusions of pyrite, galena, Te-bearing argentite in quartz in association with rhodonite and rhodochrosite or in massive form as distinct bands within veins (i.e., wurtzite) (Figures 5 and 6).

Pyrite is the dominant sulfide in rhodonite–quartz–rhodochrosite-bearing veins. It forms inclusions in quartz in association with rhodonite (Figure 6a). The chemical analysis of pyrite is given in Table 1 and Table S1. The analyzed pyrite contains As up to 1 wt.%. Ag (up to 0.36 wt.%) in pyrite is probably attributed to submicroscopic inclusions of Ag-bearing phases (Table 1, Figure 6b).

Te-bearing Argentite (Ag_2S) forms inclusions (up to 2 μm) in pyrite alongside galena (Figure 6b). Based on SEM-EDS data (Table S1), argentite contains up to 9.09 wt.% Te.

Galena forms inclusions in pyrite from rhodonite–quartz–rhodochrosite-bearing veins (Figure 6b). It also forms inclusions in silver-rich manganese oxides (Figure 6c). EDS analyses of galena are given in Table S1.

Sphalerite is observed in the rhodonite–quartz matrix and contains up to 2.6 wt.% Mn and 0.57 wt.% Fe, corresponding to 2.44 mole % FeS (Figure 6d, Table 1).

Alabandite (MnS) is found as small grains up to 5 μm in size in association with manganese oxides and seems to postdate the formation of adjacent Ag-todorokite (Figure 6e).

Wurtzite, a $(Zn,Fe)S$ polymorph, was verified from its X-ray diffraction pattern (Figure S1). It occurs as massive, reddish-brown bands overlaid by manganese oxides such as todorokite–hetaerolite–chalcophanite (Figure 5).

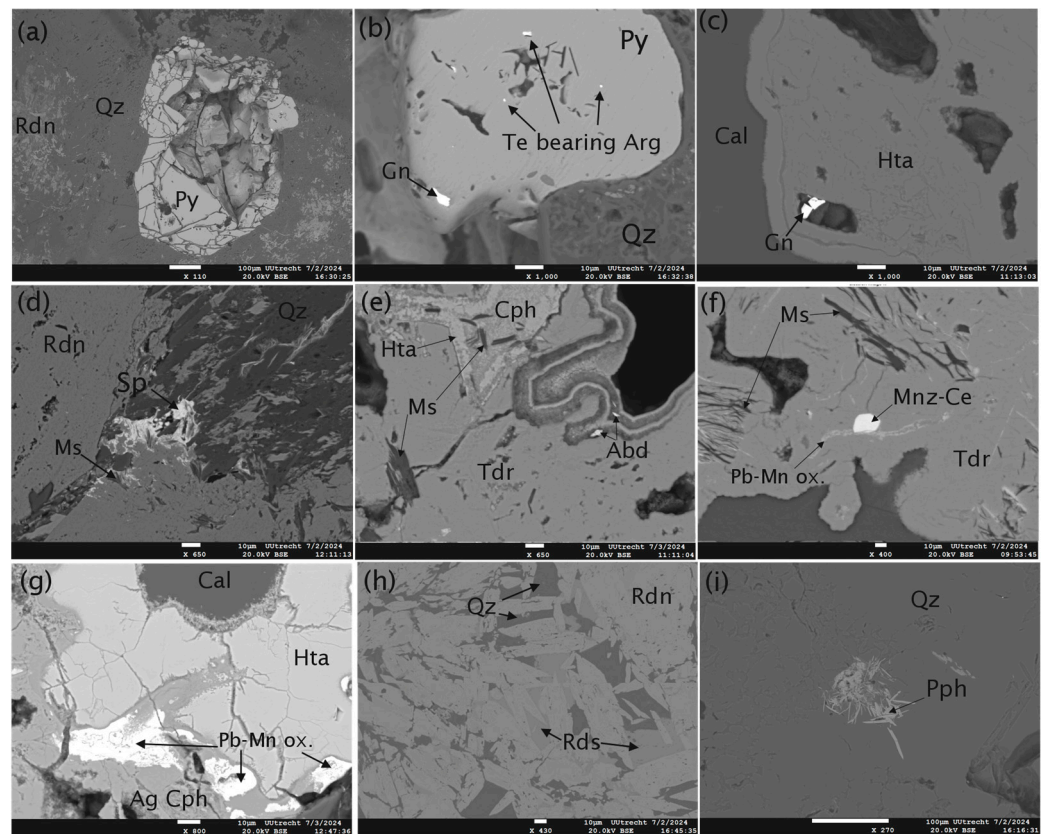


Figure 6. Microphotographs (BSE images) of sulfides, Mn oxides, and non-metallic minerals from the (a,b,d,h,i) rhodonite–quartz–rhodochrosite–sulfide-rich samples and (c,e–g) the silver-rich Mn oxide samples from Mavro Xylo. (a) Pyrite (Py) grains in association with rhodonite (Rdn) surrounded by quartz (Qz); (b) Te-bearing argentite (Arg) and galena (Gn) as inclusions in pyrite; (c) galena (Gn) is present as an inclusion in hetaerolite (Hta) and surrounded by calcite (cal); (d) sphalerite (Sp) occurs together with hydrothermal muscovite (Ms) and quartz (Qz) and rimming rhodonite; (e) early alabandite (Abd) followed by todorokite (Tdr), which is replaced by hetaerolite/hydrohetaerolite (Hta) and late chalcophanite (Cph). Hydrothermal muscovite (Ms) formed contemporaneously with manganese oxides; (f) monazite in association with hydrothermal muscovite (Ms) included in todorokite (Tdr) and in contact with the hydrous Pb-Mn oxide mineral replacing todorokite; (g) argentian chalcophanite (Ag cph) and silver-rich hydrous lead manganese oxide (Pb-Mn ox.) postdate hydrohetaerolite (Hta); (h) rhodonite (Rdn) followed by quartz (Qz) in association with rhodochrosite (Rds); (i) pyrophanite (Pph) as an inclusion in quartz (Qz).

Table 1. Representative EPMA data of sulfides from Mavro Xylo Mn mineralization (in wt.%, b.d. = below detection): 1–3 Pyrite; 4–5 sphalerite; 6 alabandite.

	1	2	3	4	5	6
Fe	46.84	45.37	46.58	0.57	0.2	0.22
S	52.76	51.46	53.37	32.85	33.01	35.15
Mn	0.82	0.03	0.03	2.3	2.56	64.9
Cu	0.06	0.05	0.02	0.05	0.04	0.02
As	0.01	1.07	b.d.	b.d.	b.d.	b.d.
Pb	0.18	0.19	0.25	0.1	0.06	0.11
Zn	b.d.	0.01	0.02	64.71	64.78	0.08
Ag	b.d.	0.36	0.02	0.02	0.09	0.03
Total	99.6	98.54	100.29	100.6	100.74	100.49

Table 1. Cont.

	1	2	3	4	5	6
	Chemical Formula					
Fe	1.006	1.000	1.000	0.010	0.003	0.003
S	1.974	1.976	1.997	0.992	0.994	0.961
Mn	0.018	0.001	0.001	0.040	0.045	1.034
Cu	0.001	0.001	0.000	0.001	0.001	0.000
As	0.000	0.017	b.d.	b.d.	b.d.	b.d.
Pb	0.001	0.001	0.001	0.000	0.000	0.001
Zn	b.d.	0.000	0.000	0.957	0.956	0.001
Ag	b.d.	0.004	0.000	0.000	0.001	0.000
Total	3.000	3.000	3.000	2.000	2.000	2.000

4.2.2. Manganese Oxides

Todorokite $[(Na,Ca,K,Ba,Sr)_{1-x}Mn_6O_{12} \cdot 3-4.5(H_2O)]$ is the most abundant Mn oxide in Mavro Xylo, accompanying wurtzite in the vein-style mineralization. While it can occur either as a hypogene or supergene mineral in manganese deposits [1,3,40], *todorokite* at Mavro Xylo is thought to be of hydrothermal origin, and the first phase of manganese oxide to form followed by hydrothermal calcite and quartz (Figure 6e,f). EPMA and SEM-EDS data (Table 2 and Table S2) show that, except for Ca and K, which are common in *todorokite* in various concentrations, it also contains up to 3.65 wt.% Zn and 2 wt.% Ag. The average structural formula of *todorokite*, based on EMPA data, is $(Mn_{1.76}^{2+}K_{0.02}Ca_{0.09}Zn_{0.10}Ag_{0.03})_2Mn_6O_{12} \cdot 4H_2O$, demonstrating the incorporation of 1.76 apfu Mn^{2+} in the structure. The assemblage of *todorokite*–*wurtzite* in Mavro Xylo was verified by X-ray diffraction (Figures S1 and S2).

Table 2. Representative EPMA data of Mn-oxides/hydroxides from Mavro Xylo Mn mineralization (in wt.%, b.d. = below detection): 1–2 hetaerolite; 3–4 hydrohetaerolite; 5–6 *todorokite*; 7–8 hydrous lead manganese oxide; 9–11 *chalcophanite*.

Oxide	1	2	3	4	5	6	7	8	9	10	11
SiO ₂	0.11	0.12	0.16	0.18	0.06	0.03	0.1	0.08	0.11	0.09	0.06
Al ₂ O ₃	0.02	b.d.	b.d.	0.02	b.d.	b.d.	0.08	0.1	0.15	0.07	0.03
FeO	0.23	0.18	0.12	0.13	0.16	0.2	0.84	0.45	0.43	0.8	0.29
Mn ₃ O ₄	66.2	66.06	62.16	62.26	-	-	-	-	-	-	-
MnO ₂	-	-	-	-	87.01	85.55	68.82	71.93	69.28	76.83	79.52
MgO	b.d.	b.d.	b.d.	b.d.	0.06	0.02	0.02	0.29	0.35	0.34	0.5
CaO	0.04	b.d.	0.13	0.09	0.93	0.83	0.95	1.46	1.09	1.79	3.01
K ₂ O	0.02	b.d.	0.03	0.04	0.18	0.18	0.2	0.41	0.22	0.64	0.78
Cu ₂ O	0.05	0.02	0.11	0.12	0.03	0.03	0.52	0.56	0.09	0.53	0.09
As ₂ O ₃	b.d.	b.d.	b.d.	b.d.	b.d.	b.d.	0.87	0.58	0.31	0.24	0.17
PbO	0.03	b.d.	0.02	0.07	0.03	0.06	17.19	9.82	0.05	0.31	1.5
ZnO	33.78	33.6	35.2	35.12	2.48	2.99	4.86	5.17	22.58	7.4	4.68
Ag ₂ O	b.d.	b.d.	b.d.	b.d.	0.67	1.56	0.73	1.46	0.46	1.81	2.2
Total	100.25	99.98	97.93	98.03	91.61	91.45	95.18	92.31	95.01	90.85	93.74

Hetaerolite ($ZnMn_2O_4$) and *hydrohetaerolite* ($Zn_2Mn_4O_8 \cdot H_2O$) (IMA unapproved) are rare zinc–manganese minerals found in the Mavro Xylo area. Both mineral phases postdate *todorokite* and contain up to 27 wt.% Zn (Tables 3 and 4; Figure 6c). Even though all other manganese oxide minerals at Mavro Xylo have considerable Ag concentrations, *hetaerolite* and *hydrohetaerolite* analysis showed negligible Ag content (Tables 2 and S2). This is likely because their spinel-like structure, like *hausmannite*, exhibits the weakest adsorption capacity among manganese oxides since the adsorption properties of manganese oxides are closely linked to their structural characteristics [1,41]. The presence of *hetaerolite*/*hydrohetaerolite* together with *todorokite* and *chalcophanite* was verified by X-ray diffraction patterns (Figure S2).

Table 3. Representative EPMA data of Mn-carbonates and Mn-silicates from Mavro Xylo Mn mineralization (in wt.%, b.d. = below detection): 1 Mn-bearing Calcite; 2–3 rhodochrosite; 4–5 rhodonite.

Oxide	1	2	3	4	5
SiO ₂	b.d.	0.39	0.17	44.77	44.62
Al ₂ O ₃	b.d.	0.03	0.03	0.89	1.04
FeO	b.d.	0.16	0.12	0.41	0.36
MnO	1.9	59.63	47.36	46.16	44.61
MgO	0.33	0.21	0.68	0.58	0.4
CaO	54.52	1.3	11.72	5.41	7.11
K ₂ O	b.d.	0.01	0.02	0.02	b.d.
Cu ₂ O	0.03	0.03	0.02	0.01	0.02
As ₂ O ₃	b.d.	b.d.	0.01	0.03	b.d.
PbO	0.02	b.d.	b.d.	0.04	0.06
ZnO	0.06	0.09	0.01	0.02	0.01
Ag ₂ O	0.02	b.d.	b.d.	0.01	b.d.
CO ₂ *	42.93	36.90	38.01	-	-
Total	99.48	98.75	98.15	97.95	98.23

* CO₂ is estimated by stoichiometry.

Chalcophanite (ZnMn₃O₇*3H₂O) appears to replace hetaerolite at Mavro Xylo (Figure 6e,g). The Zn concentration varies from 5 wt.% up to 19 wt.% (Tables 2 and S2), suggesting a zinc-deficient variety of chalcophanite [9,42,43]. Chalcophanite, together with todorokite, represent two Mn-oxide mineral phases with the highest Ag concentrations in the mineralization. The Ag content in chalcophanite ranges from 0.6 wt.% to 2.2 wt.% (Tables 2 and S2). The Ca content also reaches values up to 2.26 wt.%. Based on EPMA data, the structural formula of the chalcophanite studied here is (Ca_{0.1}Mn_{0.60}²⁺Zn_{0.21}Ag_{0.09})Mn₃O₇*3H₂O.

Hydrous lead manganese oxide (PbMn₅O₁₁*5H₂O) is a minor constituent occurring with chalcophanite or within todorokite after galena (Figure 6f,g). This mineral phase was first described at Aurora mines together with argentiferous manganese oxides [9] and is also reported from Mavro Xylo. The Pb content in this mineral phase ranges from 9.82 to 20.86 wt.% (Tables 2 and S2). Additionally, Ag contents reach values of up to 1 wt.%. The structural formula of hydrous Pb-Mn oxide is (Fe_{0.13}Mn_{0.05}²⁺Zn_{0.14}Pb_{0.62}Ag_{0.03})Mn₅O₁₁*5H₂O.

4.2.3. Gangue Minerals

Rhodonite [CaMn₃Mn(Si₅O₁₅)], a manganese silicate mineral, was found in the Mavro Xylo area and is a dominant early mineral phase (Figure 6a,d,h) in hydrothermal veins. It incorporates minor amounts of Al₂O₃ substituting for SiO₂ (up to 0.85 wt.%), and Ca, Mg, and Fe (up to 5.07, 0.26, and 0.2 wt.%, respectively) substituting for Mn (Tables 3 and S3).

Quartz occurs following rhodonite, a major host of sulfides and Mn oxides in mineralization (Figure 6a). The mineral assemblage of rhodonite–quartz–rhodochrosite was verified by X-ray diffraction analysis (Figure S3).

Rhodochrosite is a Mn-carbonate mineral phase found together with quartz, postdating rhodonite (Figure 6h). Its chemical composition is given in Table 3. Its Ca concentration varies from 1 to 12 wt.%.

Pyrophanite (MnTiO₃) has needle-like inclusions in quartz (Figure 6i).

Muscovite accompanies sulfides and oxides in Mavro Xylo mineralization (Figure 6d,e). Low amounts of manganese are present in muscovite, reaching values up to 1.78 wt.% (Table S3).

Calcite is abundant in Mavro Xylo, either as mangiferous *black calcite* alongside brecciated marble (Figure 4e) or as grey–white calcite in manganese oxide-bearing veins (Figure 6a,b). Manganese content in calcite varies from 1.5 to 1.9 wt.% (Table 3).

Monazite [(Ce,La,Nd)PO₄] occurs mainly as minute grains (10–15 µm in size), included in todorokite. Monazite grains display a close textural association with muscovite (Figure 6f). Praseodymium, Gd, and Sm were found at values of 2.92 wt.%, 1.96 wt.%, and 1.7 wt.%, respectively (Table S3).

4.3. Bulk Ore Geochemistry

Six Mn ore samples from the Mavro Xylo vein were analyzed by X-ray fluorescence, and the results are shown in Table 4. The samples record manganese abundances from 48.6 wt.% to 66 wt.%. Notable base metal impurities in the manganese oxide ore reflect the mineral chemical characteristics already described: Pb content varies from 0.01 wt.% to 0.66 wt.%, Zn content ranges from 0.31 wt.% to 16.2 wt.%, Cu ranges from 0.01 wt.% to 0.8 wt.%, and S content ranges from 0.06 wt.% to 0.56 wt.%. Ag concentrations are particularly notable, ranging from 0.01 wt.% to 0.57 wt.%, although, in two samples, Ag was below the detection limit (b.d.).

Table 4. XRF results (wt.%) of bulk manganese oxide ore from Mavro Xylo.

Sample	K	Mg	Ca	Al	Si	Mn	Fe	Zn	Pb	Cu	Ag	As	Sb	S
MX23-1	0.5	0.1	6.59	0.36	0.79	48.6	0.24	0.31	0.08	0.08	0.01	0.18	0.09	b.d.
MX23-2	0.3	b.d.	4.56	1.24	1.89	50.3	0.53	0.99	0.01	b.d.	b.d.	0.05	b.d.	b.d.
MX23-4	0.12	b.d.	0.92	0.61	1.2	55.5	0.31	1.01	0.24	0.01	b.d.	0.05	b.d.	b.d.
MX23-5	0.31	2.13	12	1.09	0.86	66	0.5	7.09	0.66	0.8	0.43	0.08	0.02	0.06
MX23-6	0.5	1.02	3.98	3	1.89	59.8	0.82	16.2	0.38	0.71	0.29	0.03	0.02	0.23
MX23-7	0.34	2.01	11.4	0.96	3.07	64.5	0.55	6.07	0.6	0.74	0.57	0.04	0.04	0.56

5. Discussion

5.1. Paragenetic Sequence and Physicochemical Conditions of Formation

Based on field relationships and petrographic data (optical microscopy, SEM, EPMA), we present a paragenetic sequence for the vein-type mineralization at Mavro Xylo below (Figure 7). We suggest two-stage evolution for mineralization in the area:

- Stage I ore is dominated by the presence of disseminated sulfides, in accordance with previous findings of [15–17] for the broad Kato Nevrokopi area. At Mavro Xylo, initial deposition of the manganese silicate rhodonite is followed by rhodochrosite and quartz, the latter also including lesser pyrite, galena, Te-bearing argentite, and sphalerite (Figure 6a,b,d). Additionally, this stage is characterized by the deposition of wurtzite and alabandite. Stage I thus records notable enrichments in Mn-, Zn-, Ag-, and Te.
- The second stage (stage II) is characterized by the dominance of manganese oxide minerals. Stage II is marked by the early deposition of Ag-Zn-bearing todorokite, followed by hetaerolite and hydrohetaerolite, and paragenetically later by Ag-bearing chalcophanite and hydrous Pb-Mn oxides. Quartz, calcite, muscovite, and monazite-(Ce) are gangue minerals.

Todorokite and chalcophanite are complex manganese oxide minerals with structures ([3 × 3] tunnel structure for todorokite and layered for chalcophanite) that can host many cations due to their strong adsorption capability for alkali and alkaline earth and transition metals [1]. Although Ag-Mn ore deposits are globally significant as metal sources, there are limited studies on the distribution of Ag in manganese oxides *sensu stricto* [6,44]. SEM-EDS and EPMA results on todorokite and chalcophanite from Mavro Xylo constrained their elemental compositions with respect to both Ag and Zn. For further understanding of the partitioning of Ag and Zn into both manganese oxides, correlation diagrams are presented in Figure 8. A broadly positive correlation between Ag and Zn in todorokite indicates that both elements occupy the tunnel structure of todorokite (Figure 8a). Binary plots between Mn-Ag and Mn-Zn display an apparent negative correlation in both cases (Figure 8b,c), suggesting that Ag and Zn substitute for Mn²⁺, thus supporting the late-stage origin and metal uptake of these minerals [45]. In contrast, the EPMA data of chalcophanite define a broadly negative correlation between Ag and Zn, indicating that these two metals substitute each other in the structure of chalcophanite (Figure 8d).

Mineral	Stage I	Stage II
Rhodonite	—————	
Quartz	—————	
Rhodochrosite	—————	
Pyrophanite	———	
Muscovite	—————	—————
Monazite		———
Calcite	—————	—————
Pyrite	—————	
Te bearing Argentite	—————	
Galena	—————	
Sphalerite	—————	
Wurtzite		—————
Alabandite		———
Ag-Todorokite		—————
Hydrohetaerolite		—————
Hetaerolite		—————
Ag-Chalcophanite		—————
Ag-Pb-Mn hydrous ox.		—————

Figure 7. The paragenetic sequence of Ag-rich Mn-Zn-Pb vein-type mineralization at Mavro Xylo.

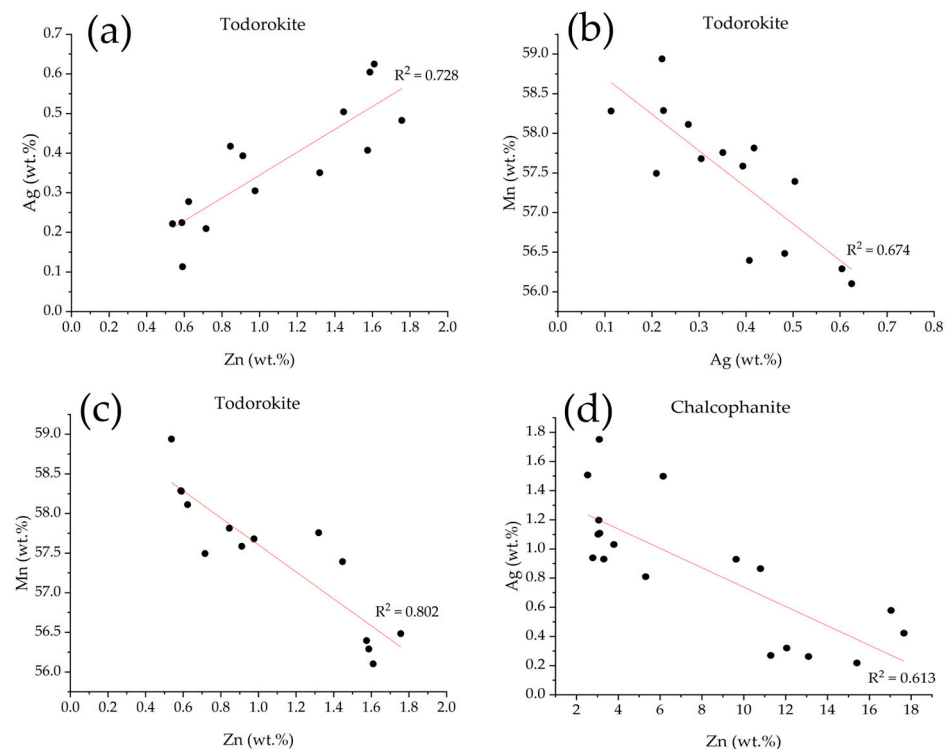


Figure 8. Correlation plots of (a) Ag vs. Zn, (b) Mn vs. Ag, and (c) Mn vs. Zn in Todorokite, and (d) Ag vs. Zn in chalcophanite from Mavro Xylo Ag-Pb-Zn-Mn mineralization.

Manganese incorporation into early silicates (rhodonite), carbonates (rhodochrosite), oxides (pyrophanite), and sulfides (alabandite) takes place in its divalent form (Mn^{2+}), supporting more reducing fluid conditions during the initial stages of mineralization. Manganese incorporated into stage-II minerals (todorokite, hetaerolite, hydro-hetaerolite, and chalcophanite) occurs mainly in the trivalent and/or tetravalent form, thus suggesting

increasingly oxidized conditions during stage II ore deposition, likely due to meteoric fluid infiltration [46,47]. The presence of Te during mineralization indicates a primary magmatic contribution, given that Te is usually transported in the form of magmatic vapors [48]. In summary, Mavro Xylo vein-type mineralization is thought to have evolved from earlier, relatively reducing magmatic–hydrothermal conditions towards more oxidizing conditions due to the later incursion of meteoric waters. Future applications of stable isotope analyses and fluid inclusion studies are bound to provide critical constraints on the conditions of ore formation during both ore-forming stages.

5.2. Comparison of Mavro Xylo Veins with Other Epithermal Mn-Precious Metal Mineralization

The vein-type mineralization at Mavro Xylo is structurally controlled and shares common structural attributes (i.e., banding and brecciation) with epithermal styles of mineralization elsewhere [49]. Although rhodonite has been reported from carbonate replacement [50,51] and skarn deposits [52], it is also a typical mineral in epithermal-style mineralization when found together with Mn carbonates [53–56]. Moreover, the studied mineralization lacks other skarn-type mineralogy of diagnostic value (e.g., johannsenite, spessartine, and piedmontite) [20] that would support a contact metasomatic environment of deposition. Similarly to Mavro Xylo, the presence of early stage rhodochrosite, together with rhodonite, quartz, and sulfides, has been previously reported in hydrothermal manganese deposits of Hokkaido, Japan [53,57], Bisbee and Tombstone, Arizona [53,58,59], and Philipsburg and Butte, Montana [53,58,60]. Such assemblage is typical of intermediate sulfidation epithermal mineralization [53,61,62], as is, for example, the precious and base metal epithermal deposit of Banská Hodruša in Slovakia [56,63].

Two ZnS polymorphs are present within the epithermal NW–SE trending veins at Mavro Xylo, namely wurtzite and sphalerite. The presence of both wurtzite and sphalerite has also been reported from other epithermal mineralization in Greece, for example, at St. Philippos in western Thrace [64], Achla Tarla [65], Panormos in Tinos Island [66], and at Lavrion [67,68]. The presence of sphalerite with 2.4 mole % FeS at Mavro Xylo is compatible with intermediate sulfidation fluid states during mineralization [49]. Sphalerite, with a similar composition to that found at Mavro Xylo, is described from the intermediate sulfidation Mn-rich epithermal veins of the Rosia Montana Au–Ag deposit in Romania [69]. Moreover, the alabandite-bearing silver-rich manganese oxide mineralization at Mavro Xylo resembles other Ag- and Mn-rich epithermal deposits, such as the Santo Toribio epithermal deposit in Northern Peru [70].

Among the manganese oxides, todorokite, hetaerolite, and hydrohetaerolite are common constituents in Mn-rich epithermal-style deposits [1,3]. The minerals hetaerolite and hydrohetaerolite have been previously reported at Milos Island [3], Madjarovo, Eastern Rhodope [71], Rodna, Romania [72], as well as Hokkaido, Japan [73], in all cases in connection with vein-type Pb–Zn–Ag–Mn epithermal mineralization.

Silver-rich manganese oxides/hydroxides are considered quite rare and are typically found near Ag–Pb–Zn or Ag–Mn deposits as part of the epithermal environment [6,9,74]. In Mavro Xylo, todorokite records high concentrations of Zn and up to 2 wt.% Ag and can thus be reported as argentian todorokite. Argentian todorokite was initially identified in the Aurora mines (Treasure Hill), Hamilton, Nevada, USA [9], where it is associated with black calcite and has silver concentrations reaching up to 4 wt.% [9,75].

The occurrence of silver in these manganese minerals is complex and debated, with suggestions of silver existing as a native element bound to manganese oxide [9,12] or within the crystal lattice of the manganese oxides (such as cryptomelane) replacing potassium or other elements [8,9,76,77]. Despite their industrial significance, these mineral phases have not been extensively studied due to the low Ag recovery in metallurgical processes [7,8,13,78].

In summary, geological, mineralogical, and textural characteristics of the studied veins at Mavro Xylo indicate a fault-controlled, intermediate sulfidation, Ag-rich Mn–Zn±Pb epithermal style of mineralization. Partial leaching and remobilization of Ag, at the expense

of earlier sulfide-dominant assemblages, could have played a key role in its subsequent incorporation into later-stage Mn oxides.

6. Conclusions

Based on the findings of this study, the following conclusions may be drawn:

- (1) New field evidence, including mineralogical and geochemical data from the Mavro Xylo Mn-Zn-Ag±Pb deposit at Kato Nevrokopi, Drama, Greece, indicates epithermal vein-type mineralization as part of the deposit.
- (2) Mineralization is interpreted to have formed during two evolutionary hydrothermal stages: (I) an early sulfide-bearing stage consisting of pyrite, galena, Te-rich argentite, sphalerite, wurtzite, and alabandite and (II) an oxide-bearing stage, with initial deposition of todorokite, followed by hetaerolite, hydrohetaerolite, and chalcophanite.
- (3) Silver was primarily introduced into the mineralization in the form of Te-bearing argentite and later remobilized and bound in the structure of Ag-bearing Mn-oxides such as todorokite and chalcophanite, as demonstrated in Mavro Xylo mineralization.
- (4) Mineralization evolved from more reducing (sulfide-bearing) towards more oxidized (Mn oxide-bearing) conditions, likely due to the increasing incursion of meteoric waters in the ore system.

Supplementary Materials: The following supporting information can be downloaded at <https://www.mdpi.com/article/10.3390/min14090955/s1>, Figure S1: X-ray diffraction pattern of the ore sample from the epithermal vein consisting of wurtzite (Wur)–todorokite (Tdr) with calcite (Cal) and quartz (Qz) as gangue minerals, Figure S2: X-ray diffraction pattern of the silver-rich manganese oxide ore sample containing hetaerolite (Hta), todorokite (Tdr), and chalcophanite (Cph), Figure S3: X-ray diffraction pattern of gangue minerals containing Rhodonite (Rdn)–Quartz (Qz)–Rhodochrosite (Rds), Table S1: Representative SEM-EDS analyses of sulfides from Mavro Xylo Mn mineralization (in wt.%), Table S2: Representative SEM-EDS data of hetaerolite and silver-rich manganese oxides from Mavro Xylo, Kato Nevrokopi area (in wt.%), Table S3: Representative SEM-EDS data of gangue minerals.

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