Mineralogical and geochemical study of pseudocoticule from the Stavelot Massif, Ardennes (Belgium), and redefinition of coticule

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Abstract: A petrographic investigation of pseudocoticules from the Salm Valley, Belgium, shows that this type of rock is characterized by a quartz + spessartine + hematite assemblage. Spessartine grains can reach *ca.* 200 μm in diameter. The rocks directly in contact with the pseudocoticules are very rich in chloritoid and spessartine, thus showing that metasomatic processes affected the pseudocoticules at the end of the Variscan orogeny. Geochemical data indicate that Fe is higher in the host rocks than in the pseudocoticules, whereas Mn shows the inverse behaviour. Cu shows a significant increase in pseudocoticules when compared to the host rocks, thus indicating that pseudocoticules may be the source for the enrichment in exotic trace elements (Cu, Te, Mo, Bi, and Pb) observed in the quartz veins of the Salm Valley. The term coticule is redefined on an historical basis, as a yellow rock characterized by small spessartine grains ($\geq$85 mol. % Sps, 5–20 μm) included in a matrix containing large amounts of phyllosilicates. Whole-rocks analyses indicate ($K_2O + Na_2O$) $\geq$ 1 wt% and $Al_2O_3 \geq$ 15 wt%. Such a rock can be used as whetstone, whereas pseudocoticules, which contain larger amounts of quartz, do not show the same technical properties. Most samples from the literature, considered as coticules, rather correspond to pseudocoticules or to almandine-bearing quartzites.

Key-words: pseudocoticules, coticules, Stavelot Massif, Belgium.

1. Introduction

The term coticule designates an unusual type of rock used as whetstone, which has been extensively mined in the region of Recht-Vielsalm-Bihain (Stavelot Massif, Belgian Ardennes, see Fig. 1, deposited as supplementary material on the GSW website, http://eurjmin.geoscience.org) since the 18th century. The first petrographic description of coticule reported in the geological literature is the paper published by Renard (1878), dealing with an occurrence on the west bank of the Salm River near Vielsalm. Since this date, publication dealing with coticule problems has been relatively regular; the studies performed by Kramm (1976), Lamens *et al.* (1986), and Krosse & Schreyer (1993) are among the latest.

Coticule occurs as beige- to yellowish-coloured layers with a thickness of 1–10 cm, interbedded with purple metapelites of Lower Ordovician age. These metamorphic Mn-rich rocks contain abundant fine-grained spessartine (5–20 μm in diameter), dispersed in a matrix essentially composed of muscovite, with accessory quartz and chlorite (Kramm, 1976; Lessuise, 1980; Krosse & Schreyer, 1993).

Besides coticule *sensu stricto*, another type of spessartine-rich rock is also known in the Vielsalm-Salmchâteau area. These rocks occur as pinkish centimetre-sized layers interstratified with chloritoid-bearing schists, and contain large spessartine grains (up to 50 μm) embedded in a matrix essentially constituted by quartz (Theunissen, 1971; Bossiroy, 1984). These rocks are called pseudocoticule (Theunissen, 1971; Bossiroy, 1984; Hatert, 1996, 2005), and can not be used as whetstone due to the abundance of quartz.

At the present time, the term coticule is frequently used in the international literature to describe spessartine-bearing quartzites (Schiller & Taylor, 1965; Doyle, 1984; Spry & Wonder, 1989; Spry, 1990; Jiménez-Millán & Velilla, 1997; Willner *et al.*, 2001), or garnet-rich quartzites in general (Spry & Wonder, 1989; Spry, 1990; Thomson, 2001). Such quartzites rather correspond to pseudocoticules, according to the petrographic observations of the rocks from the Salm Valley, where the term coticule was historically defined. It is noteworthy that in the literature several massive sulphide deposits are closely associated with pseudocoticules or spessartine quartzites, as for example the deposit associated with the Leinster granite, Ireland (Kennan *et al.*, 1986), or the Broken Hill deposit, New South Wales, Australia (Spry & Wonder, 1989).

The aim of the present paper is to present a petrographic and geochemical study of pseudocoticules from the Salm Valley, in contrast to the ''classical'' coticules from the same area, and to confirm both the unusual geochemistry and genesis of these rocks. These observations will also allow the distinction between coticule and pseudocoticule to be specified, and to redefine the term coticule on the basis of historical backgrounds.
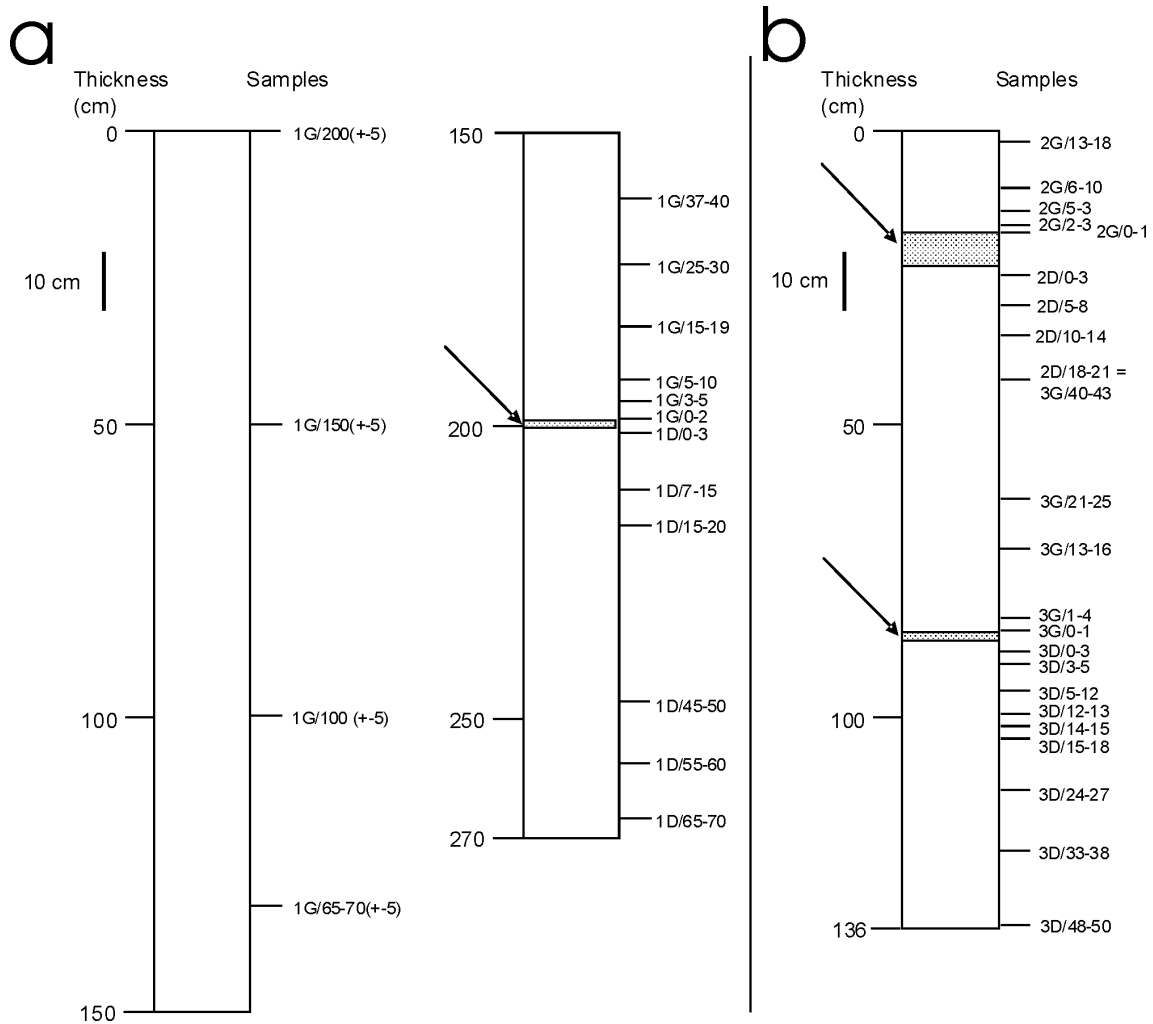
Fig. 2. Lithological profiles of the two pseudocoticule outcrops in ''Thier des Carrières'' at Cahay, Salm Valley. a. profile #1. b. profile #2.

2. Historical definition of coticule and pseudocoticule

The term ''coticule'' is derived from the Latin *coticulam,* a word which was already used by Plinius in his book *Naturalis Historia* dated from the 1st century AD (Lamens & Geukens, 1984; Goemaere *et al.*, 2009). This term designates a type of rocks which was found by Theophrastus (Greek scientist, 4th century BC) in the Tmolus river, and was also called ''Lydian rock''. This touchstone corresponds to a dark radiolarian chert, which was used to determine the fineness of gold and silver coins (Lamens & Geukens, 1984). Even if the Belgian coticule does obviously not correspond to this black chert, it seems that the term *coticulam* may be a generic word for either whetstone or touchstone in general, thus explaining the origin of the name ''coticule''.

Even if coticule was probably mined before the 17th century (Lejeune, 1982), the first coticule description was written by Christophe de Gernichamp (Fraipont, 1911),

who in 1625 mentions the existence of high-quality yellowish whetstones in the Salm valley, which were extracted and exported to Frankfurt and Venice. During the 18th and 19th centuries, coticule became famous and was exported to many parts of the world, resulting in the opening of new quarries in the Recht-Vielsalm-Bihain area. After the Second World War, cheaper artificial whetstones, modern sharpening processes, and also disposable and electric razors appeared. The coticule industry began to decrease slowly; today only the quarry ''Thier del Preu'' near Lierneux (Fig. 1) is still active.

In the Salm valley also exists another type of spessartine-bearing rocks occurring as pinkish centimetre-sized layers enclosed in chloritoid-bearing schists. Due to the large size of the spessartine grains and to the high quartz abundance in this rock, it was not suitable to manufacture whetstones, and the miners called it *cresse* meaning *filth* in local Walloon language. This rock is consequently distinct from coticule, and was described by Belgian geologists as pseudocoticule (Theunissen, 1971; Bossiroy, 1984; Hatert, 1996, 2005).

3. Geological setting and sampling

The Stavelot Massif, Belgian Ardennes, represents a large block of Cambro-Ordovician metasediments (Fig. 1) belonging to the Caledonian basement of the Rhenohercynian orogenic belt. There is an angular unconformity between the Ordovician and the overlying Devonian, Carboniferous and Permian rocks.

Although the existence of a Caledonian metamorphic event in the Stavelot Massif area is still a matter of debate (Kramm *et al.*, 1985; Ferket *et al.*, 1998), clear evidence for Hercynian metamorphism exists (*e.g.*, Schreyer, 1975), which is responsible for the crystallization of the metamorphic minerals observed in schists and quartz veins. The presence of andalusite, chloritoid and spessartine, as well as the phengite contents of the white K-micas, permit *P-T* conditions of 2 kbar/360–420°C to be estimated in the southern border of the massif (Kramm, 1982; Kramm *et al.*, 1985).

The quartz veins crystallized at the end of the Hercynian metamorphic phase. Fluid circulation through rock fractures, coupled with metasomatic processes, resulted in the concentration of numerous chemical elements, such as Mn, Ba, Cu, V, or Mo, within the quartz veins (Michot, 1954; de Béthune & Fransolet, 1986; Hatert, 1996). This explains the diversity of minerals discovered in this area (Hatert *et al.*, 2002).

Localized in the SE zone of the massif, the Salm syncline provides a geological profile in metapelites of the Salm Group (formerly Salmian, abbreviated Sm) of Lower Ordovician age, between Vielsalm and Salmchâteau (Verniers *et al.*, 2001; Fig. 1). The Ottré Formation (Sm2) belongs to this group, and is subdivided into three Members: the Meuville Member (Sm2a), the Les Plattes Member (Sm2b), and the Colanhan Member (Sm2c). The Les Plattes Member consists of red to purple schists, rich in andalusite, in which coticule is interlayered. The Colanhan Member is constituted by chloritoid-bearing schist containing the pseudocoticule layers (Geukens, 1999).

Different hypotheses have been proposed for the genesis of the coticule protolith, including clastic sedimentation of clay (Macar, 1973), sedimentation of glassy volcanic tuffs later halmyrolysed into Mn-rich montmorillonite (Kramm, 1976), or chemical deposition of manganese carbonates together with the clay fraction as in the case of calcite in marls (Lamens & Geukens, 1984). The hypothesis of a rhodochrosite precursor for spessartine was suggested by Lamens *et al.* (1986), and later confirmed by Schreyer *et al.* (1992), who observed rhodochrosite inclusions within spessartine crystals of the coticule. On the basis of a detailed geochemical investigation, Krosse & Schreyer (1993) demonstrated that both coticule and their enclosing redschists are constituted by the same type of clastic material formed by the same sedimentation process. Moreover, they concluded that the enrichment in Fe and Mn in these rocks was due to submarine hydrothermal exhalations. The inverse correlation between MnO, responsible for the crystallisation of spessartine in coticules, and Fe₂O₃, responsible for the crystallisation of hematite in the enclosing redschists, can be explained by different models (Krosse

Table 1. Average chemical analyses of chloritoid-bearing schists (28 samples) and pseudocoticules (14 samples) from the Salm Valley.

Wt%	Chloritoid schists			Pseudocoticules		
	Av.	Max	Min	Av.	Max	Min
SiO_2	54.54	56.52	52.64	66.60	82.43	51.27
TiO_2	1.00	1.06	0.93	0.48	0.83	0.32
Al_2O_3	23.05	23.61	22.03	11.35	16.24	6.31
$Fe_2O_3{}^a$	12.82	14.99	10.78	3.59	5.45	2.66
MnO	0.89	1.36	0.65	16.60	25.44	8.58
MgO	1.85	2.22	1.47	0.75	1.01	0.44
CaO	0.26	0.31	0.17	0.69	0.99	0.41
Na_2O	1.17	3.04	0.93	0.10	0.21	0.00
K_2O	3.68	3.89	3.39	0.07	0.50	0.00
P_2O_5	0.14	0.18	0.08	0.05	0.08	0.00
Total	99.40			100.30		
ppm						
Rb	177	185	167	8	17	0
Sr	256	294	218	8	30	3
Y	33	38	31	15	25	10
Zr	140	149	134	70	110	44
Nb	17	19	16	5	13	2
Th	15	17	12	2	15	0
Cu	23	58	14	939	4587	11
Ni	72	79	58	0.5	5	0
Zn	115	137	91	42	67	18
Ga	–	–	–	7	12	2
Co	–	–	–	13	27	5
Pb	–	–	–	14	35	6
U	–	–	–	11	25	2
V	–	–	–	199	304	130
Cr	–	–	–	32	40	21
S	–	–	–	134	879	0

[a] All iron occurs as Fe_2O_3, due to the preliminary calcination (1000 °C) of the samples.
–: Not determined.

& Schreyer, 1993), such as periodic variations of Eh-pH conditions (Krauskopf, 1957; Bonatti *et al.*, 1972) or precipitation of Mn-rich solutions by the action of bacteria (Campbell *et al.*, 1988).

The samples of pseudocoticule and chloritoid-bearing schist investigated herein were collected in two profiles located in the old quarries of the "Thier des Carrières" at Cahay, near Vielsalm. The first profile of 270 cm length contains one pseudocoticule layer reaching 1 cm in thickness (Fig. 2a), while the second profile of *ca.* 140 cm length contains two pseudocoticule layers reaching 5.5 and 1.5 cm in thickness, respectively (Fig. 2b). Five additional pseudocoticule samples were collected along the road close to the railway bridge at Vielsalm, as well as in the "Old Rock" mine located in the same village.

4. Analytical methods

Forty-four samples have been selected for geochemical analyses (tables with the chemical analyses of all samples are

Table 2. Mineral content of pseudocoticules (P) and chloritoid-bearing schists (S) from the Cahay profiles.

Sample #	Quartz	Spessartine	Chloritoid	Mica	Chlorite	Hematite	Rutile	Recrystallized pellets
1 (P)	XXXX	XXXX		X	X	XX	X	
1G/0–2 (S)	X	XXX	XX	XXX	XX	X	X	XX
1G/3–5 (S)	X	XXX	XX	XXXX	X	XX	X	
1G/5–10 (S)	X	XX	XXX	XXXX	X	XXX	X	
1G/15–19 (S)	X		XXX	XXXX	XX	XXXX	X	X
1G/25–30 (S)	X		XXX	XXXX	X	XXX	X	XX
1G/37–40 (S)	X		XXX	XXXX	XX	XXXX	X	X
1G/65–70 (S)	X		XX	XXXX	X	XXX	X	
1G/100 (S)	X		XX	XXXX	X	XXX	X	
1G/150 (S)	X	XX	XXX	XXXX	X	XXX	X	XXX
1G/200 (S)	X	XX	XXX	XXXX	X	XXX	X	XX
1D/0–3 (S)	XX–X	XXXX–XXX	XXXX–XXX	X–XXX	XXX	X–XX	X	
1D/7–15 (S)	X	XX	XXX	XXXX	X	XXX	X	
1D/15–20 (S)	X		XXX	XXXX	X	XXX	X	
1D/45–50 (S)	X		XXX	XXXX	X	XXX	X	XX
1D/55–60 (S)	X		XX	XXXX	XX	XXXX	X	X
2G/2–3 (S)	XX	XXX–XX	XXXX	XX	X	XX–XXX	X	
2 (P)	XXXX	XXXX		X	XX	XXX	X	
2D/0–3 (S)	XX	XXXX–XXX	XXX	XX–XXX	X	X–XX	X	
3G/1–4 (S)	X	XXX–X	XX–XXX	XXX	X	X–XXX	X	
3G/13–16 (S)	X		XXX	XXXX	X	XXX	X	
3 (P)	XXXX	XXXX		X	XXX	XXX	X	
3 (S)	XX	XXXX	XXXX–XXX	X–XXX	XX	X–XX	X	X
3D/0–3 (S)	X	XXXX	XXX	XXX	X	XX	X	XX
3D/5–12 (S)	XX	X	XXX	XXXX	XX	XXX	X	
3D/33–36 (S)	X	X	XXX	XXXX	XX	XXX	X	

XXXX = dominant mineral, XXX = abundant mineral, XX = less abundant mineral, X = accessory mineral.

available at the editorial office in Paris upon request; average chemical data are summarized in Table 1). All the samples were manually crushed with a hammer and milled in agate mortars. Whole-rock compositions were obtained for major oxides (SiO_2, Al_2O_3, TiO_2, Fe_2O_{3total}, MnO, MgO, CaO, Na_2O, K_2O, P_2O_5, LOI) and some trace elements (Rb, Sr, Y, Zr, Nb, Co, Cu, Ga, Ni, Zn, Ba, Cr and V) by X-ray fluorescence with an ARL 9400XP spectrometer. Major elements were measured on lithium tetra- and meta-borate-fused glass discs, with matrix corrections following the Traill-Lachance algorithm. Trace elements were measured on pressed powder pellets and data were corrected for matrix effects by Compton peak monitoring. Accuracy is estimated as better than 1 % for major elements and 5 % for trace elements, and was controlled using 40 international and in-house standards.

The mineralogical content of the samples (Table 2) was determined by observation of thin sections under the polarizing microscope, and by powder X-ray diffraction using a Panalytical PW 3710 diffractometer (Fe$K\alpha$ radiation, λ = 1.9373 Å).

Quantitative chemical analyses were performed with a Cameca SX-100 electron microprobe (Stuttgart, Germany) operating in the wavelength-dispersion mode, with an accelerating voltage of 15 kV, a beam current of 10 nA, and a beam diameter of 5 μm. The following standards were used: graftonite (P), wollastonite (Si, Ca), corundum (Al), periclase (Mg), sphalerite (Zn), hematite (Fe), rhodonite (Mn), albite (Na), and orthoclase (K).

5. Petrographic description, mineralogy, and geochemical data

Pseudocoticules show a typical pinkish colour and contain an assemblage characterized by the presence of spessartine, quartz, hematite, as well as accessory mica and rutile (Fig. 3a). Some veinlets containing quartz and clinochlore (Table 3) frequently cross-cut the pseudocoticule layers. Spessartine forms small rounded grains reaching 50 μm in the pseudocoticules, but larger crystals reaching 200 μm are observed in the quartz veinlets (Fig. 3b). These large crystals probably result from a re-crystallization process (see below). The electron-microprobe analyses of spessartine (Table 3) show a chemical composition with *ca.* 91 mol. % spessartine, close to the composition of garnets occurring in similar pseudocoticule layers from the Vielsalm-Salmchâteau region (89 % Sps, sample FOSS-02, Hermann, 2004). The proportions of hematite vary significantly, but are always lower than those of quartz and garnet. Hematite forms red anhedral crystals which are intimately disseminated between the garnet grains (Fig. 3a). These red crystals are responsible for the pinkish colour of pseudocoticule. Anhedral grains of quartz constitute the matrix of the pseudocoticules; they can reach 10–50 μm in diameter.

The chloritoid-bearing schists, in which the pseudocoticule layers occur, are characterized by the assemblage mica + chlorite + hematite (5–10 %) + chloritoid
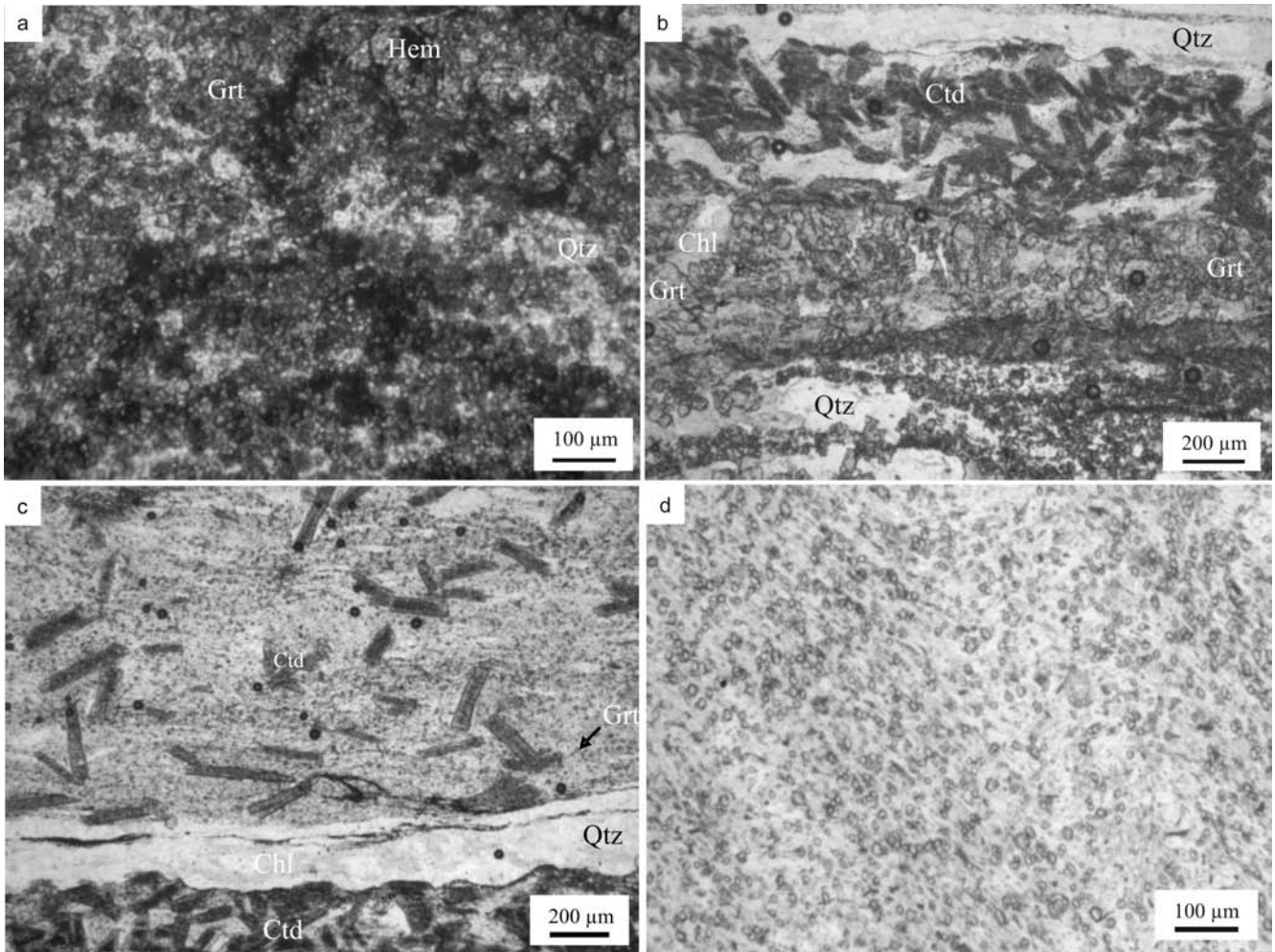
Fig. 3. (a) Assemblage spessartine + quartz + hematite in pseudocoticule. Plane polarized light, sample 1, Cahay, Salm Valley. (b) Pseudocoticule veinlet with large spessartine grains, showing the contact with a millimetre-sized layer almost exclusively constituted by chloritoid. A quartz veinlet occurs on the top of the photograph. Plane polarized light, sample 1D/0–3, Cahay, Salm Valley. (c) Assemblage of the contact zone with a quartz + chlorite vein cross-cutting a millimetre-sized layer almost exclusively constituted by chloritoid. Hematite inclusions and later rims on chloritoid are clearly observed. Plane polarized light, sample 1D/0–3, Cahay, Salm Valley. (d) Assemblage spessartine + phyllosilicates in coticule. Plane polarized light, sample L2, Moët-Fontaine, Lienne Valley. Ctd = chloritoid, Chl = chlorite, Grt = spessartine garnet, Hem = hematite, Qtz = quartz.

(10–20 %), with accessory quartz and rutile. Chloritoid crystals are idiomorphic, show a rectangular shape, and reach 200 μm in length (Fig. 3c). They exhibit a greenish colour, contain minute inclusions of hematite and do not show any zonation. The chloritoid-bearing schists show millimetre-scale layering due to the alternation between zones enriched in hematite and zones relatively poor in this mineral. Hematite forms small opaque grains (<50 μm) which follow the cleavage and surround the porphyroblasts of chloritoid. Mica occurs in the matrix of this rock, and is also the main constituent of concentric structures reaching 200 μm in diameter, interpreted by Bossiroy (1984) as relics of sedimentary pellets affected by metamorphism.

The contact zone between the pseudocoticule and the host rocks exhibits an intermediate mineralogy between those of both types of rocks. Moreover, the walls show an interesting mineral zonation. A millimetre-sized layer almost exclusively composed of chloritoid and small spessartine grains reaching 10 μm occurs directly at the contact between pseudocoticules and schists. Then, the mineral proportions progressively reach the composition of the chloritoid-bearing schists, with the disappearance of spessartine, a decrease in chloritoid, and an enrichment in hematite. It is noteworthy that the contact zone and the chloritoid-bearing schists do not show the same colour: the green colour of the contact zone is due to its high content in green chloritoid, whereas the purplish colour of the chloritoid-bearing schists is due to their high content in hematite. Chloritoid occurring in the contact zone shows a zonation characterized by a limpid pleochroic rim (yellow to green) surrounding a core which contains minute inclusions of hematite (Fig. 3b, c). However, this zonation is not obvious in the electron-microprobe analyses, which show a uniform composition of chloritoid particularly enriched in MnO and in MgO (Table 3). Electron-microprobe analyses of spessartine from the contact zone indicate a significant enrichment

Table 3. Electron-microprobe analyses of minerals occurring in pseudocoticules and in the contact zone rocks from Cahay.

	Garnet Ps (34)	Garnet contact (16)	Chloritoid contact (25)	Muscovite contact (10)	Clinochlore qtz vein (21)
SiO_2	35.43	36.03	25.08	44.59	26.05
P_2O_5	0.30	0.03	0.05	0.02	0.01
Al_2O_3	20.55	20.78	40.74	36.73	25.27
Fe_2O_3[a]	3.19	2.25	1.55	–	–
FeO[a]	0.30	3.80	12.42	1.74	11.94
MgO	0.32	0.56	4.09	0.61	21.97
MnO	39.55	36.03	9.08	0.67	1.98
ZnO	0.01	0.02	0.06	0.00	0.15
CaO	1.40	1.07	0.01	0.12	0.02
Na_2O	0.01	0.02	0.01	2.44	0.01
K_2O	0.00	0.08	0.01	7.14	0.00
H_2O[b]	–	–	7.39	4.47	12.11
Total	100.76	100.56	100.50	98.53	99.50
Cation numbers					
Si	2.898	2.934	2.035	2.988	2.580
P	0.002	0.002	0.003	0.001	0.001
Al	0.100	0.064	–	1.012	1.419
Σ	3.000	3.000	2.038	3.000	4.000
Al	1.881	1.936	3.897	1.889	1.000
Fe^{3+}	0.119	0.064	0.095	–	–
Fe^{2+}	–	–	–	0.098	–
Mg	–	–	–	0.061	–
Σ	2.000	2.000	3.992	2.048	
Al	–	–	–	–	0.531
Fe^{3+}	0.077	0.074	–	–	–
Fe^{2+}	0.020	0.259	0.843	–	0.989
Mg	0.039	0.068	0.495	–	3.244
Mn	2.740	2.492	0.624	0.039	0.166
Zn	0.001	0.001	0.003	0.000	0.011
Ca	0.122	0.094	0.001	0.009	0.002
Na	0.001	0.004	0.002	0.317	0.002
K	0.000	0.008	0.001	0.611	0.002
Σ	3.000	3.000	1.969	0.976	4.947

Analyst: T. Theye. The number of analyses is indicated in parentheses.
Cation numbers were calculated on the basis of 8 cations (garnet, chloritoid), 12 (O, OH) (muscovite), 18 (O, OH) (clinochlore).
[a]FeO and Fe_2O_3 contents were calculated to maintain the charge balance.
[b]H_2O contents were calculated according to the ideal formulae of the minerals.

in FeO, when compared to spessartine from the pseudocoticule (Table 3, Fig. 4). This enrichment is probably due to the composition of the contact zone, which is significantly richer in Fe than the pseudocoticules (Table 1).

Average geochemical data for the two profiles analyzed in the Salm Valley are presented in Table 1. The composition of the chloritoid-bearing schists is close to that of the redschists from Ottré (Krosse & Schreyer, 1993), with SiO_2, Al_2O_3 and Fe_2O_3 reaching *ca.* 50–55, 20–25, and 10–15 wt%, respectively. In the pseudocoticules, however, the Fe_2O_3 content decreases below 5 wt%, MnO increases to *ca.* 10–25 wt%, Al_2O_3 drops below 15 wt%, and SiO_2 increases up to *ca.* 65 wt% (Table 1). TiO_2, MgO, P_2O_5, Na_2O and K_2O decrease significantly in the pseudocoticule, whereas CaO increases from 0.26 to 0.69 wt% (Table 1). Trace elements show a decrease in pseudocoticule, except for Cu which increases significantly up to 939 ppm (Table 1, Fig. 5).

6. Discussion

6.1. Late metasomatic remobilization processes

Thin section examination in pseudocoticules and in rocks from the contact zone indicates that both were affected by significant later mineralogical modifications. Bossiroy (1984) already suggested a complete re-crystallisation of pseudocoticule to explain the large size of the spessartine grains observed in this rock. The contact zone was also affected by this re-crystallisation process, as shown by the abundance of chloritoid and spessartine in the vicinity of the pseudocoticule (Fig. 3b), by the presence of chloritoid rims surrounding the hematite-rich chloritoid cores (Fig. 3c), and by the disappearance of schistosity. These modifications in the contact zone of the pseudocoticule are similar to those previously observed by de Béthune & Fransolet (1986) in the schists directly in contact with the
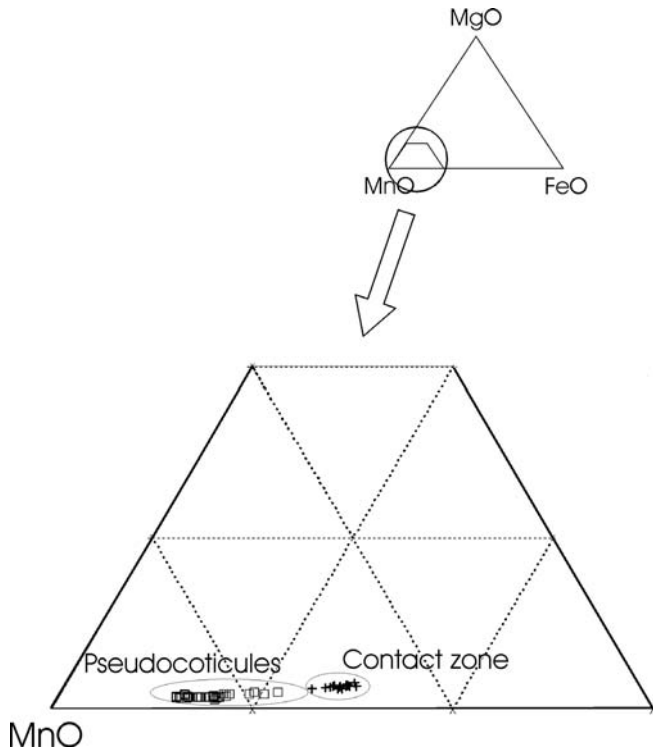
Fig. 4. Ternary MnO-MgO-FeO diagram (wt%) showing the compositions of spessartines from the pseudocoticules (squares) and from the contact zone (crosses), Cahay.

quartz vein of Ottré. The disappearance of schistosity indicates that the fluid migration responsible for these re-crystallisation processes took place after the Variscan deformational peak. However, the pressure and temperature conditions were still sufficiently high to induce the crystallisation of Mn-bearing chloritoid and spessartine, thus showing that these processes took place shortly after the Variscan metamorphic peak.

These re-crystallisation processes, which affect the contact zone over a thickness of *ca.* 10 cm, are due to the metasomatic migration of elements, necessary to reduce the chemical disequilibrium existing between the pseudocoticule and its host rocks. The spider diagram of Fig. 5, in which samples compositions were normalized to the unaffected schist composition, shows that the trace elements of samples from the contact zone and from pseudocoticules exhibit complementary trends whose amplitude decreases towards the schists. This behaviour confirms the geochemical imprint of pseudocoticules on the contact zone rocks.

In order to assess the mobility of chemical elements in the contact zone, we established correlations between pairs of major elements. These correlations are generally poor for K_2O, Na_2O, CaO, Fe_2O_3, MnO, MgO, P_2O_5, and SiO_2, with correlations coefficients between 0.00 and 0.79, demonstrating the mobile status of these elements. On the other hand, the correlation between TiO_2 and Al_2O_3 is excellent (Fig. 6), indicating that the TiO_2/Al_2O_3 ratio is
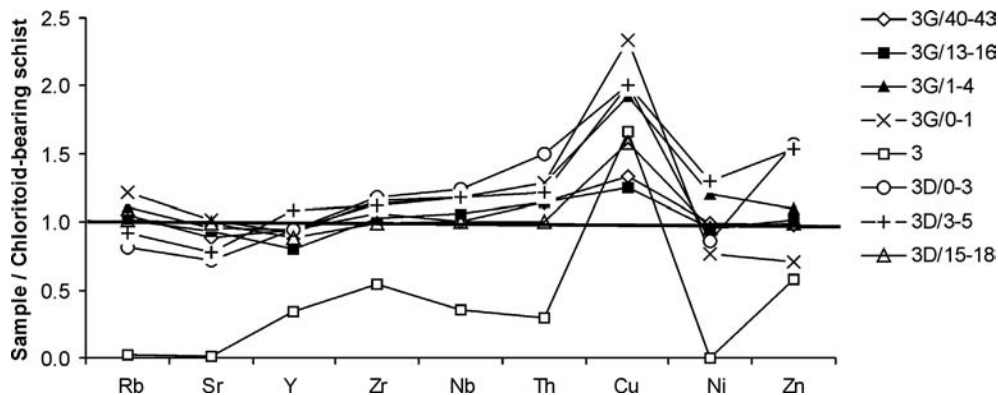

Fig. 5. Spider diagram showing the trace elements behaviour in pseudocoticules and in the host rocks, Cahay. Samples compositions were normalized to the unaffected chloritoid-bearing schist composition.
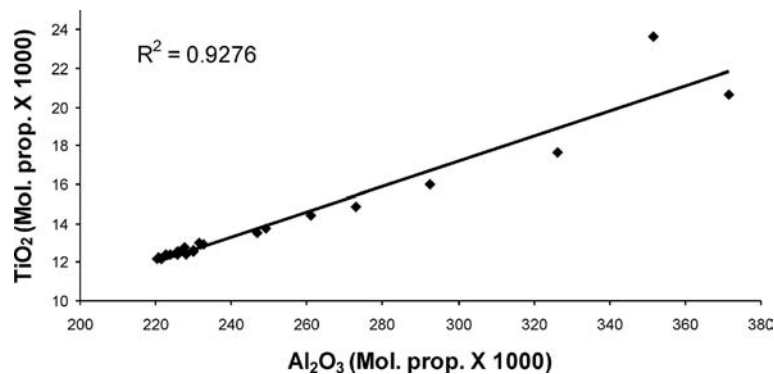

Fig. 6. Correlation between TiO_2 and Al_2O_3 (mol. prop. $\times$ 1000), for the samples of schists hosting the pseudocoticule veins, Cahay.
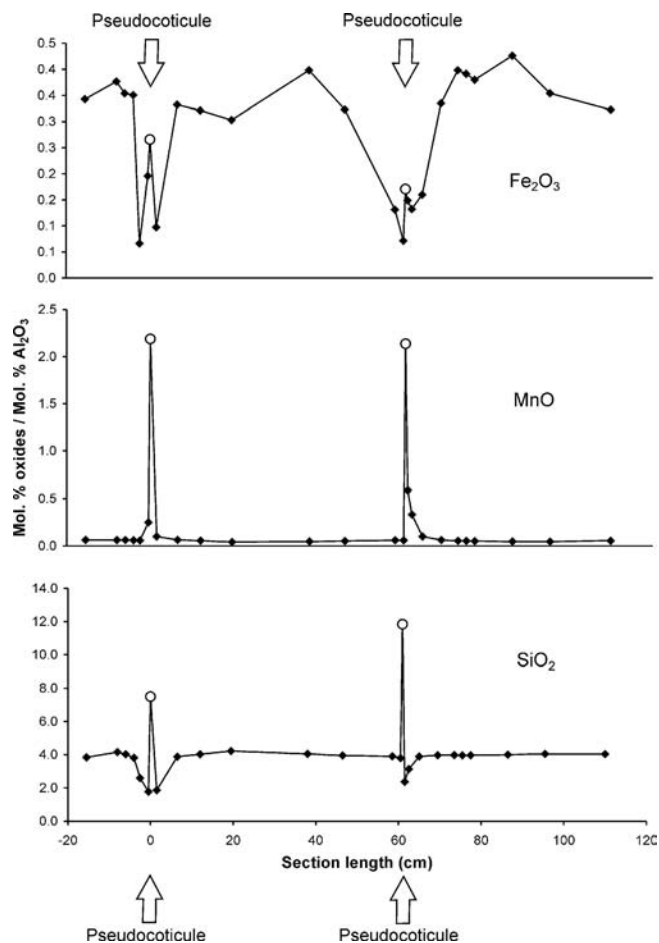
Fig. 7. Variation of the Fe_2O_3, MnO, and SiO_2 contents (Mol. % oxides/Mol. % Al_2O_3) along the second pseudocoticule profile, Cahay, Salm Valley.

Fig. 8. Variation of trace element contents along the first pseudocoticule profile, Cahay, Salm Valley.

constant in all investigated samples, and that these elements are consequently immobile. In the following discussion, the contents in major elements were normalized to immobile Al_2O_3.

The Fe_2O_3 contents show a progressive decrease in the contact zone and an increase in pseudocoticule (Fig. 7), indicating a migration of Fe from the contact zone to the pseudocoticule in order to reach chemical equilibrium. This geochemical feature explains the disappearance of hematite in the contact zone, as shown by the green colour of these rocks. The SiO_2 contents show a similar behaviour, whereas MnO increases progressively in the contact zone and in pseudocoticule (Fig. 7). This increase is due to a migration of Mn from the pseudocoticule to the contact zone, which is responsible for the re-crystallization of chloritoid rims and of spessartine.

The coticules from the Lienne and Salm Valley do not show any petrographic or geochemical evidence of these re-crystallisation processes, as already shown by Krosse & Schreyer (1993) and by Baijot (2008). The presence of fluid migration in pseudocoticule, but not in coticule, can probably be explained by the different permeability of these two types of rocks. Pseudocoticule was porous due
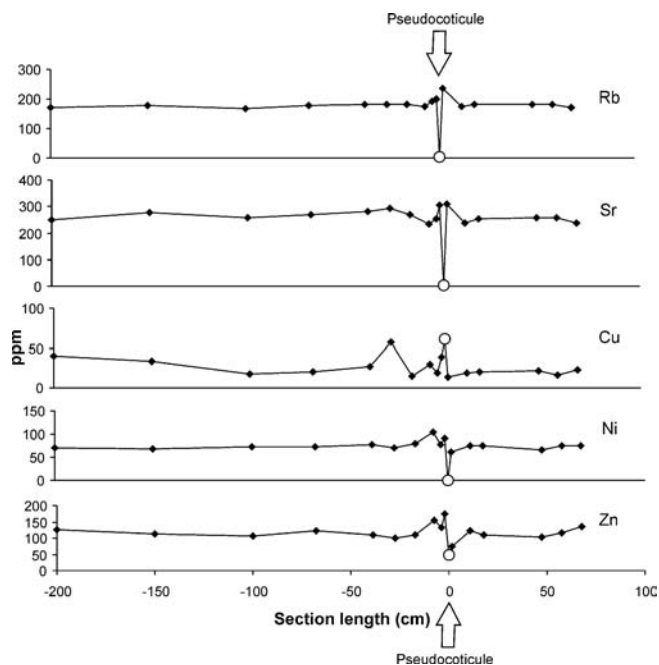
to his high quartz content, whereas coticule was certainly less porous due to its high content in phyllosilicates. The weak permeability of the chloritoid-bearing schists, due to their high contents in phyllosilicates, could also explain the limited lateral extension of the metasomatic processes affecting the contact zone of the pseudocoticules.

6.2. The origin of copper in the Salm valley mineralizations

The trace elements are lower in the pseudocoticules when compared to the host rocks except for Cu, which is significantly higher in the pseudocoticules (Fig. 8). This high Cu content, which is due to the presence of chalcocite and can reach more than 4500 ppm Cu, could confirm the hypothesis of Hatert (2005), who tentatively suggested that pseudocoticules could be the source for the trace elements Cu, Mo, Te, Pb, and Bi that occur in the quartz veins of the Vielsalm-Salmchâteau area. However, it is very difficult to determine unambiguously the source of these trace elements, since the remobilization processes could also have been responsible for the high Cu contents in the pseudocoticules.

6.3. Redefinition of coticule

Historically, the term coticule was defined in the Salm valley, where it designates a yellowish spessartine-bearing rock that can be used as a whetstone. However, Doyle (1984), on the basis of his study of spessartine quartzites from Ireland, suggested to use the term coticule for any rock containing more than 20 % spessartine. As a consequence,

Table 4. Petrographic description of coticules suitable for whetstones and pseudocoticules from the literature.

| Reference	Location	Main minerals	Accessory minerals	Garnet composition (size)	Colour of rock
Coticules					
Renard (1878)	Salm valley, Belgium	Spessartine, muscovite	Quartz, tourmaline, hematite	Spessartine (< 20 μm)	Whitish yellow
Kramm (1976)	Salm valley, Belgium	Spessartine, phengitic micas, quartz	Paragonite, chlorite	Spessartine (0.4–5 μm)	Yellow to white
Lessuise (1980)	Salm valley, Belgium	Spessartine (20–80 %), muscovite, quartz, chlorite	Rutile, hematite, tourmaline, andalusite, kaolinite	Spessartine (5–20 μm)	Creamy yellow
Lamens & Geukens (1984)	Salm valley, Belgium	Spessartine, mica	Quartz	n.g.	Pale yellow
Lamens et al. (1986)	Salm valley, Belgium	Spessartine (40 %), mica (30 %), quartz (30 %)	Hematite	Spessartine (< 20 μm)	Yellow
Schreyer et al. (1992)	Salm valley, Belgium	Spessartine, muscovite, chlorite, quartz	Hematite	n.g.	n.g.
Krosse & Schreyer (1993)	Salm valley, Belgium	Spessartine, muscovite, quartz, chlorite, paragonite	Tourmaline, zircon, hematite	n.g.	Yellow to beige
Baijot (2008)	Salm valley, Belgium	Spessartine, mica	Chlorite, quartz, hematite	Spessartine (< 50 μm)	Creamy yellow
Other similar rocks					
Schiller & Taylor (1965)	Nova Scotia, Canada	Spessartine, quartz	Chlorite, calcite, muscovite	Spessartine (10–100 μm)	Orange pink
Theunissen (1971)	Salm valley, Belgium	Spessartine, quartz	Paragonite, muscovite	Spessartine (100μm)	Pink
Bossiroy (1984)	Salm valley, Belgium	Spessartine, quartz	Paragonite, muscovite	Spessartine (100μm)	Pink
Spry & Wonder (1989)	Broken Hill, Australia	Quartz, garnet (10–80 %), biotite, muscovite, gahnite, orthoclase, plagioclase, cordierite	Amphiboles, sulfides, dyscrasite, fluorite, hedenbergite, ilmenite, orthoclase, löllingite, magnetite, staurolite, talc, wollastonite, zoiste	Almandine, spessartine, grossular (0.1 mm to 1 cm)	Orange brown to pink (garnet colour)
Kennan & Murphy (1993)	Bellewstown, Ireland	Garnet, chlorite, quartz, mica	Magnetite	n.g. (100 μm)	n.g.
Jiménez-Millán & Velilla (1997)	Ossa-Morena belt, Spain	Spessartine, quartz, dannemorite	Hematite, zircon, magnetite, tourmaline	Spessartine (25–100 μm)	Yellow
Thomson (2001)	New England Appalachians	Almandine (45–65 %), quartz	Biotite, apatite, ilmenite, tourmaline, rutile	Almandine (< 0.5 mm)	Pink
Willner et al. (2001)	Bahia Mansa, Chile	Quartz, spessartine, stilpnomelane	Muscovite, chlorite, amphibole, titanite, pyrite, albite, apatite, epidote, calcite, siderite	Spessartine (< 80 μm)	n.g.
This work	Salm valley, Belgium	Quartz, spessartine	Hematite, mica, rutile	Spessartine (50–200 μm)	Pinkish

n.g.: not given
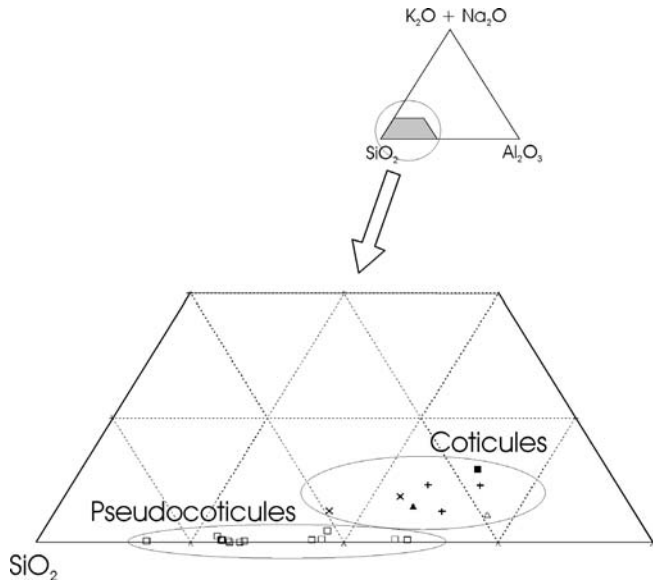
Fig. 9. Ternary (K_2O + Na_2O)-Al_2O_3-SiO_2 diagram showing the compositions (wt%) of pseudocoticules and coticules from the Stavelot Massif, Belgium. Open squares: pseudocoticules from the Salm valley (this work), vertical crosses: coticules from the Lienne valley (Baijot, 2008), diagonal crosses: coticule from the Salm Valley (Kramm, 1976), open triangle: coticule from the Salm valley (Lamens *et al.*, 1986), closed triangle: coticule from the Salm valley (Krosse & Schreyer, 1993), closed square: coticule from the Salm valley (this work).
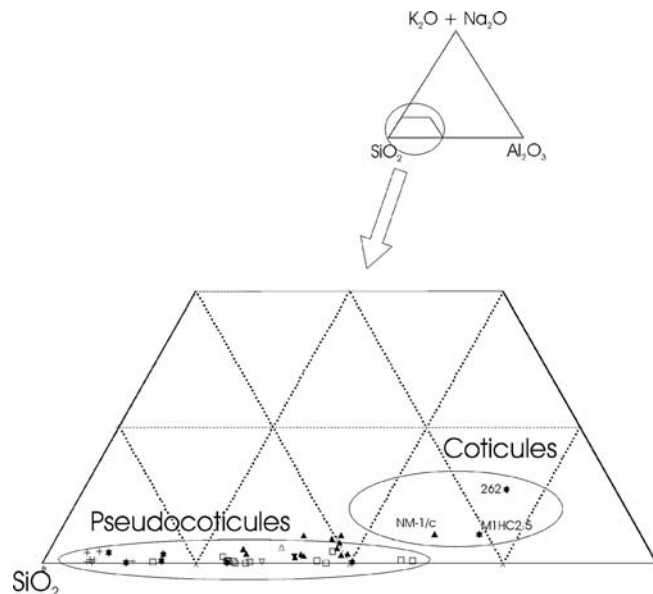

Fig. 10. Ternary (K_2O + Na_2O)-Al_2O_3-SiO_2 diagram showing the compositions (wt%) of pseudocoticules and coticules from the literature. Stars: Spry (1990), crosses: Willner *et al.* (2001), open triangles: Wonder et al. (1988) and Spry & Wonder (1989), closed triangles: Thomson (2001) and Bjerkgard & Bjorlykke (1996), open squares: pseudocoticules from the Salm valley (this work).
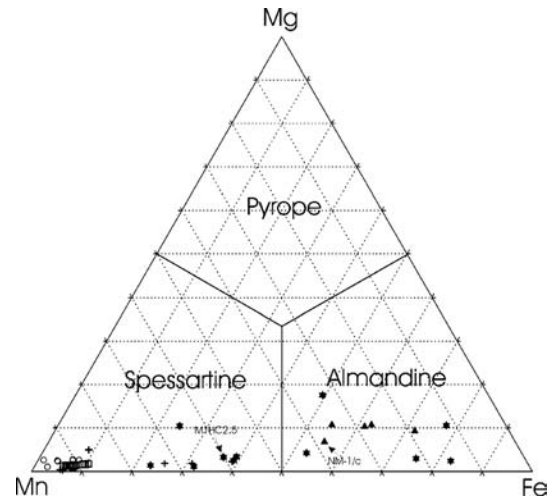

Fig. 11. Ternary MnO-MgO-FeO diagram showing the compositions (mol. %) of garnets from the literature and from Cahay. Open squares: spessartine from pseudocoticules, Cahay (this work), open circles: spessartine from coticules, Salm valley (Kramm, 1976; Schreyer *et al.*, 1992), crosses: Willner *et al.* (2001), closed triangles: Thomson (2001), stars: Spry (1990).

the term coticule is at present used in the international literature to designate spessartine-bearing quartzites in general, without any reference to the material and the localities where this type of rock was originally named and defined.

The petrographic descriptions of whetstone-type coticules from the Salm valley are summarized in Table 4, where it clearly appears that these rocks contain small spessartine grains (5–50 µm) included in a matrix mainly composed of muscovite and quartz. The presence of a significant amount of phyllosilicates in the matrix is necessary to give the material its unique properties as a coticule; this was already observed by the miners who knew that quartz-rich layers were not suitable for obtaining efficient whetstones. Pseudocoticules, which are dominated by spessartine + quartz and lack significant phyllosilicates (Theunissen, 1971; Bossiroy, 1984; this work), are clearly distinct from coticules from a petrographic point of view (Table 4), and can not be used for the manufacture of whetstones.

Table 4 also lists petrographic descriptions of rocks which were named coticules in the literature. However, these rocks generally contain high amounts of quartz (Schiller & Taylor, 1965; Spry & Wonder, 1989; Jiménez-Millán & Velilla, 1997; Thomson, 2001; Willner *et al.*, 2001), indicating that they correspond to pseudocoticule rather than to coticule.

In order to clearly define the boundary between pseudocoticules and coticules on a geochemical basis, we positioned analyses of samples from the Stavelot Massif in a (K_2O + Na_2O)-Al_2O_3-SiO_2 diagram (Fig. 9). As can be seen in Fig. 9, pseudocoticules contain lower amounts of alkalis and higher amounts of SiO_2 than coticules, due to their low contents in phyllosilicates. A comparison with

the chemical composition of samples from other occurrences (Fig. 10) indicates that most of these rocks correspond to pseudocoticules, except the two samples 262 and M1HC2.5 from Spry (1990), and the sample NM/1-c from Thomson (2001).

Another major characteristic of coticule is that the composition of the garnets included in the matrix must correspond to that of spessartine. As shown in Fig. 11, in which the chemical analyses of garnets from the literature have been plotted, all the samples investigated by Thomson (2001), including sample NM-1/c, correspond to almandine, not to spessartine. The garnets in sample 262 were not analyzed by Spry (1990), but in sample M1HC2.5, this mineral really does correspond to spessartine (Fig. 11). As a consequence, we suggest to rename the samples reported in Fig. 10 as pseudocoticules, except for sample M1HC2.5 which is a true coticule, and sample NM-1/c which corresponds to an almandine-bearing quartzite. A chemical analysis of the garnets contained in sample 262 is necessary to determine the nature of this rock.

In conclusion, the term coticule can be redefined as a yellow whetstone-type rock characterized by small spessartine grains (≥ 85 mol. % Sps, 5–20 μm), included in a matrix containing large amounts of phyllosilicates. Whole-rocks analyses must show $(K_2O + Na_2O) \geq 1$ wt% and $Al_2O_3 \geq 15$ wt% (Fig. 9).

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