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The Coticule Rocks (Spessartine Quartzites) of the Venn-Stavelot Massif, Ardennes, a Volcanoclastic Metasediment?

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Abstract. Thin spessartine-quartzite layers (coticules) are interstratified with Ordovician (Salmian) shales of the Venn-Stavelot Massif, Ardennes. These coticules indicate sudden interruptions in the sedimentation process of the shales. The lower contact of the coticules represents an abrupt change in the chemical composition from the underlying shales. In contrast, the upper limit of the coticules is chemically more diffuse. Phase relations of the phengite-bearing spessartine-quartzites including paragonite, chlorite, and chloritoid or kaolinite as subordinate phases give evidence for a manganese-montmorillonitic source material of the coticules. This is in good agreement with the internal structures observed in the coticule layers (swelling and sliding effects, Liesegang structures). Since there is a positive correlation between the oxidation ratio of the enclosing shales and the chemical composition of the coticules, it is proposed that the source material of the coticules developed in situ by halmyrolysis out of tuffs. High oxidation ratios of the shales with iron fixed in the trivalent state but with divalent and thus mobile manganese led to the formation of coticule starting material, dominantly a manganese-montmorillonite. Halmyrolysis products formed under low oxidation ratio conditions of the enclosing shales are characterized by hydrosilicates rich in iron. The Obrochishte manganese deposit, Bulgaria, is discussed as a nonmetamorphic equivalent of the coticules of the Ardennes.

1. Introduction

In the Venn-Stavelot Massif, Ardennes, Ordovician rock units are characterized by low-grade metamorphic shales of Salmian age (Tremadocian). Within the lower parts of the Upper Salmian series (= Salmian 2), yellow to white layers of a spessartine-quartz assemblage are repeatedly intercalated. This typical rock, commercially mined and used as whetstone in former times, is geographically restricted to the southwestern part of the Salmian region (Fig. 1). Following Renard (1878), these spessartine-quartzites are called coticules (cos, cotis, masc., lat. whetstone).

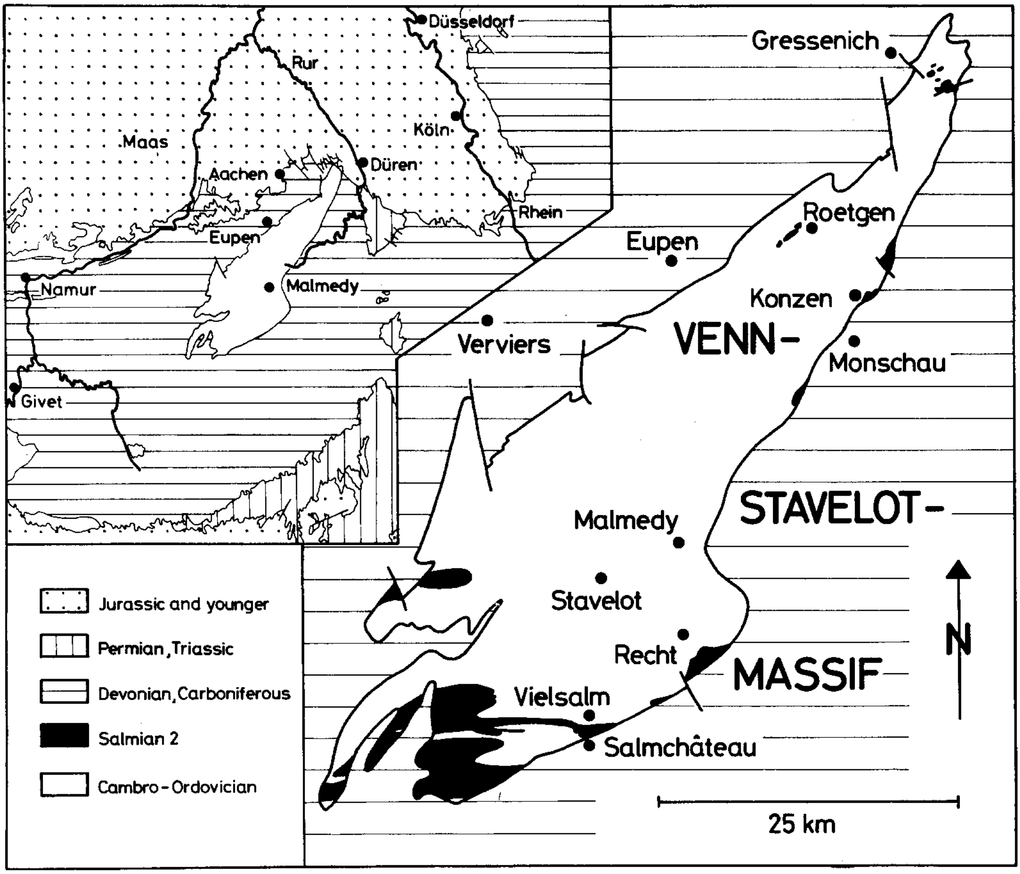

Fig. 1. Geologic map of northwestern part of Rhenish mass. Salmian 2 (= Upper Salmian) is coticule-bearing formation

In all occurrences, including others outside the Ardennes, coticules are metamorphic rocks. Their metamorphic grade varies between very low-grade greenschist facies (Ardennes) (Kramm, 1973) and amphibolite facies (Brezovica, Yugoslavia) (Karamata et al., 1970). Without any doubt, coticules are derived from sediments. However, highly contrasting interpretations as to the exact nature of the sedimentary source material are given by different investigators. Clifford (1960) derives the coticules of the New Hampshire occurrence, U.S.A., from manganese rich sandy layers. According to Schiller and Taylor (1965), the spessartine-quartzites of Nova Scotia, Canada, are formed from chert clay mineral-mixtures with manganese precipitated under oxidizing conditions. Karamata et al. (1970) propose, that the coticules of Brezovica, Yugoslavia, had been formerly cherty marine sediments, in which the deep sea manganese nodules were excessively accumulated. For the localities in the Ardennes, Richter (1969) suggests a formation out of spessartine placer deposits. Macar (1973) supports the idea of Lohest (1913) of a sedimentary origin of the coticules, but, in contrast to Richter, favors a clayey sediment as starting material. During examination of a coticule-bearing conglomerate within the transgressive Devonian sediments, Schreyer (1975) found new evidence for a Hercynian age of the metamorphism in the Venn-Stavelot Massif. This means that the "proto-coticule" pebble must have been consolidated and transportable during the Devonian transgression. For this period Schreyer proposes a cherty coticule source material perhaps containing Mn in carbonates. This assumption is in accordance with De Dycker's (1939), who believes to have found a nonmetamorphic analogue of the coticules. It consists of nearly 50% manganese carbonate. However, all these attempts at describing the original coticule source material are insufficient in that they fail to explain both the structural features and the phase relations recorded in the coticules.

Because of the unusual mineralogic and chemical composition, an explanation of the development of coticules must consider at least four main characteristic of these rocks:

1. The unusually high manganese content present in divalent form.
2. The general absence of manganese oxides.
3. The relatively high aluminum content, which is at least equivalent to the manganese content.
4. The very fine laminated structure and specific folding characteristics.

A structural analysis of the coticules of the type locality, the discussion of their phase relations, and a characterization of their geochemical surroundings with respect to material supply and oxygen fugacity allow the development of a model source material that fits all these rock parameters. The manganese ore deposit of Obrochishte, Bulgaria, is regarded as a nonmetamorphic equivalent of the coticules. Its formation, however, seems to be different from that proposed for the coticule source material.

2. Analytical Methods

Chemical rock analyses were made either by wet chemical methods (Na, K, Mg, P, Fe^{2+}) after dissolving the samples in HF-$HClO_4$ mixtures, or by *X*-ray fluorescence of $Li_2B_4O_7$ fluxes using internal and external standards (Si, Ti, Al, Fe, Ca, Mn). The determination of Fe^{2+} was carried out according to the vanadate method (Peters, 1968), using a closed reaction vessel thus preventing the oxidation of the sample during fusion. Water content as H_2O^- and H_2O^+ was titrated using Karl Fischer's reagent (Lindner and Rudert, 1969).

Chemical compositions of the minerals were determined using an ARL-EMX electron probe microanalyzer (operating conditions: 15 kV, 0.07 μA beam current, beam current-time integration). Natural standards served for calibration (Garnet standards: 12442, 7SP-1AL-1GR-1PY). Corrections for mass absorption and secondary fluorescence were done with special regard to H_2O contents using the correction factors of Albee and Ray (1970). The water content of chloritoid was presumed to be constant (theoretical H_2O content of Fe-chloritoid), and H_2O contents of chlorites were estimated from their Mg/Fe ratio using a nomogram based on data of Deer et al. (1963). Since there is no zoning in the minerals investigated, the chemical analyses given in Tables 3–5 are averages of 20 one-point measurements.

The quantitative mineral composition of the rocks was investigated by *X*-ray diffraction methods. Kaolinites were determined by the d-spacings of their basal reflections after having been submitted to an intercalation reaction to form hydrazine kaolinite (Weiss et al., 1963).

3. Petrography

The spessartine-quartzites of the Ardennes vary in thickness from less than 1 mm to several decimeters. Normally, a single coticule layer has quite a constant thickness, at least within one exposure. Beside this, lenticular, but strata-bound, coticules can be observed in a few cases. The lateral extensions of single coticule beds are estimated to amount to several square kilometers. Since all these beds are parallel to the layering of the enclosing shales, there is no doubt that the coticules are of sedimentary origin. This is confirmed by Macar (1973), who observed that the upper coticule surface (the last sedimentation surface of the coticule source material) contains erosion pits and tracks.

The coticule layers are very frequent in some beds of the Upper Salmian shales, while other strata are poor in coticules or lack them completely. There is a positive correlation between the number of coticule beds in a shale unit and the thickness of the coticules.

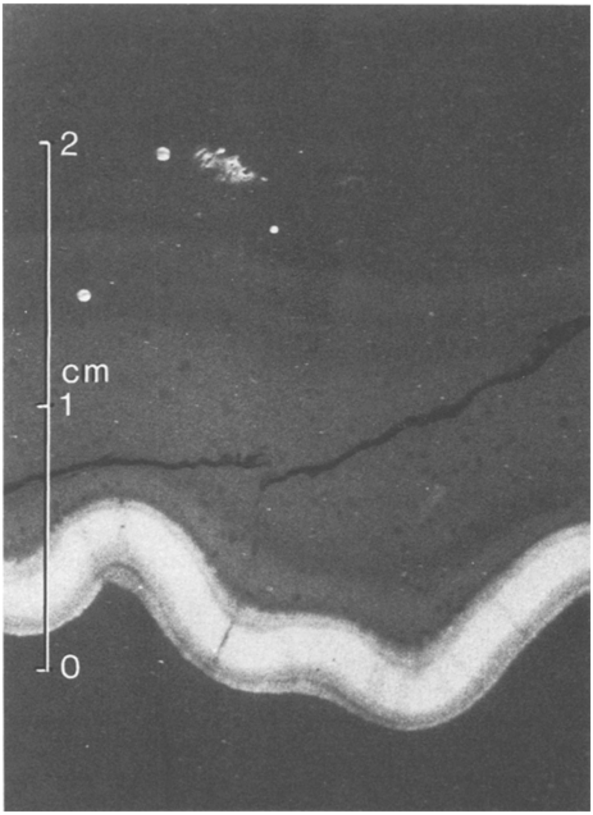

Fig. 2. Microfolding of coticule layer (type 1). Height of folds diminishes rapidly in neighboring shales, fading out some centimeters above and below layer (thickness of coticule about 0.4 cm). Shales following above coticule layer pale in color compared to usual Salmian shales and represent special chemical compositions (see Fig. 4, C1)

Frequently, coticules show microfolding. These folds gradually diminish in the enclosing shales and fade out some centimeters above and below the coticule layers (Fig. 2). Lohest (1913) interprets this feature as an interaction of a competent coticule layer and the surrounding more incompetent shales under tectonic stress. However, since the folding of the enclosing shales is independent of the contraction suffered by the whole rock unit and varies only with the height of the coticule folds, the explanation of this folding must be different from that proposed by Lohest (Macar, 1973). Unquestionably, some folds of the coticules are synsedimentary, as shown by Macar. In other cases small-scale shale units overlying the coticule beds can be observed, which are present only in the synclines of the coticule folds. These shale units are also folded, indicating a continuing syn- to postsedimentary folding. Since the underlying shales are affected in a similar way, an explanation of the folding exclusively in terms of subaquatic sliding must be rejected. Thus, this type of folding should be inherent in the coticule source material and it is assumed to be the result of a syn- to postsedimentary swelling, e.g., by the absorption of water. For comparison, similar effects can be observed in the "Schlangengips" of the German Zechstein (Upper Permian). Here the increase in volume by water absorption of anhydrite to form gypsum was compensated by microfolding. Volcanoclastic tuffs are therefore proposed for a possible source material of the coticules. They were transformed to claymineral assemblages including swelling montmorillonitetype minerals by halmyrolytical reactions penecontemporaneously with the sedimentation and during early stages of diagenesis. These clay-mineral assemblages are considered to have been the starting material for the formation of coticules during metamorphism.

Macroscopically, several types of coticules can be distinguished by their internal structures and their different colors which represent different mineralogic compositions. Since one coticule type can change gradually into another, any classification must, of necessity, be incomplete. In the present paper, only a few types are distinguished which are significant for a discussion of the development of the coticules:

Type 1

Homogeneous yellow spessartine-quartzites are usually represented by layers up to 1 cm thick.

Type 2

Coticule layers usually thicker than 1 cm, which are accompanied pseudoconcordantly by greenish gray quartzites, always contain thick spessartine-rich layers both in the upper and lower part of the bed. Only the central quartzitic part of these inhomogeneous coticules is homogeneous and poor in spessartine or free of it.

Type 3

Coticules of this type are similar to coticules of type 2. The central quartzitic part, however, is subdivided by a large number of very thin, subparallel spessartine

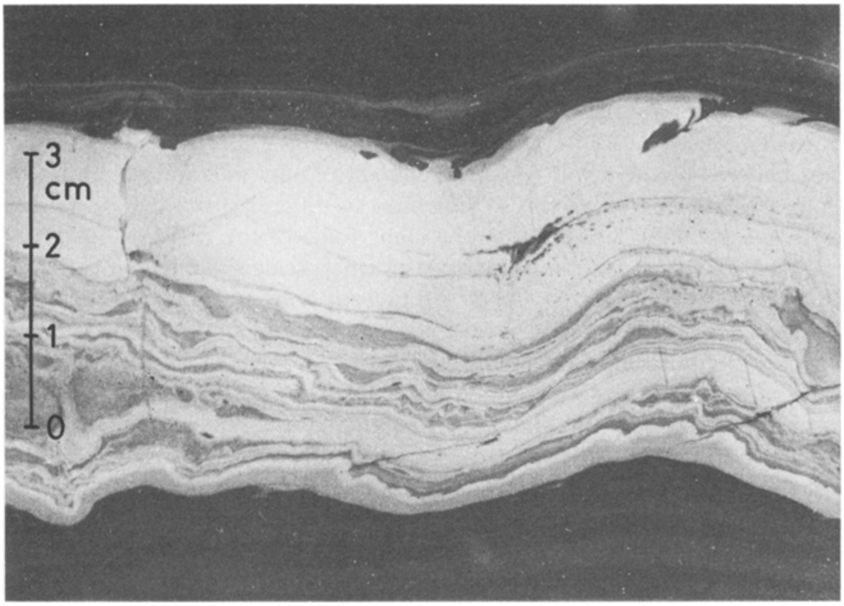

Fig. 3. Coticule section (type 3) in dark Salmian shales. Lower and upper part of coticule layer characterized by thick spessartine quartzites, central part laminated by smallest subparallel spessartine layers. Top of coticule shows small erosion pits and tracks. Thickness of coticule layer about 4 cm

layers (Fig. 3). In contrast to the marginal yellow layers, the internal spessartine-rich units are microfolded. Repeated sections perpendicular to the stratification demonstrate the very limited lateral extension of these internal layers.

Type 4

Green chlorite- and chloritoid-rich layers are intercalated in the lower and upper parts of the spessartine-quartzites. More rarely they are recognized in the central parts. In contrast to the finely laminated yellow spessartine intercalations in the central quartzitic parts of type 3, these green intercalations are without any stratification.

Type 5

Depending on the chemical composition of the enclosing shales, a strata-bound green chlorite-chloritoid assemblage can be observed which genetically belongs to the coticuletype intercalations, but, according to the definition of the coticules (=spessartine-quartzites), is no coticule.

The coticules of types 1, 2, and 3 can contain yellow to white kaolinite spots in their spessartine-rich layer units. The size of these spots varies from 0.1 to 1 mm. They are similar to the kaolinitic flakes of the neighboring shales (Theunissen, 1971; Kramm, 1973). In the adjacent rocks they are concentrated in a thin strata overlying the coticules. The thickness of this zone amounts to some centimeters. In contrast to the dark gray to violet shales, the color of this zone is light gray to reddish.

4. Chemistry of Coticules and Neighboring Rocks

Compared to the enclosing shales, the chemical composition of the coticules is distinctly different (Table 1). The concentration of Fe_2O_3 in the shales, which are usually rich in hematite, amounts to 10–20 wt %, whereas the coticules contain 0.1–1 wt % Fe_2O_3. This remarkable difference is expressed in the color of both rock types, which is due to the presence or absence of hematite. The distribution of manganese between the shales and the coticules is the reverse: The coticules are strongly enriched in manganese (MnO contents of coticule type 1 and the spessartine-rich layers of types 2 and 3 up to 25 wt %) compared to the enclosing rocks, which however still can contain up to 2 wt % MnO – much more than the average shales (Turekian and Wedepohl, 1961). MnO contents of the coticule types 2 and 3 vary between 1 wt % and 15 wt % depending on the dilution effect of the quartzitic intercalations. The average MnO content of the Salmian shales amounts to 0.6 wt %. In the coticules Fe^{2+} is always present in higher amounts than in the neighboring shales, although, for types 1, 2, and 3, 1 wt % FeO is not exceeded. SiO_2 contents of the coticules are higher, Al_2O_3 contents lower than in the surrounding shales. K_2O, too, is lower in the coticules.

Table 1. Chemical composition of coticules and enclosing rocks (weight percent)

Specimen[a] rock type	SA-2 Shale	SA-4 Coticule type 2	OT-3 Shale	OT-4 Coticule type 3	OT-5 Shale
SiO_2	51.00	63.75	56.40	73.65	55.00
TiO_2	1.04	1.10	1.05	1.27	1.02
Al_2O_3	20.77	18.67	23.08	16.43	21.09
Fe_2O_3	15.70	0.47	9.04	0.48	12.99
FeO	0.47	0.54	0.23	0.17	0.26
MnO	0.61	8.32	0.65	2.11	0.37
MgO	1.51	0.61	1.20	1.01	1.12
CaO	0.42	0.62	0.27	0.26	0.31
Na_2O	1.52	1.42	0.86	0.74	0.82
K_2O	2.32	1.75	2.48	1.58	2.46
P_2O_5	0.28	0.29	0.28	0.10	0.28
H_2O^-	0.18	0.14	0.23	0.09	0.39
H_2O^+	3.58	2.12	3.99	2.13	3.84
C	0.01	0.00	0.01	0.00	0.02
CO_2	0.00	0.00	0.00	0.00	0.00
	99.41	99.80	99.77	100.02	99.97

[a] SA-2 underlying SA-4, OT-3 underlying OT-4, OT-5 overlying OT-4

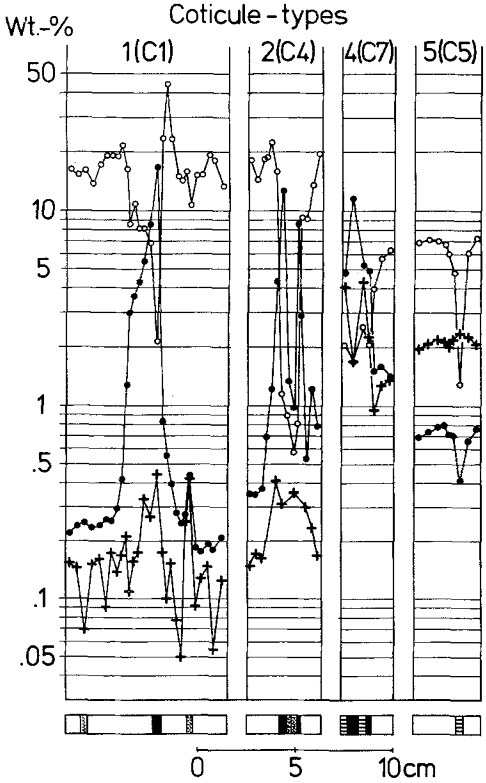

Fig. 4. Chemical profiles over coticules and enclosing rocks (FeO +—+—+, Fe_2O_3 o—o—o, MnO ●—●—●). Represented are coticules of types 1 (C1), 2 (C4), 4 (C7), and 5 (C5). Abscissa shows rock types investigated (white: shales; black: spessatine-quartzites; stippled: quartzites; horizontally striped: green chlorite-chloritoid intercalations). Left sides of profiles correspond to youngest layers

The relationship between coticules and enclosing rocks can be discussed by considering chemical profiles for FeO, Fe_2O_3, and MnO. These profiles were made for characteristic samples of coticule types 1, 2, 4, and 5 (Fig. 4) by subdividing the rocks into millimeter-thick layers according to the stratification. Larger parts of the enclosing shales above and below the coticules were included in the examination.

Most interestingly, coticules of types 1, 2, and 3 can only be found in shales with high oxidation ratios. Nearly the total amount of iron must be present in the trivalent state in these shales (mol $2\,Fe_2O_3 \times 100/2\,Fe_2O_3 + FeO > 90$). The concentration of manganese in the shales seems to be of subordinate importance for the existence of these coticules (Fig. 4, C1, C4). In contrast, coticules of types 4 and 5 are present only in shales relatively enriched in Fe^{2+} and, consequently, formed under lower E_h-p_H conditions of the sedimentation environment (Garrels, 1960). Coticule type 4 intercalations can be found in these shales, if they are rich in manganese (Fig. 4, C7). If the manganese content is low in Fe^{2+}-rich shales, only type 5 intercalations can be found instead of coticules s.s. (Fig. 4, C5).

Especially in view of the coticules of types 1, 2, and 3, MnO and Fe_2O_3 behave in a different way in the shales above and below the coticules. An abrupt increase in manganese is recognized, if the lowermost coticule layer is reached passing the underlying shale in upward direction. In contrast, the manganese content decreases more gradually by advancing from the upper coticule surface into the overlying shale. The Fe_2O_3 contents are inversely proportional to the manganese contents (Fig. 4, C1, C4).

Coticule types 2 and 3 show a different behavior of manganese in the upper and lower parts of the layer. The upper spessartine-rich units, which are considerably thicker than the lower parts, are enriched in this element.

The type 4 coticules and the type 5 chloritoid-chlorite-rich intercalations are both depleted in Fe_2O_3. But, in contrast to the other coticule types, the manganese contents in the marginal parts of the intercalations are diminished, in case of type 5 under the level of the shales. In these parts divalent iron is present in larger amounts.

5. Mineralogic Composition

In the coticule specimens investigated, garnet, phengitic mica, and quartz are the main phases, while paragonite and chlorite are present in subordinate amounts (Table 2). Kaolinite in the spessartine-rich layers (types 1, 2, 3) and chloritoid in the green, chloritic layers (types 4, 5) may be present as minor phases. Trace phases are rutile and tourmaline. In kaolinitic spots in the spessartine-rich units only, very small amounts of andalusite can occur. There is a considerable compositional variation, especially in the ratio of garnet to quartz. Type 1 coticules as well as the uppermost and lowest parts of types 2 and 3 are very rich in garnet. In contrast, the central parts of types 2 and 3 are richer in quartz. Both minerals form a very fine-grained mosaic texture.

The grain size of the *garnets* varies from 0.5 μm to 4 μm, the average diameter of the coticule garnets being 2.8 μm. Usually the subidiomorphic crystals are

Table 2. Mineralogic composition of coticules (without accessory minerals) (weight percent)

	Spessartine	Quartz	Muscovite	Paragonite	Chlorite	Kaolinite	Chloritoid
SA-4	20	38	29	<5	<5	<5	–
OT-4	5	49	36	<5	<5	<5	–
C1/coticule	41	18	20	<5	10	5	–
C8/coticule	11	24	50	<5	5	10	–
C4/lower part[a]	21	25	42	<5	10	<5	–
C4/middle part[a]	3	67	14	<5	10	<5	–
C4/upper part[a]	32	24	26	<5	10	<5	–
C7/lower part[a]	3	35	20	<5	15	–	25
C7/middle part[a]	28	42	10	<5	15	–	–
C7/upper part[a]	3	30	37	<5	10	–	20

[a] See Figure 4 for positions of the sections of the coticule layers

pale yellow to pale green. Characteristically, the garnets in the coticules are very spessartine-rich (Table 3). Within a single coticule layer, there is no significant compositional difference between spessartines from marginal or central parts (Table 3, C2). In contrast to the coticule garnets, the garnets of the appropriate shales are always somewhat enriched in iron, although their almandine component is less than 10 mol%. Very small coticule bands (less than 1 mm in width) often contain garnets which are somewhat richer in iron than those in broader coticules of the same shale unit.

Paragonite and a *phengitic mica* coexist in all types of coticules as well as in the green chloritic intercalations in the Salmian shales (type 5). This can be shown by X-ray investigations on oriented mounts. In all cases, the phengitic mica is the dominant one. Since the grain size is very small, the amount of solid solution within both micas can be estimated only by X-ray data according to which the muscovitic mica contains up to 17 mol% of the paragonite molecule, and the coexisting paragonite up to 5 mol% muscovite. From the relationship between the chemical composition of muscovite-paragonite pairs and the metamorphic grade, estimated by Zen and Albee (1964), the coexisting white micas in the coticules fit the metamorphic grade of the lower greenschist facies.

Table 3. Chemical composition of garnets in coticules and enclosing rocks

Coticule	C1	C1	C2	C2	C2	C4	C4	C4	C7
type	1	–	2	2	2	2	2	–	4
position	Garnet-rich layer	Shale	Lower gr-rich layer	Central layer	Upper gr-rich layer	Lower gr-rich layer	Upper gr-rich layer	Shale	Gr-rich layer
SiO_2	36.97	36.68	37.23	36.58	36.72	36.36	35.87	35.91	36.61
Al_2O_3	20.70	20.81	21.00	20.98	20.87	20.75	20.69	20.64	20.53
FeO[a]	1.76	2.58	2.99	3.00	3.50	1.82	1.14	3.71	3.61
MnO	40.06	39.07	38.24	38.68	37.45	39.35	40.48	38.86	39.52
MgO	0.58	0.62	0.62	0.65	0.60	0.52	0.23	0.61	0.16
CaO	0.64	0.77	0.65	0.69	0.72	0.59	0.62	0.86	0.95
	100.71	100.52	100.73	100.58	99.86	99.39	99.03	100.59	101.39
Number of cations on the basis of 24.00 oxygens:									
Si	6.02	5.98	6.03	5.97	6.01	5.99	5.95	5.90	5.97
Al	3.97	4.00	4.01	4.03	4.03	4.03	4.05	3.99	3.94
Fe	0.24	0.35	0.41	0.41	0.48	0.25	0.16	0.51	0.49
Mn	5.53	5.40	5.25	5.34	5.19	5.49	5.69	5.41	5.45
Mg	0.14	0.15	0.15	0.16	0.15	0.13	0.06	0.15	0.04
Ca	0.11	0.14	0.12	0.12	0.13	0.11	0.11	0.15	0.17
End members (mol%) approximated:									
Almandine	4	6	7	7	8	4	3	8	8
Spessartine	92	89	88	88	87	92	94	88	89
Pyrope	2	3	3	3	3	2	1	2	1
Grossularite	2	2	2	2	2	2	2	2	2

[a] Total iron as FeO

Chlorite is a relatively rare but significant phase of all coticules. It forms platy crystals up to 20 μm in diameter. The chemical composition varies considerably with the coticule types. Chlorites of types 1, 2, and 3 are very rich in magnesium and poor in iron, those of the green intercalations in the types 4 and 5 are relatively enriched in iron (Table 4). Manganese is present in low and, regarding its relationship to the coticule types, insignificant amounts. There is another small difference between chlorites from different coticule types regarding the aluminum contents in different lattice positions. Chlorites from coticule types 4 and 5 tend to have slightly higher Al$^{[4]}$/Al$^{[6]}$ ratios than those from types 1, 2, and 3. This behavior is similar to that of the chlorites in the enclosing shales (Kramm, 1973).

Kaolinite is present in some of the coticules of types 1, 2, and 3, where it prefers the spessartine-rich marginal parts. Frequently, it forms spots of 0.1–1 mm diameter, which are rich in inclusions of rutile, garnet, and quartz. *Andalusite* is observed rarely within these spots (Theunissen, 1971; Kramm, 1973).

Chloritoid was observed exclusively in the green layers of types 4 and 5, where it forms hypidiomorphic porphyroblasts ranging in size from 200 to 400 μm. The crystals contain numerous inclusions of quartz and rutile. In their chemical composition (Table 5), the chloritoids of coticule type 4 are characterized by relatively high MgO contents (3.4–4.6 wt %) and by MnO values as high as 8.4–

Table 4. Chemical composition of chlorites in coticules

Coticule	C1	C2	C2	C4	C4	C5	C7	C7
type	1	2	2	2	2	5	4	4
position	Garnet-rich layer	Gr-rich layer	Gr-poor central layer	Gr-rich layer	Gr-poor layer	Green intercalation	Gr-rich layer	Green intercalation
SiO_2	26.10	25.91	27.06	26.84	27.80	24.46	25.76	26.01
Al_2O_3	25.65	26.32	25.85	26.16	26.08	24.92	25.08	25.40
FeO[a]	3.44	4.58	4.86	3.24	3.40	14.11	9.00	9.23
MnO	2.33	1.92	1.60	1.65	1.61	1.61	2.30	1.55
MgO	27.08	25.97	26.03	26.60	26.25	20.27	23.86	23.66
	84.60	84.71	85.40	84.49	85.15	85.37	86.00	85.85
Number of cations on the basis of 28.00 oxygens:								
Si	5.12	5.09	5.26	5.23	5.37	5.02	5.12	5.16
Al[4]	2.88	2.91	2.74	2.77	2.63	2.98	2.88	2.84
	8.00	8.00	8.00	8.00	8.00	8.00	8.00	8.00
Al[6]	3.05	3.19	3.18	3.24	3.31	3.05	2.99	3.10
Fe	0.57	0.75	0.79	0.53	0.55	2.43	1.50	1.53
Mn	0.39	0.32	0.26	0.28	0.26	0.28	0.39	0.26
Mg	7.92	7.60	7.54	7.73	7.55	6.21	7.07	6.99
	11.93	11.86	11.77	11.78	11.67	11.97	11.95	11.88

[a] Total iron as FeO

Table 5. Chemical composition of chloritoids in coticules and enclosing rocks

Coticuletype	C5	C5	C7	C7	C7
position	5	–	4	4	–
	Green intercalation	Shale	Green intercalation	Gr-rich layer	Shale
SiO_2	24.38	24.12	25.30	24.89	24.75
Al_2O_3	40.10	39.97	39.50	40.21	40.03
FeO^a	15.95	16.39	13.31	13.34	13.96
MnO	8.42	8.37	8.70	9.04	8.93
MgO	3.48	3.43	4.41	4.57	4.47
H_2O^b	7.15	7.15	7.15	7.15	7.15
	99.49	99.43	98.37	99.19	99.28
Number of cations on the basis of 14.00 oxygens:					
Si	2.02	2.00	2.09	2.05	2.04
Al	3.91	3.91	3.85	3.90	3.89
Fe	1.10	1.14	0.92	0.92	0.96
Mn	0.59	0.59	0.61	0.63	0.62
Mg	0.43	0.42	0.54	0.56	0.55
	2.12	2.15	2.07	2.11	2.13
OH	3.95	3.96	3.94	3.92	3.93

[a] Total iron as FeO

[b] Fixed water content

9.0 wt %. These chloritoids are similar in composition to the chloritoids of the Salmian shales with the highest oxidation ratio (Kramm, 1973; Table 5, No. 72). In contrast, Salmian shales with lower oxidation ratio contain chloritoids poorer in MgO and MnO.

6. Phase Relations

Regarding the chemical composition of the coticules, at least twelve components should be considered for the discussion of the coticule phase relations. However, confining the discussion to the main components and to the main and subordinate phases of the coticules, the discussion of the phase relations seems to be possible in two subsystems: $Na_2O-(Mg, Fe)O-Al_2O_3-SiO_2$ and $MnO-(Mg, Fe)O-Al_2O_3-SiO_2$. H_2O as a volatile is considered to be present in excess. K_2O, by quantity the largest of the excluded components, is represented mainly by the phengitic mica because the K_2O content of paragonite is very low. Since the existence of a phengitic mica in metasediments under greenschist facies conditions is not of great importance in view of the discussion of the metasedimentary source material, the exclusion of K_2O seems to be justified as a first approximation. For the purpose of clearness, paragonite will be regarded as pure Na-phase. The trace phases rutile and tourmaline are excluded from the discussion, since they seem to be of little significance concerning the formation of the coticules.

Kaolinite and chloritoid do not coexist in the coticules investigated. Kaolinite, if present, is always confined to coticule types 1, 2, and 3, chloritoid to the type-5 intercalations and to the green units of the type-4 coticules. Regarding a chloritoid formation from kaolinite and hematite which is described for the surrounding Salmian shales by Kramm (1973), this incompatibility behavior can be discussed in terms of oxygen fugacity during metamorphism. It can be stated in the rock only, if hematite is an excess phase. Coticules of all types, however, are essentially free of hematite. Thus the incompatibility of koalinite and chloritoid observed here must be of a different origin. Since the existence of different types of coticules correlates with different oxidation ratios of the adjacent shales, it can be assumed that there is a relationship between the chemical composition of the shales and the coticules. FeO amounts of the coticules are high, for example, if the oxidation ratios of the neighboring shales are low, and vice versa. Assuming an acidic tuff very poor in iron as coticule starting material (as will be discussed in detail below) and quite constant E_h-p_H conditions of the sedimentation environment during the deposition of tuff and enclosing sediments, there should be an increase in iron in the halmyrolysis products of the tuff caused at least by the concentration gradient between the two rock units, if iron *can* migrate into the tuff. Because divalent iron is much more mobile than iron in its trivalent state under sedimentary and early diagenetic conditions (Krauskopf, 1957), it is assumed that Fe^{2+}, if it was present, has migrated into the changing tuff out of the shales, thereby yielding a bulk rock composition suitable for the formation of chloritoid. In the case of high oxidation ratios of the shales, the tuffs under halmyrolysis remained unchanged with respect to divalent iron, thus giving way to the existence of kaolinite. Therefore, the incompatibility of kaolinite and chloritoid is a function of the chemical supply to the starting material of the coticules which, for its part, depends on the E_h-p_H conditions under which the sediments have formed. The oxidation ratios of the shales reflect these conditions. For clarity, the coticule phase relations will be discussed later for two different oxidation ratios of the shales: a high one, referring to coticules with very low iron contents (kaolinite assemblages), and a low one, which means that iron is present in larger amounts in its divalent state in the coticules (chloritoid assemblages).

The subassemblages quartz-chlorite-paragonite-kaolinite (high oxidation ratio) and quartz-chlorite-paragonite-chloritoid (low oxidation ratio) plot into the subsystem $Na_2O-(Mg, Fe)O-Al_2O_3-SiO_2$ (Fig. 5). The compositions of both chlorite and chloritoid are in the plane $(Mg, Fe)O-Al_2O_3-SiO_2$. Paragonite as a relatively rare phase in low-grade metamorphic rocks is of special interest in view of describing the coticule starting material. Chatterjee (1973) discusses the compatibility relations of quartz-paragonite-assemblages in the system $Na_2O-Al_2O_3-SiO_2-H_2O$, which can be regarded as coticule subsystem (basal plane of the tetrahedron $Na_2O-(Mg, Fe)O-Al_2O_3-SiO_2$ in Fig. 5). Under p-T-conditions of low grade greenschist facies, thus comparable with the metamorphic grade of the Venn-Stavelot Massif (p-T estimate: 2 kb, 360–400° C, Kramm, 1973), he obtains a kaolinite-paragonite-quartz assemblage, in agreement with the observed coticule assemblage. Experimentally, it is formed either by a breakdown reaction of Na-montmorillonite (T– constant or decreasing; p_{H_2O} rising) or by a reaction of albite and kaolinite (p_{H_2O}– constant; T rising).

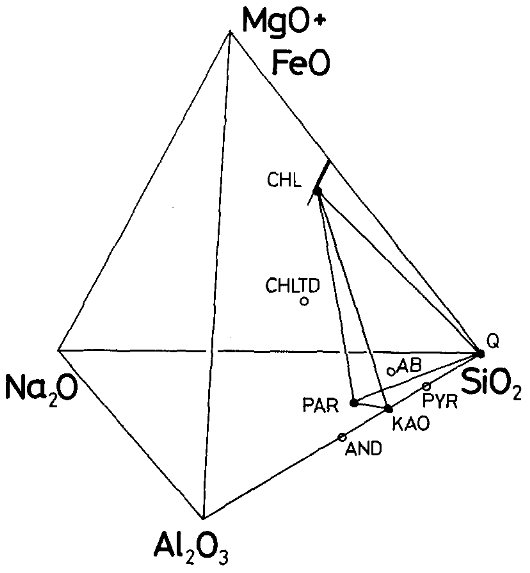

Fig. 5. High f_{O_2} coticule assemblage in system $Na_2O-(Mg, Fe)O-Al_2O_3-SiO_2$ (*CHL* chlorite, *CHLTD* chloritoid, *AB* albite, *PAR* paragonite, *AND* andalusite, *KAO* kaolinite, *PYR* pyrophyllite, *Q* quartz)

Thus the paragonite formation out of sedimentary source materials can be discussed assuming clay mineral assemblages which contain montmorillonite and/or kaolinite. However, extrapolating Chatterjee's stability relations between montmorillonite and the assemblage quartz-kaolinite-albite to surface or near surface conditions, it is seen that montmorillonite is stable at lower values of p and T, compared to quartz-kaolinite-albite, and should thus be favored as the sedimentary starting material.

Extending Chatterjee's experiments intellectually to natural Na-montmorillonites as starting phases of paragonite assemblages, MgO has to be regarded as another component in the system. Natural montmorillonites have an average Mg content of 3.5 wt% MgO (Weaver and Pollard, 1973). This oxide is not taken up in the lattice of paragonite in larger amounts (Radoslovich, 1963; Franz and Althaus, 1974), and its coexistent phases quartz and kaolinite. It should form an independent Mg phase along with the crystallization of the paragonite assemblage. Comparing paragonite-bearing low-grade metamorphic rocks, this postulated phase should be a chlorite. Thus, the coticule subassemblage quartz-chlorite-paragonite-kaolinite can be obtained by a breakdown reaction of natural montmorillonite.

The subassemblages spessartine-chlorite-quartz-kaolinite and spessartine-chlorite-quartz-chloritoid can be described in the subsystem $MnO-(Mg, Fe)O-Al_2O_3-SiO_2$ (Figs. 6, 7). Both spessartine assemblages reflect source materials in which either manganese was present in the divalent state a priori, or manganese has been reduced from a higher oxidation state during metamorphism after deposition in an oxidizing environment. Reducing effects under metamorphic

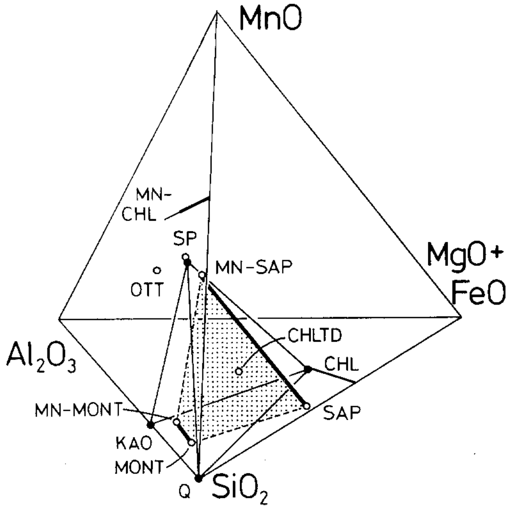

Fig. 6. High f_{O_2} coticule assemblage in system MnO – (Mg, Fe)O – Al_2O_3 – SiO_2 (*Mn–CHL* manganese chlorite; *OTT* manganese chloritoid; *SP* spessartine; *SAP* saponite; *Mn–SAP* manganese saponite; *MONT* montmorillonite; *Mn–MONT* manganese montmorillonite, other symbols see Fig. 5). Coticule assemblage represented by four-phase space with spessartine-chlorite kaolinite-quartz. Within the plane Mn–MONT – MONT – Mn–SAP – SAP (dotted) plots assumed starting material of coticules

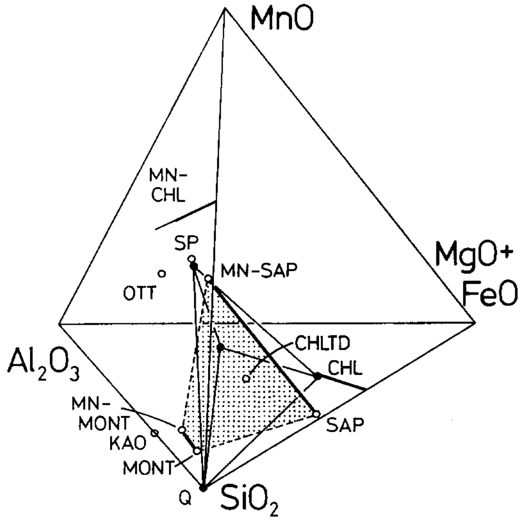

Fig. 7. Low f_{O_2} coticule assemblage in system MnO – (Mg, Fe)O – Al_2O_3 – SiO_2. This coticule assemblage forms four phase space spessartine-chlorite-Mn-Fe-chloritoid-quartz

conditions are known in many cases (Eugster, 1959; Frey, 1969), and are described for special rock positions adjacent to quartz-veins in the Venn-Stavelot Massif, too (Kramm, 1973). Here the rock units cannot be regarded as closed systems with respect to the vapor phase. Therefore, only in these areas does a large-scale reduction of the shales seem possible, caused by the different mobility of the dissociation products of the main component of the vapor phase, H_2O. Since, however, coticules are not situated in these special geologic environments in general, this reduction mechanism cannot be realized for the spessartine-quartzites. On the other hand, there are no indications of tetravalent or trivalent manganese in the coticules (in contrast to braunite- and viridine-bearing Salmian shales). Thus, it can be assumed that manganese was present a priori in its divalent state in the coticule source material. Carbonate and silicate minerals containing divalent manganese are stable under surface or near surface conditions and special oxygen fugacities (e.g., Ross, 1946; Aleksiev and Bogdanova, 1974).

Generally, metamorphic mineral assemblages can be formed by a reaction of a previous mineral assemblage or by a breakdown reaction of one mineral. In a mineral breakdown, the starting phase is consumed totally by the reaction. In the other case, the starting mineral assemblage vanishes totally only in the very rare case of primary stoichiometric composition. Otherwise, after the reaction, the excess phase (or phases) can be found in the new assemblage.

Assuming a coticule formation out of two or more phases, the Mn-bearing starting phase(s) could plot outside the four phase volumes kaolinite-quartz-chlorite-spessartine (Fig. 6) or chloritoid-quartz-chlorite-spessartine (Fig. 7). Considering a coticule formation by a mineral breakdown reaction, the starting phase has to plot within the four phase volumes. Possible phases with chemical compositions in these volumes are montmorillonite group minerals, which, as derived above, could also account for the formation of paragonite and the microfolding structures. Possible manganese-bearing phases outside the four phase volumes are rhodochrosite, Mn chlorites and, Mn saponites.

In the coticules the manganese content of the source material was used up for the formation of spessartine and chlorite or spessartine, chlorite, and chloritoid. Relics of any possible Mn-bearing source material are never observed. In view of a Mn carbonate starting phase this is particularly remarkable, since rhodochrosite-kaolinite-quartz-spessartine-chlorite-phengite-hematite assemblages are not rare in the area investigated, forming thick red shale units. In addition, for a rhodochrosite-containing starting material, but also for Mn saponites, Al_2O_3 must be present at least in amounts allowing the formation of spessartine. Al_2O_3 can be obtained from clay minerals. Since, however, rhodochrosite and Mn saponite are never present in the coticules, even when there are no excess clay minerals, these two phases are not believed to be the starting material. On the other hand, information about both natural Mn montmorillonite and Mn chlorite of sedimentary origin is very scarce. Since up to now no Mn chlorite beds are known in sedimentary environments, Mn montmorillonite is the favored coticule source material. Through breakdown, Mn montmorillonites of suitable chemical compositions should be able to form the whole coticule assemblage under low-grade greenschist facies conditions, e.g.

$$\text{Mn montmorillonite} \rightleftharpoons$$

$$\text{spessartine} + \text{paragonite} + \text{chlorite} + \text{kaolinite} + \text{quartz} + \text{water}$$

(high oxidation ratio assemblage)

$$\begin{aligned}&40\,(\mathrm{Al_{1.60}Mn_{0.35}Mg_{0.05}})(\mathrm{Si_4O_{10}})(\mathrm{OH})_2\mathrm{Na_{0.40}} \rightleftharpoons 4.7\,\mathrm{Mn_3Al_2Si_3O_{12}}\\&\quad + 16\,\mathrm{NaAl_2(Si_3AlO_{10})(OH)_2} + 0.4\,\mathrm{Mg_5Al(Si_3AlO_{10})(OH)_8}\\&\quad + 1.45\,\mathrm{Al_4Si_4O_{10}(OH)_8} + 91\,\mathrm{SiO_2} + 16.6\,\mathrm{H_2O}\end{aligned}$$

With decreasing oxidation ratios of the shales, an increasing amount of divalent iron is incorporated into the montmorillonites. These montmorillonites are assumed to be able to form the chloritoid-assemblage, e.g.

Mn montmorillonite $\rightleftharpoons$

spessartine + paragonite + chlorite + chloritoid + quartz + water

(low oxidation ratio assemblage)

$$\begin{aligned}&40\,(\mathrm{Al_{1.60}Mn_{0.20}Fe_{0.15}Mg_{0.05}})(\mathrm{Si_4O_{10}})(\mathrm{OH})_2\mathrm{Na_{0.40}} \rightleftharpoons 2\,\mathrm{Mn_3Al_2Si_3O_{12}}\\&\quad + 16\,\mathrm{NaAl_2(Si_3AlO_{10})(OH)_2} + (\mathrm{Mg_2Fe_3Al})(\mathrm{Si_3AlO_{10}})(\mathrm{OH})_8\\&\quad + 5\,\mathrm{Mn_{0.4}Fe_{0.6}Al_2SiO_5(OH)_2} + 98\,\mathrm{SiO_2} + 15\,\mathrm{H_2O}.\end{aligned}$$

The Mn montmorillonite compositions used here are derived from chemical analyses of Mg montmorillonites (Weaver and Pollard, 1973) by replacing most of Mg by Mn (and Fe). By replacing the interlayer sodium by Mn in the hypothetical montmorillonite the amount of garnet, which is underrepresented in the breakdown assemblage cited above, compared to the modal analysis (Table 2), and the amount of paragonite, which is overrepresented, can be varied. It cannot be excluded that other Mn-rich silicate phases (especially Mn saponites) also occur in minor amounts in these reactions.

7. Mineralogy and Genesis of Mn Hydrosilicates in the Obrochishte Manganese Ore Deposit, Bulgaria

The Obrochishte manganese ore deposit, Bulgaria, situated northeast of Varna/Black Sea, is one of the few manganese deposits that has a mineralogic composition similar to that postulated for the coticule starting material. Its mineralogy will be described below to get a more precise idea of natural occurrences of Mn-bearing smectites that fit the composition of the coticule starting material. The genesis of this deposit, however, seems to be different from that proposed for the coticules, as will be shown in detail below.

The Obrochishte deposit, part of the northeast Bulgarian manganese mineralization, is a volcanosedimentary formation of Lower Oligocene age (Aleksiev and Bogdanova, 1974). Being intercalated in glauconitic sediments, there is no doubt about its marine origin. Beside minor amounts of allogenic minerals such as quartz, feldspars, epidote, garnet, muscovite (terrigenous) and volcanic glass, quartz, sanidine, biotite, amphibole (volcanoclastic), the mineralogic composition of this ore consists of authigenic minerals. In this regard manganese hydrosilicates, which are assumed to have been formed by coagulation of silica- and manganese-rich hydrothermal solutions, and calcite (sedimentary and biogenic), rhodochrosite (epigenetic and diagenetic), montmorillonite, phillipsite, glauconite, and pyrite (diagenetic) must be mentioned (Aleksiev and Bogdanova, 1974). Hydrothermal minerals such as alabandite and barite are rare. Both the terrigenous and the volcanoclastic minerals are sometimes altered and are often recognized only by their alteration products. However, since unaltered volcanic glass and other detrital minerals in the Mn-hydrosilicate precipitates can still be found, it must be assumed that the pyroclastics were not affected by the hydrosilicate formation.

Almost all the minerals with high manganese contents belong to the authigenic group. The main representatives are the Mn hydrosilicates and the Mn carbonates. Since the Mn carbonates, together with opal and an unspecified clay mineral, are formed from the Mn hydrosilicates by percolating waters in epigenetic or diagenetic processes (Aleksiev and Bogdanova, 1974), the Mn hydrosilicates must be regarded as the primary manganese minerals. Detailed studies have shown that the hydrosilicates are represented by a series of compositions, starting with neotocite (a strongly disordered Mn smectite), passing through a more or less ordered Mn–Mg sheet silicate and ending with a ordered Mn-bearing Mg smectite of saponite type (Puliev and Aleksiev, 1972). The special chemical compositions of these different Mn hydrosilicates are not given. Assuming a composition similar to the general compositions of Mg montmorillonite, Mn montmorillonite, saponite, and a saponitelike neotocite (Strunz, 1957), the hydrosilicate series plots into the system $MnO-(Mg, Fe)O-Al_2O_3-SiO_2$, traced out by the dotted planes in Figures 6 and 7. Excluding the almost Al-free, pure Mn saponites (neotocite) and Mg saponites, and, in case of the chloritoid assemblage of the coticules (Fig. 7) the almost pure Mn montmorillonites, Mn hydrosilicates with their chemical compositions in these planes can be regarded as possible coticule starting material. Coticule type 1 as well as the upper and lower parts of types 2 and 3 and the finely laminated spessartine rich intercalations within the type 3 point to a Mn montmorillonite, whereas the central quartzitic parts poorer in spessartine and richer in chlorite point to a magnesian montmorillonite.

8. Formation of the Coticule Source Material

Within the Salmian rocks, the coticules represent a repeated and sudden change in sedimentation. This change can only be interpreted by differences in material supply into the sedimentation basin. The environmental factors (E_h, p_H) cannot produce coticule source materials out of shales, since there is no suitable geochemical process known that carries away iron from manganese (and not vice versa) in sedimentary environments. Assuming a quite constant sedimentation rate for the Salmian shales, the sedimentation rate for the coticule source material must be different and very high, since a cosedimentation of shale and coticule material cannot be observed within the coticules. This is demonstrated by the general lack of hematite in the coticules.

Considering montmorillonite as a starting material of the coticules, the sudden changes in sedimentation can be explained by assuming volcanic tuffs to be deposited in the Salmian sedimentation basin. The largest part of these tuffs was deposited very quickly. Since the sedimentation rate of the shale source material was much lower than that of the tuffs, shale materials are diluted below the detection limit in the tuffs. Only the very fine particles of the tuffs sedimented more slowly and thus mixed with the continuously sedimenting shales to a larger extent. In addition, in these coticule-shale mixtures overlying the pure coticules, there should be coticule material redeposited from newly sedimented, but reworked beds, leaving, for example, lenticular coticule beds in the primary deposition site. Deposited in the marine Salmian environment, these volcanic tuffs were assumed to have been altered to montmorillonite assemblages by halmyrolysis.

Halmyrolytical processes are the weathering processes under submarine conditions (Hummel, 1922; Füchtbauer and Müller, 1970). Many of the known montmorillonite deposits have been formed out of volcanic tuff layers by this kind of alteration (Weaver and Pollard, 1973). Chemically, the dominant process during this alteration is the contemporaneous absorption of Mg and H_2O by the rocks out of the marine environment. Especially the presence of Mg seems to be of great importance for the stabilization of the montmorillonite lattice, since, under marine p_H-conditions (basic), aluminum prefers a tetrahedral coordination in silicate systems, thus preventing a montmorillonite formation (De Kimpe et al., 1961). Here Mg may be necessary to nucleate the octahedral lattice units.

In contrast to this process forming Mg montmorillonite, we have to assume a high participation of manganese in the montmorillonitization process of the coticule beds in the Venn-Stavelot area. This manganese was present in the Upper Salmian sedimentation basin as indicated by the high manganese contents of the Salmian shales. It can be discussed together with the proposed volcanism, since the contemporaneous occurrence of volcanic activity and manganiferous solutions is recorded for many localities (Berger, 1968). Contemporaneously occurring volcanics and manganiferous solutions are mentioned for the Obrochishte deposit, too. However, despite this similarity, it must be mentioned that the assumed process of montmorillonite formation for the coticule beds is distinctly different from that of the Obrochishte manganese hydrosilicates which are proposed to have been formed by coagulation (Aleksiev and Bogdanova, 1974). In the Obrochishte deposit are found unaltered volcanic minerals and even fresh volcanic glass within the manganese hydrosilicate layers.

Coticules of types 1, 2, and 3 are intercalated only in shales with oxidation ratios >90, whereas coticules of types 4 and 5 occur in shales more rich in divalent iron. Since there must be available divalent cations (Mg^{++}, Mn^{++}, Fe^{++}) in sufficiently large amounts for the montmorillonitization process, this relationship can be discussed in terms of the mobility of elements in the shale source material and the seawater under varying E_h–p_H conditions. In aqueous solutions the most mobile form of both manganese and iron is the divalent form (Garrels, 1960). Under low E_h–low p_H conditions both Fe^{++} and Mn^{++} can coexist. But since the oxidation potential of Fe^{++} is lower than that of Mn^{++}, there are E_h–p_H conditions under which manganese will remain in the divalent state while iron is oxidized and forms poorly soluble Fe^{+++} oxides and hydroxides. Now only manganese is in the mobile state and a separation of the two elements is possible, leaving iron insoluble in the residue (Krauskopf, 1957). Only under these conditions can Mn montmorillonite be formed by diffusion of manganese from the shale source material and the seawater into the volcanic tuffs during halmyrolytical processes. However, with decreasing E_h–p_H conditions in the aqueous environment, the formation of manganese montmorillonite becomes more difficult because of the increasing amount of migrating iron. Now an increasing amount of Fe^{++}-containing decomposition products of the tuffs can be formed. Finally, with an excessive supply of divalent iron, very iron-rich hydrosilicates can be formed, which may react to chloritoid-rich assemblages during the metamorphism.

The diffusion of manganese into the tuffs led to the formation of very thin and subparallel manganese montmorillonite layers in the central parts of type 3 coticules. They can be interpreted as Liesegang structures, formed by local conditions favorable for the montmorillonitization during the diffusion of the divalent manganese.

Summarizing the facts, volcanoclastic sediments as primary source material of the coticules are considered to be indicated by:

1. The generally very thin layers with large lateral extension.
2. The characteristic type of folding of the coticules, assumed to be generated by swelling processes.
3. The very abruptly changing chemical composition in the sedimentation sequence, especially with the beginning of the coticule source material sedimentation.
4. The metamorphic phase relations of the coticules, indicating a montmorillonitic starting material, which can be interpreted as a common alteration product of volcanic tuffs in marine environments.

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