

GEOCHEMISTRY AND ORIGIN OF BANDED ORE OF MANGANESE BELT, EASTERN CARPATHIANS, ROMANIA

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Abstract. The Manganese Belt has a great mineralogical diversity and rarity containing more than 350 minerals and mineral varieties, of which 182 are new for Romania, being one of the most complex deposit in the world. The manganese ores are of carbonate-silicate type with a few oxides and sulfides. The chemical composition of many manganese carbonates, silicates, and oxides have high Mn/Fe ratios. The all manganese ores/manganiferous rocks have well-developed laminations/bandings, that appeared in hand samples and thin sections, representing distinct lithologies/petrographic types. The following types were established: metachert, quartzite with alkali pyroxenes and amphiboles, tephroite, Mn-humites, spessartine, pyroxmangite, rhodonite, mangancummingtonite, nambulite and natronambulite, pyrosmalte, and vein type (bannisterite, ganophyllite, and stilplomelane), all host by Tulgheş Series 1 (TG1) rocks. Each type was geochemical analysed. All lithology types show low concentrations of Ni, Co, Cu, Zn, U, Th, and REE trace elements, being similar to the trace element concentrations reported from sediments which are forming in hydrothermally active regions on the present sea floor. The metachert shows similar, but in low concentrations of trace elements, as the type ore. The metachert and manganese ore have high Li concentrations as trace element. The association of the manganiferous lithologies with metachert and meta-igneous rocks of TG1 is consistent with deposition of the original sediments in a rifting environment, such as a back-arc basin. The current tectonic and structural setting of Mn ore correspond to their development and evolution in a subduction/rift zone, a narrow and long active paleotrench area, reflected in their line development as belt.

Key words: TG1, metachert, manganiferous banded lithologies, high Mn/Fe ratios, low concentrations of trace elements (especially Ni, Co, and Cu), ocean-rifting environment, subduction zone, hydrothermal submarine genesis.

Résumé. Les gisements cambriens métamorphiques de Mn dans les monts Bistriței (Ceinture de Mn) présentent une grande diversité minéralogique. Le minerai de Mn est rubané/en couches, chaque bande/couche représentant un type pétrographique de minerai/roche de manganèse. Les types pétrographiques suivants ont été établis: téphroïte, Mn-humites, spessartine, rhodonite, pyroxmangite, mangangrunerite, pyroxène et amphiboles alcalines, minéraux de lithium, manganpyrosmalte, filonien (bannisterite, ganophyllite et stilplomelane), métachert, et la roche hôte (série Tulgheş). Chaque type a été analysé géochimiquement. Tous les types pétrographiques analyses ont montré de faibles concentrations d'éléments traces, Ni, Co, Cu, Zn, U, Th et d'éléments des terres rares (ETR), étant similaires aux concentrations signalées dans les sédiments qui se forment aujourd'hui dans les régions hydrothermales actives du fond océanique. Métachert a des concentrations similaires, mais dans de faibles concentrations d'oligo-éléments, comme le minerai de Mn. Le minerai de Mn et le métachert ont des concentrations élevées de Li comme élément trace. Métachert est la gangue de minerai de Mn. Le cadre tectonique et structural des gisements de Mn correspond à leur développement et à leur évolution dans une zone de subduction, une zone active longue et étroite (paléotranchée), reflétée par leur développement linéaire, à la manière d'une ceinture. Le cadre / environnement de subduction paléodépositionnelle est également matérialisé dans la grande épaisseur de milliers de mètres des roches de la série Tulgheş, l'hôte de Mn. Les concentrations en éléments traces des types pétrographiques projetées dans le diagramme $(Cu + Ni + Co) \times 10$ se situent dans le domaine hydrothermal sous-marin.

Mots-clés: TG1 roche hôte, métachert, minerai/roche de manganèse rubané, faibles concentrations d'éléments traces, (Ni, Co et Cu), subduction zone, hydrothermal sous-marin genèse.

INTRODUCTION

The Cambrian metamorphic Tulgheş Series (TG) has large development in Bistriţa Mts, and has also less development in the South and North of them, in the Giurgeu Mts, and Maramureş and Mestecăniş Mts, respectively. The TG hosts four mineralized belts with line development, which are oriented NW–SE, from West to East, and from bottom to upper part: Manganese (MnB), Barium (BaB), Sulfide (SB), and Uranium (UB) (Hirtopanu, 2019). These mineralized belts have been established using the recently determined minerals and mineral varieties occurring in each belt. The interferences of mineralogical compositions of these four belts indicate a genetic link, which suggests that all were formed during the same submarine hydrothermal process on the Cambrian sea floor. The MnB is situated in TG1, the bottom of TG. In the low middle Cambrian (TG2), the sea floor was pushed toward the East of MnB, and the Ba mineralizations were deposited at some distance from and over the Mn ore body. The SB hosted by TG3, forms an alignment of 200Km of deposits situated from NW to SE (Maramureş, Mestecăniş, Bistriţa, and Giurgeu Mts) and has the same orientation as MnB and BaB, and at some distance of them. In the upper Cambrian (TG4) the sea floor was more pushed towards East, under the oldest Bretila Group, and the U mineralization was deposited at some distance from the SB and with the same orientation. Nevertheless, it was tectonically strongly transformed and remobilized from its original source (TG4), being pushed more under the older Bretila Group. The current tectonic-structural setting of Tulgheş Series corresponds to its development and evolution in a narrow deep active subduction zone. The paleotectonic subduction is materialized in its great thickness of thousands of meters (4,000–6,000m). The rocks of TG are gradually and retrogressively metamorphosed, just with a recurrent metamorphic facies and subfacies, repeated and superimposed metamorphic events.

COUNTRY ROCKS OF MANGANESE BELT

The Manganese Belt is situated at the bottom of Tulgheş Series (TG1) whose main constituents, hornblende, biotite, and almandine, are strongly carbonated and chloritized. The ilmenite, an important constituent of TG1, is a Cr bearing variety. The titanite, magnetite, calcite, graphite, oligoclase, and less pyrite also occur as important constituents. The TG1 looks like a retromorphosed amphibolite. The decarbonation reactions of the rhodochrosite of the premetamorphic bulk of Mn ore were the source of large CO₂ volumes of petrological importance. The Ti bearing minerals is tightly linked to the evolution of metamorphic processes indicating the polymetamorphism of the formation of the country rock. The ilmenite is a mineral that persists over a long period of metamorphism between the kyanite and staurolite zone, and biotite zone. Therefore, we appreciate that the first metamorphic peak of TG1 belongs to at least biotite/almandine zone of amphibolite facies. Instead, the Mn-ore (tephroite, old pyroxmangite, old rhodonite, and old mangancummingtonite, ferroan johannsenite) shows higher metamorphic conditions than its host rocks. The first occurrence of **ferroan johannsenite** (Hirtopanu & Scott, 2002) with a composition closer to that of diopsidhedenbergite, belongs to upper amphibolite facies. The johannsenite structure is less stable than other pyroxenes and is substituted by the ferrorhodonite, new mineral recently discovered (Shchipalkina *et al.*, 2017), and grossularite. The chemical composition of TG1 shows very low MnO content (0.3–0.8wt%). There is no textural or chemical evidence for the replacement of Mn-poor by Mn-rich minerals in TG1. There are no correlations among the Tg1 and its hosted manganese ore. A few sample were analysed (Table I) and they show big scarcity of concentrations of trace elements which differ that those of metachert and Mn-ore. The contents of Ba, As, Sb, Bi, Mo and Yb are not present or very low. The low Cr content comes from ilmenite. The Li absence as trace element in TG1 and its large concentrations in metachert and manganese ores, show no genetic links of them.

Table I

The trace elements in the TG1 rocks (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BPO33	–	–	4.8	130	7.5	–	135	6.5	–	–	32	50	5.5	75	–	4
BRS9	–	–	10.5	380	24	–	65	26	–	15	32	70	40	55	–	2
BS72	–	–	–	380	24	–	65	23	–	5	14	50	21	5	–	–
BOS151T	–	–	–	11	–	–	–	18	–	–	–	50	20	5	–	–
BAGS55	–	–	–	60	7.5	–	–	–	–	–	20	–	–	40	–	–
BA51Or	–	–	–	130	7.5	–	100	13	–	3	160	–	–	30	–	–

Analyst: Mihai Popescu

TEXTURE, MINERALOGY, AND GEOCHEMISTRY OF MN-POOR AND MN-RICH LITHOLOGIES

The manganese ores and manganiferous rocks have well-developed laminations/bandings, that appeared in hand samples and thin sections, representing distinct lithologies/distinct petrographic types. Were established the following types: metachert, quartzite with alkali pyroxenes and amphiboles, rhodochrosite, tephroite, Mn-humites, spessartine, rhodonite, pyroxmangite, mangancummingtonite, nambulite and natronambulite, manganpyrosmalite, and vein type (bannisterite, ganophyllite, and stilplomelane). Each type was geochemically analysed.

1. THE METACHERT, THE GANGUE OF THE MN-ORE

The metachert was known as inadequate term of “black quartzite” (Buţureanu, 1911; Munteanu *et al.*, 2004), because of the presence of small graphite and altered pyrite. It is white medium grained recrystallized quartzite, with massive or thin-bedded texture. The quartz proportion of metachert is high and variable (80–99.5%). The microscope study established four mineralogical metachert types with: (a) a few graphite (+small apatite, muscovite, chlorite, calcite, pyrite); (b) ferrostilplomelane, retromorphe on biotite (+chlorite, pyrite, magnetite, apatite, alkali feldspars, spessartine, biotite); (c) rare small alkali pyroxenes and amphiboles (+microcline, albite, magnetite, apatite, hematite, almandine-spessartine); (d) very small and rare spessartine (+a little mangancummingtonite, graphite, pyrite, chlorite). When the alkali pyroxenes and amphiboles are abundant, the (c)-metachert type becomes a quartzite with alkali pyroxenes and amphiboles, and when the spessartine is abundant, the (d)-metachert type becomes a spessartine/gondite type. All these metachert types occur as bands around and inside Mn-ores. The (b)- metachert which has the biotite transformed in ferrostilplomelane is banded with pyroxmangite rich bands (Fig. 9 right). The metachert could be considered the gangue of ore. The chemical composition of metachert shows that it has a smaller Mn/Fe than Mn ore, but the large amount of dominated silica tends to dilute the concentration of all other constituents. Under the microscope the (c)-metachert has approximately the same composition such the quartzite with alkali pyroxenes and amphiboles, but its constituents have smaller dimensions and low proportions. This (c)-metachert has a diluted composition of that of the quartzite with alkali pyroxenes and amphiboles. In terms of absolute concentrations, the (c)-metachert has relatively high Na, K, and Li contents. The thin bands of this (c)-metachert type are banded with quartzite with alkali pyroxenes and amphiboles (Figs. 1 left and right). It has relatively high concentration of minor and trace elements (Table II) which geochemically is different of the nearly pure metachert of other Mn deposits. The Li (30–3,000ppm) as trace element come from low Li content of the microscopic alkali pyroxenes and amphiboles, and Cr (100–210ppm) could be explained by the presence of microscopic Cr bearing ilmenite. The relatively high Ti content (80–1,500ppm) is directly correlated with the presence of a few ilmenite, rutile, and titanite. The ilmenite, when occur in the massive metachert, gives to it a faint banded. The

relatively high Ba content (60–900ppm) could be linked with the presence of the hyalophane. Low U and Th concentrations in MnB metachert are values comparable to those found in the other Mn ore deposits, which have been identified as submarine hydrothermal in origin. The source of low Zr and Hf (detrital elements, derived primary from nonmafic continental sources) contents as trace elements could be the sporadically zircon occurrence. The relatively high content of some trace elements (Li and Ba) of some samples, similar with that of Mn ore, shows their strong genetic link and common evolution. The relatively high Li content (3,000ppm) as trace element in (c)-metachert is due to the presence of microscopic magnesioriebeckite/ferrihoseite in its mineralogical composition, which could contain some amount of Li. The Rb as trace element has low contents, specifically in the minerals which contain Li-Na-K-amphiboles. The Rubidium is never major constituent in minerals, but its chemistry is similar to that of alkali metals.

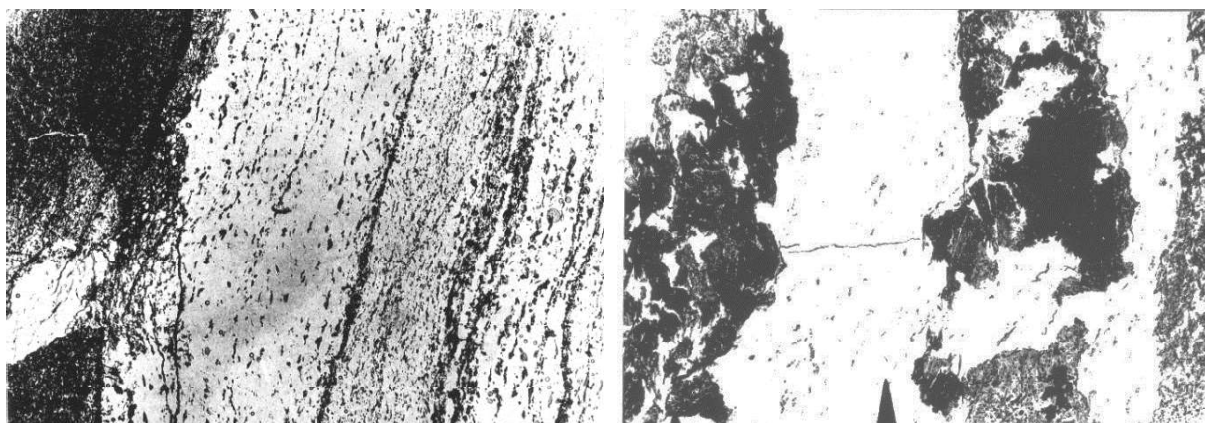


Fig. 1. Metachert-(c) with small alkali amphiboles (centre and right) banded with quartzite with large alkali pyroxenes and amphibole+magnetite+Ba-feldspars (black, left) (left); Metachert-(c) near pure (white) with small alkali amphiboles banded with large alkali amphibole+magnetite+albite+Ba-feldspars (right), photos of polished thin sections (PTSs), x5.

Table II

The trace elements in the metacherts type rocks (ppm)

Samples	Cr	Ti	Li	Rb	Sr	Y	Zr	Ba	Yb	Hf	Th	U
BSx	100	150	90	1.40	300	40	15	70	2.20	0.30	0.50	0.70
BS3	100	210	100	1.70	100	9	10	140	0.10	0.29	8.50	0.50
BS72	100	780	300	1.40	200	35	14	80	2.00	0.30	0.50	0.70
BS74	100	780	1,100	1.40	300	20	13	60	2.50	0.50	0.30	0.80
BOS151R	210	400	520	80	250	25	120	800	2.70	3.50	8.00	3.50
BUA	100	850	610	70	100	25	120	900	2.50	3.50	8.00	3.50
BOS77	260	1,150	950	1.90	30	8	9	140	0.70	0.20	1.35	1.10
BOS15	210	1,500	3,000	2.50	100	25	5	900	2.50	3.00	8.00	3.50
BAGS13	210	1,500	3,000	3.50	100	20	15	800	2.50	3.50	8.00	3.50
BAGS4	160	700	860	80	100	25	120	900	2.70	3.00	3.20	0.30
BAGS55	100	1,050	1,600	90	100	30	110	900	2.70	3.00	3.00	0.30
BA510R	100	390	370	90	100	25	100	800	2.50	3.00	3.00	0.30
BE(?)..25	100	320	160	80	100	25	100	800	2.30	3.00	3.00	0.30
BTM514	210	80	300	60	100	30	50	800	2.50	3.00	3.00	0.30
BVBorca4	100	160	230	50	100	25	50	900	2.50	3.00	3.00	0.30
BRsA	100	320	30	90	100	20	30	800	2.70	0.50	3.00	0.30
BMdx	100	180	95	80	100	20	30	800	2.70	0.50	3.00	0.30
BP56	210	110	300	70	100	20	30	800	2.70	0.50	8.00	3.00
BP33	210	3,000	320	70	100	20	30	800	2.70	0.50	8.00	0.30

Analysts: Veronica Alexe and Anca Uscătescu

The protolith of MnB metachert is represented by silica jaspis, resulting from submarine basic rocks alterations, or even by a flux of SiO_2 of hydrothermal origin. The massive and thin-bedded/banded metachert has high $\text{Fe}_2\text{O}_3/\text{FeO}$ ratio, indicating that silica was more rapidly precipitated under extreme oxidizing conditions, such as happened in subduction zone. This may be caused by such a nature of hydrothermal water, more oxidizing than the conditions of the sea bottom, gushing out from a submarine hot spring (Watanabe *et al.*, 1970).

2. THE QUARTZITE WITH LARGE ALKALI PYROXENES AND AMPHIBOLES TYPE

The quartzite with large alkali pyroxenes and amphiboles type rock are fine bedded/banded with the (c)-metachert (Figs. 2 left and right) and old carbonate ore, on the scale of a thin section and in hand samples. Inside bands of quartzite with large alkali pyroxenes and amphiboles occur the (c) metachert and pyroxmangite (Fig. 2 left) rich bands/lens. The minerals of this manganiferous lithology are: quartz, brown Mn-aegirine-augite, blue alkali Mn-Mg-riebeckite, yellow alkali Mg-Li-amphibole (ferrighoseite), microcline, albite, spessartine-almandine, magnetite, and hematite.

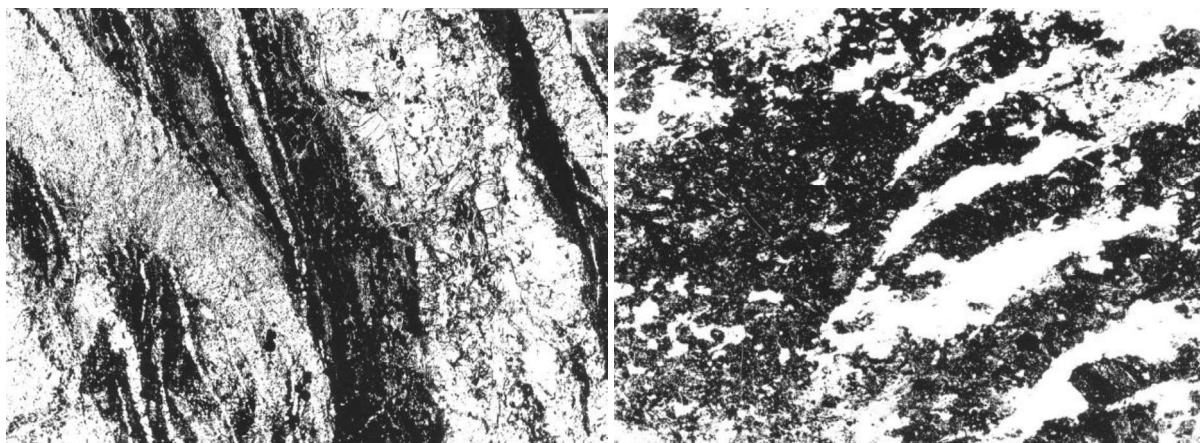


Fig. 2. Banded from left to right: metachert (c) with small magnesioriebeckite (grey in white quartz, bottom corner)/quartzite with large alkali pyroxenes and amphiboles (black), (c)-metachert with small magnesioriebeckite/quartzite with large alkali pyroxenes and amphiboles (black)/rich pyroxmangite (large grey band)/narrow band of quartzite with large alkali pyroxenes and amphiboles (black)/metachert- (c) with small magnesioriebeckite (right top corner) (left); Quartzite with large alkali pyroxenes and amphiboles (black) banded with (c)-metachert (white) (right), photos of PTSs, x5.

The forming conditions of this rock, $P > 9\text{Kb}$ and $T < 450^\circ\text{C}$, has been evaluated from experimental Jadeite /Glaucofane-Aegirine/Mg-riebeckite diagram (Wood, 1980) and from the Jd-Ae-Q diagram (Brown & Ghent, 1983), based on the jadeite component of aegirine, and that of glaucophane component of Mg-riebeckite. The paragenesis aegirine-magnesioriebeckite is newly formed on older one. The presence of fine microscopic exsolutions inside alkali pyroxene and amphibole, by cooling, indicates that they are formed at the expense of older homogenous chemically minerals of higher T and P. It can suggest that this old initial paragenesis was hedenbergite/ omphacite/ johannsenite/jadeite pyroxene+ magnesiocummingtonite/glaucophane amphibole. The protolith of the quartzite with alkali pyroxenes and and amphiboles was probable a mafic gabbroic/ basaltic rocks. Its high quartz content could be due to the presence of jaspis.

The relatively high Ba content as trace element (500–3,200ppm) (Table III) is explained by the presence of hyalophane, which was identified in thin sections and by X-ray analyses. Low concentrations of Cu (0–250), Pb (0–80), Co (10–105), Zn (0–210), Ni (50–380), and Yb (0–10ppm)

are characteristic of hydrothermal manganese deposits that are forming on the present sea floor (Toth, 1980). The Li content exceeds the value as trace element, being a constituent in the chemical composition of Li-Na-K alkali amphiboles of these rocks. Also, the aegirine of this association could have a few Li content.

Table III

The trace elements of quartzite with large alkali pyroxenes and amphiboles type bands (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Yb
BOS37	400	–	40	5	10	100	60	150	–	2	–	70	70	2	–
BT339x	–	1,000	40	3	5	–	–	160	–	2	–	70	60	2	–
BT1002Px	100	700	10	5	5	20	40	180	–	2	–	–	60	3	–
BTdS5	50	–	10	1	10	–	50	70	–	–	–	–	10	2	–
BT268x	170	–	50	4	80	3,200	30	190	10	2	–	80	55	3	–
BT258x	–	800	30	3	10	–	40	150	–	2	–	40	45	2	–
BT339	60	500	30	5	15	–	–	140	–	2	–	50	55	10	–
BS3	–	–	7	250	3	–	30	60	–	4	30	20	15	2	5
BTD3	–	1,000	5	10	4	30	60	100	–	–	–	20	25	5	–
BT1500	120	500	10	10	2	–	–	120	–	5	30	150	60	2	10
BS101	–	–	15	28	90	–	65	90	–	7.5	11	210	25	–	–
BTD9	–	3,100	–	6.5	–	–	125	50	–	–	–	–	105	10	2
BTD1	–	3,200	–	6.5	–	–	115	150	–	–	–	–	47	40	4
BAG39C	–	–	15	60	–	–	170	380	–	5	–	170	200	–	–

Analyst Mihai Popescu

3. THE RHODOCHROSITE TYPE ORE.

The main constituent of manganese ore is the old rhodochrosite with small FeO content ($\approx 5\%$ wt) and lower MgO content ($\approx 0.6\text{--}1\%$). It was described before as old name “ponite” (Buțureanu, 1911). The old large rhodochrosite bands host/alternate with jacobsonite, tephroite, Mn-humites, and ferriferous tephroite bands. It forms fine grained, compact, grey or brown masses. The experimental data showed that the stability field of rhodochrosite at high X_{CO_2} shifts to higher T and lower f_{O_2} . The graphite absence indicates for the rhodochrosite the lowest possible boundary of $f_{\text{O}_2} = 10^{-30}\text{--}10^{-28}$. Increasing of FeCO_3 component of old rhodochrosite, widens the solvus and raises it upper T limit to some extent. The effects of FeCO_3 on the solvus are the same as MgCO_3 are at low concentrations (Goldsmith & Graf, 1960). The old rhodochrosite represents probably the original composition which survived during metamorphism. It is known that the rhodochrosite is ubiquitous up to amphibolites facies, however it does not survive in granulite facies. The concentrations of the trace elements in the old rhodochrosite (Table IV) are very low: Cu=2–130ppm, Ni=30–60ppm, and Mo=2.5–7.5. The Ba, Pb, Sb, Cr, Bi, V, Zn, Co, Ga, Yb, and Li have been not detected in these few analysed samples.

Table IV

The trace elements in rhodochrosite type ore (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BCPS14	–	–	31	41	–	–	–	60	–	7.5	–	–	–	–	–	–
BMD30	–	–	–	13	–	–	–	30	–	2.5	–	–	–	–	–	–
BP59	–	–	–	2	–	–	–	30	–	4.4	–	–	–	–	–	–
BAG41B	–	–	150	130	–	–	–	50	–	5.5	–	–	–	–	–	–
BAG538	105	–	370	60	–	–	–	34	–	4.6	–	–	–	–	–	–

Analyst: Mihai Popescu

4. TEPHROITE TYPE ORE

The oldest silicate minerals are Mn-olivines (tephroite, ferroan tephroite, and ferroan rich tephroite) of silica-undersaturated ore and the spessartine of silica-saturated type rocks. No direct contact between the undersaturated tephroite type ore and saturated spessartine rock type: between them always exists a band of fibrous rhodonite (Fig. 3 right). The absence of quartz in the tephroite association rules out the existence of a medium greenschists facies of its formation. The MnB tephroite near-end member composition was formed under anhydrous conditions, where only CO₂ is present in fluid. Its temperature formation is in acord with experimental data at 580±10⁰C (Peters *et al.*, 1973). Considering that P was much higher in the MnB tephroite ore than in experiment, then the equilibrium T was more higher. The mineral reactions of decarbonation type took place at high T when X_{CO2} is high in metamorphic fluid (Peters *et al.*, 1973). The f_{O2} for jacobsite association (jacobsite/Mn-humites/rhodochrosite/tephroite/jacobsite/kellyite) is situated into a large stability field between 10⁻²⁵–10⁻²², and the presence of tephroite indicates upper boundary of 10⁻¹⁵ (Essene & Peacor, 1983).

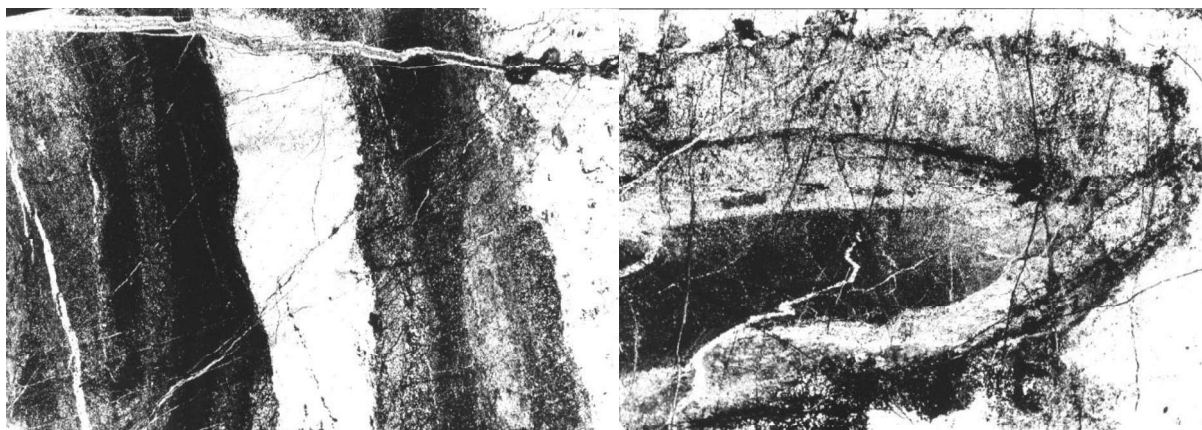


Fig. 3. Tephroite (large, grey, grains, left) banded with small tephroite+jacobsite (dark grey, black) and with Mn-humites (white) (left); Tephroite (large gray white outside) banded around small jacobsite-tephroite grains (black, centre (right)). Photos of PTSs, x5.

Table V

The trace elements in the tephroite type ore (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BS27	–	–	90	12	–	–	–	65	–	43	–	–	13	2	–	–
BOS43	420	–	400	80	75	–	–	95	–	60	–	–	23	2	–	–
BOS42	–	–	135	18	–	–	–	75	–	50	–	260	23	3	–	–
BS59	–	–	190	12	–	–	–	95	–	43	–	–	16	2	–	–
BS11	420	–	90	40	65	–	–	95	–	43	–	260	17	–	–	–
BAGS58	2,000	–	340	40	–	–	–	210	–	43	–	–	60	2	–	–
BOr8	600	–	135	11	250	–	–	140	–	60	–	270	34	–	–	–
BS23	–	–	240	40	170	–	–	140	–	50	–	270	25	2	–	–
BSGS	–	–	135	30	–	–	–	140	–	65	–	–	50	3	–	–
BP56	–	–	140	80	65	–	–	95	–	60	–	–	35	2	–	–
BS28	–	–	240	40	65	–	–	95	–	65	–	–	35	2	–	–

Analyst: Mihai Popescu

The near end member composition tephroite is banded with Mn-humites (Fig. 3 left). The band of small tephroite+jacobsite grains are banded with large tephroite grains (Figs. 3 left and right). In Fig. 3 left

the large tephroite, small tephroite, and Mn-humites are banded. The layers/bands range in width from about 2–5mm (the scale of a thin section) to more cm/dm on the field. The high bulk concentration of As in some samples (Table V) may indicate the presence of cobaltite (CoAsS) as accessory phase which was identified optically and with microprobe. The relatively high B in all tephroite samples is linked with the accidental presence of some borates (homilite, manganaxinite). Low concentration of Co, Ni, Cu, and Zn are characteristic of hydrothermal Mn deposits that contain 34–52 wt % Mn and that are forming on the present sea floor (Toth, 1980). In the tephroite type ore no Ba, Sb, Cr, Bi, V, and Li as minor elements were detected. The protolith of Mn rich tephroite ore has high Mn/Fe with low concentrations of Ca, Al, Ti, Co, Ni, Cu, Th and REE (Huebner *et al.*, 1992). The low Al of tephroite ore type is reflected by the absence of spessartine, and low Ca by the absence of rhodonite in its association.

5. MN-HUMITES/JACOBSITE/ALABANDITE/RHODOCHROSITE TYPE ORE

The terms of manganese humites are sonolite, alleghanyite, manganhumite, jerrygibbsite, ribbeite, and leucophoenicite. Alleghanyite is fine-scale banding with jacobsite+alabandite (Fig. 6 left) and sonolite is banded with tephroite (Fig. 6 right). The manganese humites contain the highest Mn, amongst the manganese silicates. The domain of stability of Mn humites, strongly undersaturated and hydroxylate, depends on $a_{\text{H}_2\text{O}}$, a_{SiO_2} , and the ratio $X_{\text{CO}_2}/X_{\text{H}_2\text{O}}$ (Winter *et al.*, 1983). The manganese humites were formed by metamorphic reactions of hydration and decarbonation with rhodochrosite consumption and formation of richer Mn terms with CO_2 liberation (Winter *et al.*, 1983). The f_{O_2} and f_{S_2} for alabandite association have been determined with Fukuoka diagram (Fukuoka, 1981), that shows for $\log f_{\text{O}_2}$ a value of -17/-20 (near QFM buffer) and for f_{S_2} a value of about -5/-2, at $T > 500^\circ\text{C}$. According low ratio $f_{\text{O}_2}/f_{\text{S}_2}$ the alabandite protolith comes from an oxygen poor and sulphur rich protolith, also rich in rhodochrosite and poor in Mn-oxides. The Mn-humites, jacobsite and alabandite assemblage has fine-scale laminations (Figs. 6 left and right). The bands are both continuous and discontinuous. The jacobsite may have formed from an Fe-Mn protolith that was deposited with carbonaceous sediments. The alabandite, and other Co sulfides (cattierite, carollite, cobaltite, glaucodote, and linnaeite) as accessory, were deposited in the the same time with the old rhodochrosite. The alabandite associated to Mn-humites has pure composition, and when it is associated to tephroite and jacobsite has low Fe content (2–5mol% FeS). There is positive correlations between compositions of coexisting minerals indicating that they were into a chemical equilibrium.

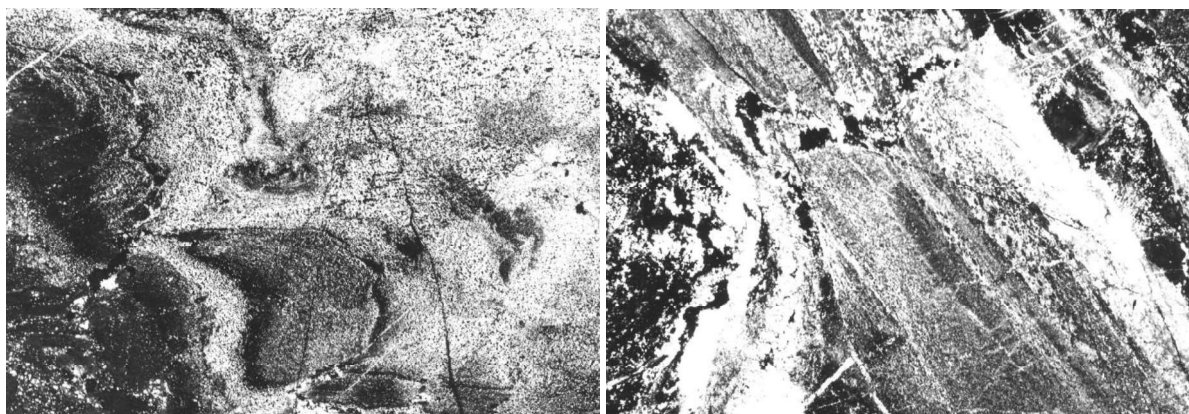


Fig. 6. Banded jacobsite (small, black), alabandite (large, black), and rhodochrosite+alleghanyite (white, grey) (left); Banded sonolite+rhodochrosite (white)/jacobsite (small black)+tephroite (small grey)/alabandite (large, black), all cut by late alabandite (large black grains), photos of polished thin sections, x5.

Table VI

The trace elements in Mn-humites/alabandite type ore (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BA508	1,000	5,000	500	3.3	–	–	–	50	–	50	–	–	20	3	–	–
BOS64	850	–	500	3.3	–	–	–	75	–	43	–	–	23	–	–	–
BA600	–	–	280	3.3	–	–	–	110	–	36	–	–	25	–	–	–
BA15	550	3,800	550	3.3	–	–	–	110	–	140	–	–	43	10	–	–
BA501	–	–	280	4	–	–	–	110	–	95	–	–	32	–	–	–
BP69	–	1,200	35	14	–	–	–	75	–	60	–	–	21	2	–	–

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The common occurrences of alabandite, cobaltite, and cattierite require a reduced and sulfidizing local metamorphic environment. Their protolith was S rich and oxygen poor. The trace element data of Mn-humites type ore are listed in Table VI. The As could be linked to presence of accessory cobaltite (CoAsS) and cattierite (CoS₂). High Ba is explained by the accidentally presence of barite, determined by electron microprobe analysis, as very little grains in the manganese humite association. The B as trace element in the Mn-humites band is linked with some sporadically presence of borates. The low concentrations of Cu, Co, Zn, Ni, and Yb are characteristic of hydrothermal Mn deposits that contain to 34–51%wt Mn and that are forming on the present sea floor (Toth, 1980). A possible precursor of Mn-humites could be Mn-rich silicate gageite [Mn₅Si₂O_{9-x}(OH)_{2x}] (Huebner *et al*, 1992). In the sample of Buckeye Mn deposit, the authors established a fair correlation between abundance of gageite and W concentration, suggesting that significant W in Mn-rich silicate layers may indicate a gageite precursor. In the Mn-humite type ore of Manganese Belt the hübnerite (MnWO₄) has been determined microscopically and confirmed by X-ray diffraction and electron microprobe analyses.

6. SPESSARTINE MANGANIFEROUS LITHOLOGY TYPE

The old spessartine is associated with quartz in gondite type, which are saturated in silica rocks. The gondite type of MnB is totally subordinated to the quelusite, which is undersaturated and constituted mostly of carbonate/silicate ore (olivines, johannsenite, manganese humites, rhodonites, and rhodochrosite). The old spessartine is contemporaneous with tephroite, being the oldest minerals. The association spessartine /quartz/mangancummingtonite/old rhodochrosite/apatite has an equilibrium relation with tephroite reduced association. The spessartine rich lens are banded with (b)-metachert (Fig. 7 left), mangancummingtonite, quartzite with alkali pyroxenes and amphiboles, and pyroxmangite type rocks (Fig. 7 right). The banding can be seen in hand samples and in thin sections (when the lamination is fine). The boundaries between adjacent bands are distinct. The dimensions of spessartine-rich lens/bands have big variation, between microscopic to a few dm in size. The small bands of old spessartine are both continuous or discontinuous on the scale of thin section, especially when they are enclosed in carbonate ore.

The garnets of deposits belong to four major varieties: old spessartine, calderite-rich spessartine, manganoan grossularite, and anisotropic spessartine-andradite-grossularite/noncubic garnets, all having a big variations of their compositions. Garnets of compositions intermediate between spessartine and andradite („spandite”) and between spessartine and grossularite varieties are common in the ore. The changes in oxygen fugacities in different areas produced local variations in mineralogy and mineral composition-mainly in garnets. The old primary spessartine is associated with abundance quartz in gondite type ore. A few mangancummingtonite, Fe rich-rhodochrosite, and graphite are the associated minerals to spessartine band. In this association the spessartine has a composition near end-member. The spessartine associated with mangancummingtonite has some Mn substituted by Fe.

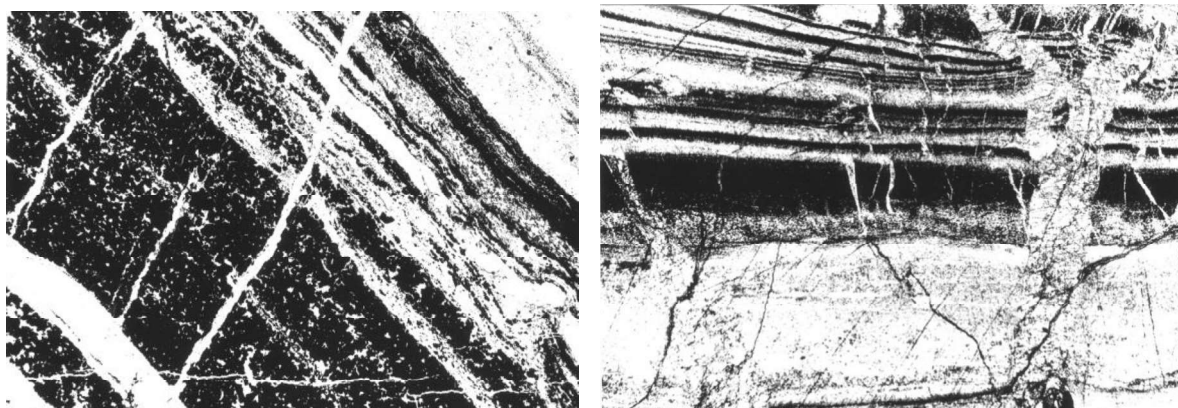


Fig. 7. Old small spessartine grain mass (large, black, centre) banded with narrow (b)-metachert with very rare small alkali pyroxene and amphiboles (grey, white grey), and with narrow pure metachert (white) (left); Banded old spessartine (black mass), mangancummingtonite (narrow bands, dark grey), pyroxmangite large band (bottom, light grey), all cut by new pyroxmangite vein, photos of PTSs, x5.

The small grains (0.02mm) of Fe rich-spessartine/Mn almandine occur in metachert, alongside with hematite and magnetite. In the associations where spessartine coexists with pyrophanite, there is a good correlation between the Fe content of pyrophanite and that of spessartine. In the oxidate quartzite with large alkali pyroxenes and amphiboles the spessartine has a small calderite compound. The new spessartine-andradite/noncubic garnets are typically to oxidate associations and the new spessartine-grossularite occurs in johannsenite-ferrohodonite association. There is a good correlation of chemical compositions of garnets with coexisting minerals. The four garnet varieties are a sensitive factor of the metamorphism conditions (P, T, f_{CO_2} , f_{O_2}) of ores/rocks. At high f_{O_2} occurs spessartine-andradite, at low f_{O_2} occurs the pure spessartine. The spessartine-grossularite occurs in the high Ca of manganese silicate (johannsenite-ferrohodonite-grossularite). In addition to Al, the Ti, Zr, Hf, Ta, Th, and Y from some marine manganese deposits have been identified as detrial in origin, derived from a nonmetalliferous, nonmafic continental source (Flohr and Huebner, 1992). The Al content of spessartine varies (16.32–17.26% wt). The Ti content of spessartines, determined by electron microprobe, has low proportions (0–0.15%wt). The Cr as trace element in some spessartines (Table VII)

Table VII

The trace elements in spessartine rich type lithology (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BCPS32	–	–	190	250	–	–	–	260	–	160	–	750	165	–	–	2
BAGC39	–	–	110	11	–	–	–	95	–	30	–	–	85	–	–	1
BMD41	–	–	85	7	–	–	–	65	–	30	–	–	34	3	–	2
BMD40	–	–	80	3.3	–	–	–	65	–	38	–	–	30	2	–	2
BT422	–	–	80	18	–	–	135	210	–	22	–	210	100	2	–	–
BAGS63A	–	–	85	26	–	–	–	110	–	20	–	–	60	3	–	–
BAGS44	1,500	–	110	7	–	–	–	170	–	32	–	210	120	2	–	–
BAGS63B	550	–	75	7	–	–	–	170	–	28	55	320	165	30	–	–
BRS17	–	–	55	7	–	–	–	95	–	30	–	210	50	2	–	–
BAGS5	–	–	38	250	–	–	–	95	–	17	–	550	120	35	–	3
???	–	–	55	250	–	–	–	50	–	24	–	260	50	–	–	3
BS91	–	–	125	12	–	–	–	65	–	36	–	190	19	–	–	–
BP92	–	9,500	110	12	–	–	–	110	–	43	–	190	43	3	–	–
BP91	–	3,200	105	250	–	–	–	75	–	50	–	240	43	2	–	–

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is due to its presence in their composition as constituent oxide (0.0–0.8wt %). The Zr, Hf, Ta, Th and Y were not determined. The protolith of the spessartine-rich rocks was a Ca-Mn rich carbonate mixed with significant amounts of siliceous and aluminous detritus. The compositions of garnets of MnB are good indices of variations in oxygen fugacities. The presence of Al rich garnets could be explained by the deposition of detrital material at the same time with the manganese hydrothermal components. The garnet rich bands represent period of greater influx of detritus or a decrease in the influx of hydrothermal material. In the same time, other Mn-silicates like tephroite, pyroxmangite, rhodonite, and mangancummingtonite rich bands would be formed by admixture of siliceous material either volcanic ash or biogenic detritus within carbonate layers, or also the aforementioned silicates have been formed in the reaction zone between premetamorphic carbonates and quartz layers (Flohr, 1992).

7. RHODONITE RICH BAND TYPE ORE.

The two pyroxenoids, rhodonite and pyroxmangite, of the MnB never appear associated. The rhodonite type ore is banded with manganese humites and tephroite in undersaturated associations, while pyroxmangite type ore is banded with spessartine, mangancummingtonite, and Mn-magnetite in saturated associations. The boundaries between adjacent bands layers are distinct in both hand samples and in thin sections (Figs. 8 left and right). The two bands, rich tephroite and rich rhodonite, have had different premetamorphic bulk composition: tephroite bands with relatively high Mn and low silice, and rhodonite bands with more silice and Ca rich. The rhodonite rich-bands situated between tephroite and metachert bands (Fig. 8 right) could be formed by the reaction $\text{SiO}_2 + \text{MnCO}_3 = \text{MnSiO}_3 + \text{CO}_2$ (Flohr and Huebner, 1992), or by the reaction $\text{Mn}_2\text{SiO}_4 + \text{CO}_2 = \text{MnSiO}_3 + \text{MnCO}_3$ (Peters *et al.*, 1973). The trace elements of rhodonite rich bands can be seen in Table VIII. The As content in some samples indicates the presence of cobaltite and other arsenides as well as the presence of some phyllosilicates with As (shallerite and nelenite). The Co concentrations could be correlated with the presence of cattietrite. Low concentrations of Cu (7–40ppm), Ni (36–360ppm), and Co (43–165ppm) are characteristic of rich manganese hydrothermal deposits that are forming on the present sea floor (Cann *et al.*, 1977; Toth, 1980). The rich rhodonite bands have not Sb, Cr, Bi, V, Ga, and Li. The detrital elements Ti, Zr, Hf, Ta, Th, and Y have been derived primarily from a nonmafic, nonmetalliferous continental source, have been not detected.

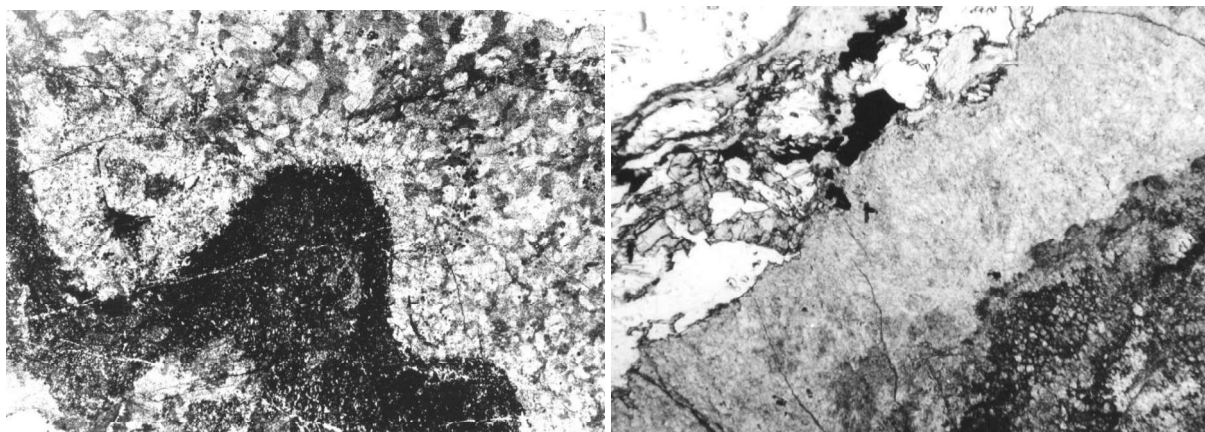


Fig. 8. Banded rhodonite (large, grey, fibrous, top) with small folded tephroite grains (dark grey, black, centre), and with large tephroite grey grains left corner, bottom), (left); banded rhodonite (light grey, centre), tephroite (large, dark grey, right bottom corner), and (d) metachert with spessartine and mangancummingtonite (left top corner), Photos of PTSs.

Table VIII

The trace elements in rhodonite type ore (ppm).

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BCP102	240	–	95	11	–	–	–	360	–	80	–	260	165	–	–	–
BTM420	–	–	90	12	–	–	–	170	–	50	–	300	85	–	–	–
BAGS77	–	3,200	190	7	–	–	–	170	–	50	–	–	120	–	–	–
BOS105	240	–	110	18	–	–	–	140	–	36	–	260	100	–	–	–
BCP99/14	175	–	180	18	–	–	–	140	–	50	–	260	50	–	–	–
BOS42A	–	–	190	40	–	–	–	170	–	43	–	180	85	–	–	8
BAGS61	–	–	110	18	–	–	–	360	–	105	–	–	170	–	–	–
BAGS46	–	–	135	8.5	–	–	–	210	–	60	–	220	170	–	–	–
BA525	–	–	135	8.5	–	–	–	310	–	50	–	220	120	–	–	–
BT2009	–	–	135	7	–	–	–	170	–	50	–	220	140	–	–	–
BOS422R	–	2,300	55	11	39	–	–	170	–	18	–	350	36	–	–	–
BOR56	–	–	160	26	–	–	–	36	–	32	–	440	43	–	–	–
BOS424	–	–	195	12	26	–	–	75	–	50	–	220	140	–	–	–

Analyst: Mihai Popescu

8. PYROXMANGITE-RICH BAND TYPE ORE

The old primary pyroxmangite type ore, which is silica-undersaturated, is banded with old spessartine and old mangancumingtonit rich type ore/rocks, which are saturated in silica. The old Fe-rhodochrosite, Mn-rich magnetite, and new mangancumingtonite (grown on pyroxmangite) are the associated minerals to pyroxmangite. The stability of pyroxmangite strongly depends by X_{CO_2} at low T. It has been formed from rhodochrosite+quartz protolith at relatively low T and relatively high P, conform the experimental data (Candia *et al.*, 1975). At high a_{H_2O} it is substituted by new mangancumingtonite.

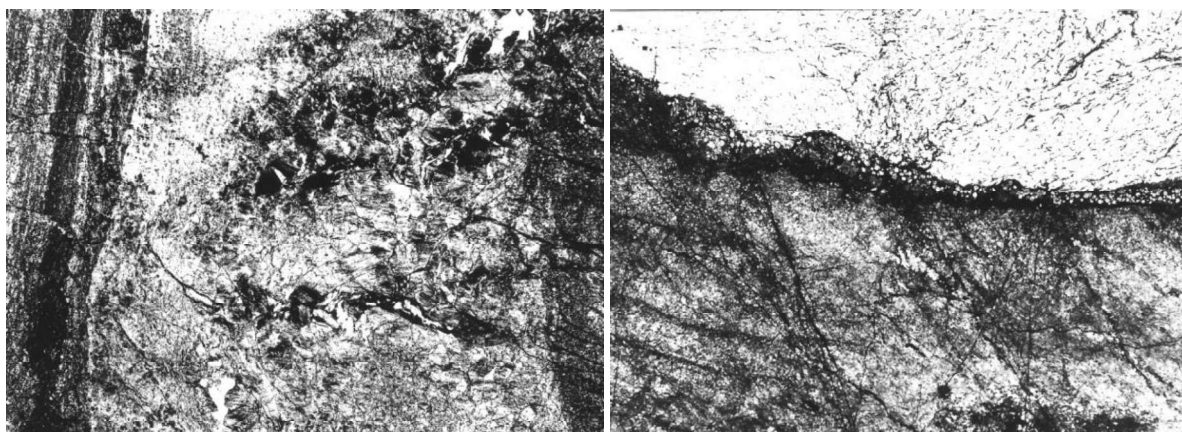


Fig. 9. Pyroxmangite rich band (grey, large grains, centre) between two spessartine bands (dark grey, black) (left); Banded pyroxmangite (large, dark grey, bottom), white (b)-metachert (with small stilplomelane), and narrow anisotropic new white rounded garnets band (grown on old black spessartine) between them. Photos of PTSS.

The As concentration (0–550ppm) (Table IX) as trace element in pyroxmangite type rocks could be explained by its association with some secondary minerals that have As in their compositions (nelenite, shallerite, and various arsenates). The Ba could come from bannisterite which occurs sometimes in pyroxmangite band as little vein, and that has barite along its cleavage. The following trace elements Sb, Cr, Bi, Ga, Co, Ga, Li, and Yb were not detected in pyroxmangite type bands.

Table IX

The trace elements in pyroxmangite type ore (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BP70	–	–	135	250	–	–	–	65	–	36	–	–	17.5	–	–	–
BAGS36	–	1,200	46	1.8	–	–	–	65	–	15	–	160	43	–	–	2
BT225b	350	–	55	2.7	–	–	–	24	–	140	–	750	43	–	–	–
BORS	–	–	110	8	–	–	–	24	–	25	–	300	–	–	–	–
BAGS3	550	–	75	1.1	55	–	–	140	–	14	–	220	60	–	–	–
BAGS35	240	–	40	1.1	–	–	–	65	–	12	55	170	60	–	–	3
BCPS48	300	–	280	7	–	–	–	50	–	21	–	–	60	–	–	–
BMD40	–	–	65	4.9	–	–	–	24	–	21	–	–	13	–	–	–
BDS8	–	–	55	4	–	–	–	32	–	19	–	210	50	–	–	–
BAG52	–	–	105	1.8	–	–	–	20	–	13.5	–	210	22	–	–	–

Analyst: Mihai Popescu

9. MANGANCUMMINGTONITE TYPE ORE/ROCK

The MnB amphiboles belong to four groups/many generations: a. The old Fe-Mn-Mg amphiboles: grünerite, mangangrünerite, mangancummingtonite and cummingtonite; b. Calcic amphiboles: Mn tremolite and Mn actinolite; c. Sodo-calcic amphiboles: winchite, ferriwinchite and Mn richterite; d. Na/K/Li amphiboles: kōzulite, riebeckite, Mn-riebeckite, ferrighoseite and magnesioriebeckite. The relations between these amphiboles observed under the microscope, led to the assumption that there are some hydration reactions which have consumed the Fe-Mg amphiboles, thus producing manganian Na/K, K, Li and Na-Ca amphiboles. The compositional zonations of amphiboles with the cummingtonite core and magnesioriebeckite margins reflect the radical changes in their chemical composition, caused by changes of the f_{O_2} , and the ratio a_{Na}/a_{H^+} , at constant P and T. However, the riebeckite/magnesioriebeckite can be retromorphically formed on cummingtonite, if there is Na available, and the ferrighoseite can be formed on cummingtonite, if there is the Li available. The intermediary terms between mangancummingtonite-magnesioriebeckite and cummingtonite-ferrighoseite occur frequently. Based on the mangancummingtonite stability curve determined experimentally (Dasgupta *et al*, 1985, 1988), the substitution of pyroxmangite by mangancummingtonite/coexisting of pyroxmanite with mangancummingtonite occurs at $T=550-600^{\circ}C$ and $P=6Kb$ (amphibolite facies). In this substitution Mn-rich mineral, pyroxmangite, is substituted by Mn-poor mineral, newly forming Mn-cummingtonite. The mangancummingtonite rich-layers are banded with (b)-metachert, rich pyroxmangite, and rich spessartine bands (Figs. 10 left and right). The rich bands of mangancummingtonite are poor in trace elements (Table X). The Ba is linked by rare presence of kinoshitalite. The low trace element concentrations are consistent with a hydrothermal source. The mangancummingtonite bands most probably have been formed in the reaction zones between quartz and carbonate, from an admixture of more siliceous material and less carbonate layers protoliths.

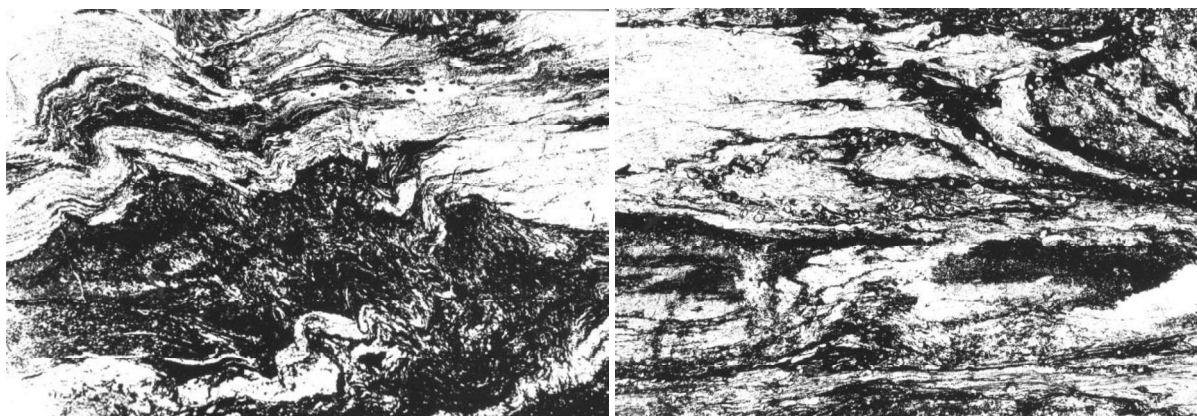


Fig.10. Folded old mangancummingtonite (grey, white grey), spessartine (black, compact), and quartz (white) (left); Mangancummingtonite (large white grey prisms), old spessartine (black), new anisotropic spessartine (small white rounded grains) grown on the old one, and quartz (white) (right), Photos of PTSs, x5.

Table X

The trace elements in mangancummingtonite type ore (ppm).

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BSS4	–	–	17	4	2	–	–	75	–	4	–	60	2	2	–	4
BAGS12	–	–	10	8	2	–	–	200	–	4	25	60	60	8	–	4
BAGS9	–	600	5	10	2	–	–	210	–	5	5	65	85	3	–	5
BA61	–	–	5	3	2	–	–	80	–	2	4	60	2	2	–	3
BTdS5	–	–	10	5	2	–	–	85	–	2	3	40	2	2	–	4
BMD21	110	–	5	5	–	–	–	110	–	2	60	30	100	4	–	3
BOS94	–	–	5	350	7	–	40	100	–	8	80	35	80	2	–	10
BMD49	–	–	20	540	5	–	30	70	–	3	4	25	20	2	–	3
BOS77	–	1,600	10	400	2	–	30	75	–	6	70	20	20	3	–	7

Analyst: Mihai Popescu

10. NAMBULITE, NATRONAMBULITE, AND LI-ALKALI AMPHIBOLE/BAND/TYPE ORE

This type ore contains the oxidate association which occurs as small lenses/bands inside Mn-ore, near/inside of rhodonite type bands. These rare minerals of the pyroxenoids group, nambulite and natronambulite, were determined in MnB for the first time in România (Hirtopanu and Scott, 1999). The nambulite and natronambulite are associated with aegirine, ferrigoseite, albite, braunite, magnetite, hausmannite (Fig. 11 left), kutnohorite, hematite, hematophanite, Ba-feldspars, microcline, and quartz. Under the microscope have not observed the substitution of rhodonite by nambulite. The nambulite is substituted by ferrigoseite, such it happens with the substitution of aegirine-augite by magnesianiebeckite in the quartzite with large alkali pyroxenes and amphiboles. There is a strong affinity of nambulite to aegirine (Fig. 11 right). The nambulite association could have the same protolith such has the (c)-metachert with small alkali pyroxenes and amphiboles (which also has Li as constituent of its alkali Na-K-Mg-Fe³⁺-amphiboles), and with quartzite with large alkali pyroxenes and amphiboles. The Na-pyroxene, an important constituent of this association belongs to aegirine-augite, with great compositional variations, reflected by the frequently marginal and sectorial zonations. The nambulite/natronambulite/ aegirine/ferrigoseite/hausmannite/albite oxidated association was formed at the same time with quartzite with large alkali pyroxenes and amphiboles, and with (c)-metachert but under more higher f_{O_2} conditions.

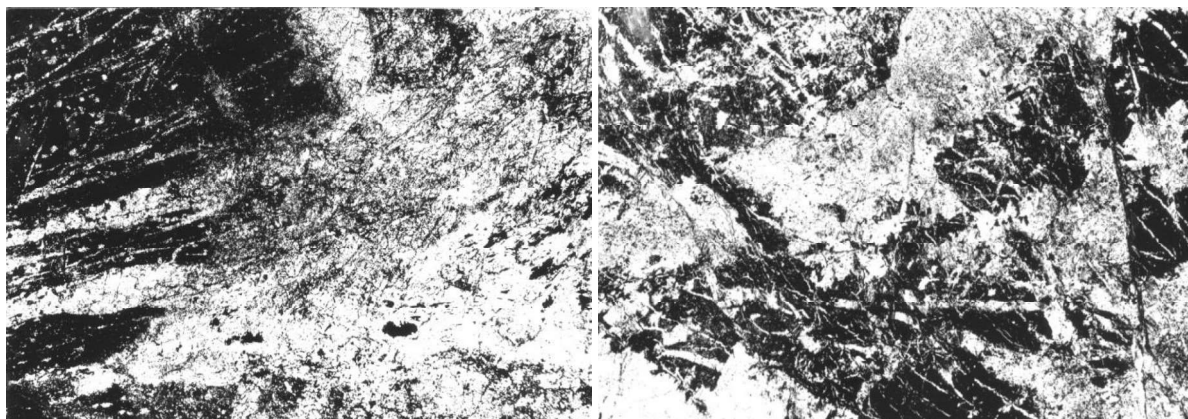


Fig. 11. Nambulite (large, white grey), Mn-aegirin (black), and Ba-feldspars (white, left corner, bottom) (left); Hausmannite (large, black), nambulite (large, grey white), and Ba-feldspars (white), photos of PTS x5.

The three lithologies types are also contemporaneous with Mn ore types that were formed under reduction conditions, therefore from different protolith and oxidizing conditions. The primary minerals, Mn silicates and Mn oxides of the manganese ore were formed at a high range of oxygen fugacities. The f_{O_2} varied within different parts of the Mn-ore, just within a small area. The varying oxygen fugacities were not externally imposed, but were internally inherited (Sivaprakash, 1980), and the mobility of oxygen was restricted during metamorphism. Internally inherited variations f_{O_2} have produced local variations in primary mineralogy and mineral compositions. Strong internally buffering of f_{O_2} by mineral reactions during prograde metamorphism produced such diverse assemblages in closely spaced units. The hausmannite is nearly pure Mn_3O_4 and the braunite is a neltnerite variety. In the bixbyite-braunite association the Fe^{3+} is incorporated in bixbyite and the stability field of braunite extends inside stability field of hausmannite (Sivaprakash, 1980). The natural association with nambulite and natronambulite lowers the f_{O_2} , because these two minerals are unable to host the Fe^{3+} . The trace element concentrations can be seen in Table XI. High Ba (500–3,200ppm) is explained by the presence of hyalophane. The Ni concentrations (105–550ppm) belong to Ni-norrishite. Very low Pb, Cr, Co, Cu, Zn and Ga, and no Bi, V, and Yb, are also characteristic of hydrothermal high Mn-deposits (Toth, 1980).

Table XI

The trace elements in Nambulite and natronambulite type ore (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Yb
BT1002Nb	50	2,700	15	60	–	–	–	180	–	5	–	140	34	2	–
BT1002A	160	600	15	380	–	–	–	380	–	5	–	270	200	5	–
BT1002x	105	300	10.5	380	55	120	–	260	–	2	–	400	105	10	–
BT224	–	2,400	5	41	–	–	55	105	–	2	–	410	40	2	–
BT262a	105	1,100	12.5	380	–	–	–	550	–	2	–	420	105	30	–
BT1002C	105	3,400	31	60	–	1,100	55	180	–	7.5	–	440	75	2	–
BT268N	160	3,800	44	16	–	1,600	55	180	–	7.5	–	180	34	2	–
BT2007	–	1,200	10.5	130	–	–	–	130	–	3.9	–	510	65	2	–
BT1002AE	300	–	125	380	38	120	–	550	–	1.5	–	310	65	40	–

Anlyst: Mihai Popescu

The possible precursors of Li bearing minerals were probable the todorokite and buserite, typically manganese hydrothermal minerals, whose crystal tunnel structure hosts Li, Ba, and Mg. Both minerals occur in the modern submarine hydrothermal manganese deposits (Cann *et al.*, 1977). The more oxidized conditions in this band are originated in some local domains that behaved as closed

systems with respect to f_{O_2} , being internally banded through the silicate-carbonate lens, which are formed in reducing conditions. The Li_2O content of nambulite of 3.56wt% and Na_2O content of 0.83 wt %, and that of natronambulite of 1.34 wt% Li_2O and 3.11 wt % Na_2O , respectively, were determined by Absorbtion Atomic Spectroscopy (AAS).

11. PYROSMALITE TYPE ORE

A rare group of Mn-phyllsilicates with Cl, the pyrosmalites, comprise a solid solution of the Fe rich end term, pyrosmalite, and the Mn rich end term, manganpyrosmalite. The presence of pyrosmalites preferentially incorporating Cl in their structure indicates a fluid with high salinity from which they were formed. The phyllosilicates with As, schallerite and nelenite, also occur in this associations. The exclusive occurrence of pyrosmalites only in the Manganese and Sulfide deposits of Manganese Belt and Sulfide Belt, respectively, is evidence of the origin of Cl deep within these deposits in the original hydrothermal submarine solutions. A special composition of bulk rock, high Cl activity and low oxygen fugacity are needed for the pyrosmalites formation (Watanabe *et al.*, 1981). Apparently, the manganpyrosmalite are retrograde phases, being formed through the substitution of the older anhydrous manganese minerals such as tephroite (Fig. 12 left) and pyroxmangite (Fig. 12 right). The replacement of the pyrosmalite by amphibole (Kazachenko *et al.*, 1979) is evidence for its forming prior to deposition of the main ore bulk. (Vaughan, 1986) suggests that the manganpyrosmalites have a prograde metamorphic origin, from metalliferous brines, rather than a retrogressive breakdown of anhydrous Fe-Mn silicates in areas locally enriched in water and Cl in the later stage. The initial Cl-enrichment in the old host lithologies may have occurred during seafloor hydrothermal alteration as an integral part of the syngenetic ore-forming processes for the associated base-metal mineralization (Vaughan, 1986). Therefore, the pyrosmalites /manganpyrosmalites could be formed in Manganese Belt at the beginning, as old minerals, coexisting with tephroite/pyroxmangite along metamorphic history through the metamorphism of some forms of primitive Cl-bearing metalliferous brines Mn-Fe rich gel or clay precursors. In view of currently accepted ideas the pyrosmalite bands of manganese deposits of MnB and SB may reflect an original layering rather than a replacement texture.

Very low B, Cu, Pb, Sb, Cr, Ni, and Co, and no As, Ba, Sb, Bi, V, Li, and Yb (Table XII) trace element concentrations of pyrosmalite rich bands are characteristic of hydrothermal high Mn deposits.

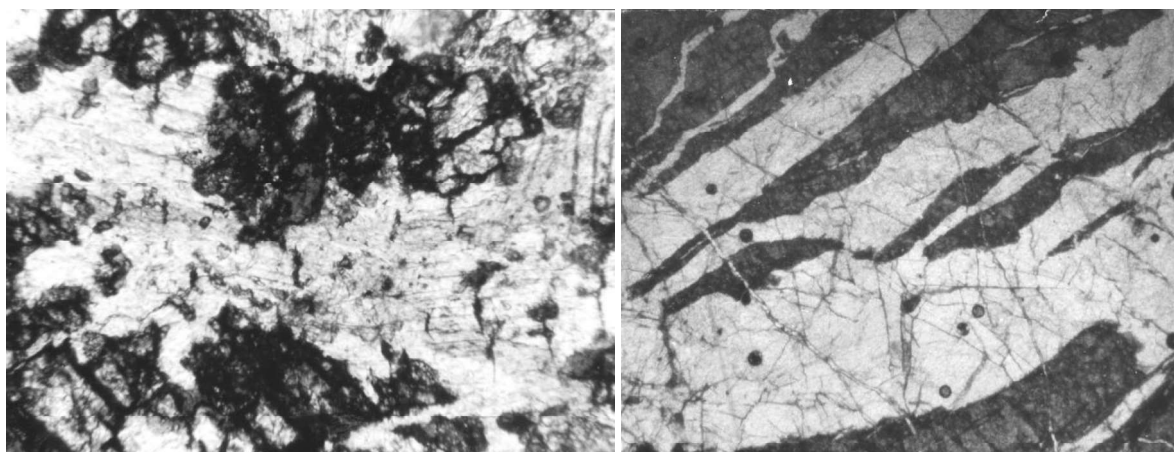


Fig. 12. Manganpyrosmalite (large, white grey, cleavage) vein in tephroite ore (large, dark grey, high refringence) (left); Pyrosmalite (large, white grey) vein/substituted pyroxmangite (dark grey relics) (right), TL, NII, x20.

Table XII

The trace elements in pyrosmalite type ore (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BOS73	–	–	44	380	–	–	130	130	–	8.5	–	–	55	2	–	–
BDS13	–	–	15	28	–	–	55	130	–	8.5	–	110	40	2	–	–
BOM695	–	–	31	28	–	–	80	130	–	11.5	–	–	34	3	–	–
BD267B	–	–	4.2	1.6	46	–	–	–	–	–	–	–	–	4	–	–
BMD1	–	–	90	20	–	–	–	105	–	5	–	210	34	5	–	4
BPrBalab1	–	–	44	41	–	–	–	105	–	10	–	175	47	6	–	–
BPrBalab2	–	–	–	1.6	–	–	–	60	–	–	–	–	–	7	–	–

Analyst: Mihai Popescu

12. BANNISTERITE/GANOPHYLLITE/STILPLOMELANE VEIN ROCK TYPE

The bannisterite and ganophyllite of the mica group, and the parsettensite of the stilplomelane group, have been described as new minerals for the MnB (Hirtopanu, 2004). This type lithology forms veins in pyroxmangite rich bands. The ferrostilplomelane occurs also as retromorph mineral at the expense of biotite in (b)-metachert and in veins through the carbonate ore. The associations ferrostilplomelane/quartz/pyrite and ferrostilplomelane/quartz/apatite/magnetite as small veins cut the bands of older associations. The ferrostilplomelane/ferristilplomelane/parssettensite veins occur at the same time with later Ca-rich carbonates veins (calcite, Mn-calcite, Ca-rhodochrosite, kutnohorite), that cut frequently the thephroite, Mn-humites, rhodonite, and johannsenite rich bands. The relatively high As (Table XIII) in a few samples of the type vein rocks could be linked with the presence of some secondary arsenates. The high Ba content (700–4,700ppm) of bannisterite type veins comes from the presence of barite (determined by SEM analyses) on its cleavages.

Table. XIII

The trace elements of the bannisterite, ganophyllite, and stilplomelane vein type (ppm)

Samples	As	Ba	B	Cu	Pb	Sb	Cr	Ni	Bi	Mo	V	Zn	Co	Ga	Li	Yb
BOS14	800	1,200	22	380	–	–	–	50	–	15	–	15	145	60	–	6
BAGS37	–	700	21	130	–	–	110	105	–	55	–	150	285	30	–	4
BAGS56	300	–	–	380	–	–	–	105	–	3.9	160	150	380	30	–	4
BAGS54	–	–	–	380	–	–	–	105	–	–	160	200	380	40	–	5
BOS18	–	–	31	380	–	–	–	34	–	31	–	120	47	25	–	7
BOS15	–	–	–	28	–	–	100	150	–	–	55	110	305	60	–	3
BCPS32	–	–	2.5	130	14	–	–	–	–	–	–	70	–	60	–	–
BT337	75	–	30	5	5	–	5	250	–	5	–	70	40	–	–	–
BAG14A	80	4,700	10	200	5	–	200	270	–	2	30	90	42	5	–	5
BAGS34	–	–	50	170	5	–	170	260	–	2	–	95	40	5	–	2
BOS93	–	400	5	5	5	–	5	210	–	3	10	90	37	7	–	4
BT323	–	–	30	15	5	–	15	230	–	2	–	70	40	–	–	1
BCPS16	130	–	10	15	–	–	15	240	–	5	–	65	40	–	–	6
BTm427	120	3,500	10	17	–	–	17	250	–	5	20	130	50	6	–	9

Analyst: Mihai Popescu

Low concentrations of Ni (0–270ppm), Cu (5–380ppm), Zn (15–200ppm), Co (0–380ppm) are characteristic of the hydrothermal manganese deposits that contain 34–51%wt Mn and that are formed on the present sea floor (Cann *et al.*, 1977; Corliss *et al.*, 1978; Toth, 1980). No Sb, Bi, and Li contents, and very low B, Pb, Cr, Bi, Mo, V, Zn, Co, Ga, and Yb concentrations were also determined (Table XIII).

CONCLUSIONS

The textural (banded layers with clear boundaries), mineralogical (presence of many end terms of manganese minerals), and geochemical (sharp separation of Mn from Fe, high Mn/Fe ratio, and low content of Co+Ni+Cu trace elements) features are all arguments in submarine hydrothermal origin's favor of Mn-ore of Manganese Belt. In the ternary [(Ni+Co+Cu)x10]-Fe-Mn diagram (Bonnati *et al.*, 1972, 1976) the all types of Mn-ore and manganiferrous lithologies plot within or near the hydrothermal field (Hirtopanu, 2004, 2019). There are no correlations between manganiferrous lithologies and country rocks.

The banding/laminations with contrasting compositions and the presence of low concentrations of most trace elements, including Th, U, Ni, Cu, and REE in the manganese lithologies from Manganese Belt, are consistent with its formation as a submarine hydrothermal deposit. Also, the low terrigenous contents (Al and Ti) and correlations between Ba and Mn typify oceanic hydrothermal deposits. The association of manganese ore with meta-igneous rocks/metabazalts of TG1 indicates that a heat source was probably available to drive a circulating hydrothermal submarine system. The geochemistry of Mn ore is similar to the hydrothermal deposits that are presently forming in the active rifting environments.

The presence of the Barium mineralization in TG2, sulfide mineralization in (TG3), and Uranium mineralization in TG4, indicates that almost all time, a hydrothermal system was active. Although the four mineralized belts are at a different stratigraphically levels, they are cogenetic. The four mineralized belts indicate that a Cambrian hydrothermal submarine system have been active/reactivated from TG1 to TG4. The submarine hydrothermal activity was fluctuant, a phenomenon also occurring in the current hydrothermal submarine deposits. The metamorphic evolution of the Mn, Ba, Sulfide, and U belts, and their host rocks, were achieved through repeated and superimposed metamorphic events, each metamorphic event being a source of new minerals. According to the trace element concentrations of manganese ore types from the Manganese Belt, the banded manganese ore/manganiferrous rock types have been mainly formed by submarine hydrothermal activity. The trace element data of TG1 and that of the manganese ore hosted by it, are consistent with paleodepositional environment of ocean-floor basalt, suggesting an oceanic-rifting environment, approached it to a subduction zone.

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