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# Low-Temperature, Low-Pressure Metamorphism of Mn-rich Rocks in the Lienne Syncline, Venn–Stavelot Massif (Belgian Ardennes), and the Role of Carpholite

*Low-grade Mn-rich metamorphic rocks of the Lienne syncline (western part of the Venn–Stavelot Massif, Belgian Ardennes) have been re-examined to evaluate the petrological significance of carpholite proper,  $Mn^{2+}Al_2[Si_2O_6](OH)_4$ . Metamorphic P–T conditions of these rocks are estimated to be  $\sim 300^\circ\text{C}$ , 1–2 kbar, which is in accordance with the exclusive occurrence of carpholite in low-P rocks such as hydrothermal environments elsewhere. Carpholite of the Lienne syncline exclusively occurs in quartz-rich segregations. Its composition is close to end-member. Thermodynamic calculations confirm that carpholite is a stable phase at low-pressure–low-temperature conditions, in contrast to ferro- and magnesiocarpholite, which are high-pressure minerals. No information is available on the high-P behaviour of carpholite. The occurrence of carpholite is partly closely associated with spessartine-bearing country rocks, or carpholite is altered to assemblages with spessartine, sudoite, chlorite, muscovite and paragonite. Spessartine in these rocks contains minor amounts of hydrogarnet component  $\{(H/4)/(Si+(H/4)) = 0.03–0.06\}$ . The presence of carpholite–spessartine assemblages in these low-P rocks is in contrast to high-pressure metamorphic rocks from other areas, where parageneses such as ferro/magnesiocarpholite–chloritoid or magnesiocarpholite–chlorite–kyanite occur. The appearance of carpholite–garnet assemblages in low-P Mn-rich rocks can be explained by contrasting phase relations because of a high Mn–Mg partition coefficient between the minerals under consideration. In rhodochrosite-bearing veins in the Lienne syncline, nearly complete replacement of carpholite by spessartine and chlorite is due to the continuous reaction  $\text{carpholite} + \text{rhodochrosite} + \text{quartz} =$*

*spessartine + chlorite +  $H_2O$  +  $CO_2$ , which defines a very low  $X_{CO_2}$ , in the temperature range under consideration. It is suggested that spessartine (possibly containing some hydrogarnet component), during prograde metamorphism at low pressure, becomes stable at a temperature of  $\sim 300^\circ\text{C}$ .*

KEY WORDS: carpholite; spessartine; sudoite; Venn–Stavelot Massif; Ardennes

## INTRODUCTION

The most common members of the carpholite group can be represented by the general formula  $(Fe^{2+}, Mn^{2+}, Mg)(Al, Fe^{3+})_2[Si_2O_6](OH, F)_4$ . Mineral names so far defined are for the end-members containing Mn, Fe and Mg as divalent cations, i.e. carpholite, ferrocapholite and magnesiocarpholite (e.g. De Roever, 1951; Goffé *et al.*, 1973; Mottana & Schreyer, 1977; Viswanathan & Seidel, 1979). Fluorine occurs as a minor but significant constituent in natural carpholite group minerals. Ferric iron is generally very low. A non-stoichiometric type of carpholite containing K, Li and F was recently described by Ghose *et al.* (1989).

The members of the carpholite group occur in hydrothermal or low-grade metamorphic environments rich in aluminium such as metapelites, metabauxites and related vein mineralizations. Recent findings of magnesio- and ferrocapholite attracted

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particular attention because they solely occur in high-pressure–low-temperature metamorphic rocks formed at pressure >7 kbar at 300–450°C. These two minerals can now be regarded as indicators for such a type of metamorphism (Seidel, 1978; Goffé, 1982; Chopin & Schreyer, 1983; Goffé & Chopin, 1986; Schreyer, 1988; Theye *et al.*, 1992; Vidal *et al.*, 1992). In contrast, the long known manganese end-member of the carpholite group is only known in low-*P*–low-*T* metamorphic and hydrothermal environments. Carpholite was first described by Werner in 1817 [cited by Dana (1914)] in hydrothermal veins of a tin mine in Schlaggenwald, now Slavkov in the Czech Republic, where it is associated with rhodochrosite and fluorite. Examples of occurrences of carpholite in low-grade metamorphic Mn-rich pelites include, for example, the Wippra Zone of the Harz, Germany (Mügge, 1918) and the Venn–Stavelot Massif in the Ardennes, Belgium (De Koninck, 1879; Fransolet, 1972). Mottana & Schreyer (1977) compiled the then known occurrences of the carpholite group.

A recent re-investigation of low-grade metamorphic rocks in the Wippra Zone of the Harz (Theye & Siedel, 1993) demonstrated that mineral parageneses involving carpholite are well suited for a characterization of metamorphic *P*–*T* conditions. In this paper, we are presenting new data on carpholite-bearing rocks from the Lienne syncline in the western part of the Venn–Stavelot Massif, with emphasis on their phase relationships, geothermobarometry and petrological significance. These data are compared with data on Mn-rich rocks from other parts of the Venn–Stavelot Massif and from the Wippra Zone. Particular attention is also paid to the relation between carpholite and spessartine, and to the appearance of spessartine during prograde metamorphism.

## GEOLOGICAL SETTING OF THE VENN–STAVELOT MASSIF

The Venn–Stavelot Massif of the Belgian Ardennes represents a large block of Cambro-Ordovician metasediments belonging to the Rhenohercynian of the Variscan orogenic belt. From overlying Devonian and Carboniferous rocks, the Venn–Stavelot Massif is separated by an angular unconformity [for a recent outline of the regional geology, see Fielitz (1992)]. The age of major deformation and metamorphism in the Venn–Stavelot Massif is proved to be Upper Carboniferous although already in the Caledonian period deformation took place

(Schreyer, 1975; Kramm, 1982; Geukens, 1984; Kramm *et al.*, 1985*a,b*).

Metamorphism of the Venn–Stavelot Massif is of very low to low-grade type in the sense of Winkler (1979). The highest-grade rocks are present in the SE portion of the massif (region of Recht–Ottre–Lierneux). Kramm (1982) and Kramm *et al.* (1985*b*) estimated 360–420°C at 2 kbar, based on the presence of andalusite, chloritoid and spessartine as well as on white K-mica composition. A lower temperature seems to hold, however, for the Lienne syncline in the western part of the massif (Kramm, 1982), to be discussed here.

Mineralogically, manganese-rich metasediments of the Upper Salmian (middle Ordovician) are of particular interest. In the region of Recht–Ottre–Lierneux, these rocks contain various assemblages involving silicate minerals such as spessartine, andalusite–kanonaite ('viridine'), sudoite, Fe–Mn-rich members of the chloritoid group, and also rare mineral species such as ardennite and davreuxite [Kramm, 1979; Theye & Fransolet, 1994; Pasero *et al.*, 1994; for a compilation see Mélon *et al.* (1976) and Fransolet *et al.* (1977, 1984)]. Carpholite only occurs in the lower-grade rocks of the Lienne syncline.

In contrast, in the Mn-poor metasediments of the underlying Lower Salmian (lower Ordovician), no *P*–*T* indicative mineral assemblages are known.

## PETROGRAPHY OF THE LIENNE SYNCLINE ROCKS

The petrographic description is based on ~100 thin sections of rocks from the Lienne syncline. The observed mineral assemblages are compiled in Table 1. Unless otherwise indicated, all descriptions refer to rocks of the Upper Salmian in the Lienne syncline.

### Metapelites and metapsammites

The majority of rocks consist of green or red metapelites and metapsammites. Particularly in metapsammites, detrital relics such as quartz grains and muscovite flakes are often well preserved. Alternating layers distinguished by their grain size and by the amount of haematite reflect sedimentary bedding that is preserved on a millimetre to centimetre size.

A ubiquitous metamorphic foliation *S*<sub>1</sub>, which, in most cases, appears parallel to sedimentary bedding, is defined by parallel alignment of phyllosilicates and elongated quartz grains. Occasionally, a crenulation cleavage *S*<sub>2</sub> oblique to *S*<sub>1</sub> is developed. Quartz-rich segregations are parallel to or crosscut the foliation.

*Table 1: Mineral assemblages of Salmian (Ordovician) rocks in the Lienne syncline (western part of the Venn–Stavelot Massif)*

<i>Upper Salmian</i>	
Chloritoid schists	
Qtz–Ms–Chl–Cld	
Qtz–Ms–Chl–Cld–Haem	
Red schists	
Qtz–Ms–Pg–Chl–Haem	
Qtz–Ms–Pg–Chl–Sud–Haem	
Qtz–Ms–Pg–Sud–Grt–Haem	
Spessartine-rich layers	
Qtz–Ms–Pg–Chl–Sud–Grt	
Carpholite-bearing segregations	
Qtz–Cph–(Chl)–(Sud)–(Grt)–(Ms)–(Pg)	
Qtz–Cph–Rds	
Manganese ore	
Qtz–Ms–Rds–Kut–Haem	
Qtz–Chl–Grt–Rds–Kut	
Qtz–Cph–Rds–Chl–Grt–(Ms)–(Chl)–(Grt)	
<i>Lower Salmian</i>	
Qtz–Ms–Chl	

Minerals replacing carpholite are shown in parentheses. Chl, chlorite; Cph, carpholite; Cld, chloritoid; Grt, garnet; Haem, haematite; Kln, kaolinite; Kut, kutnahorite; Mgs, magnesite; Ms, muscovite; Pg, paragonite; Prl, pyrophyllite; Qtz, quartz; Rds, rhodochrosite; Sud, sudoite; Sps, spessartine.

A first type of metasediments is represented by green chloritoid schists that consist mineralogically of chloritoid (up to 0.1 mm in size), chlorite, muscovite and quartz. They are intercalated with red schists containing fine-grained haematite in addition. The phyllosilicates are oriented parallel to the foliation, and chloritoid is grown syn- to post-tectonically with respect to the foliation  $S_1$ , but pre- $S_2$ . No microstructural indications of non-equilibrium between the minerals have been observed. Quartz-rich segregations present in this rock type contain quartz, chlorite, haematite and small crystals of rhodochrosite.

Besides chloritoid-bearing metapelites and meta-psammites, red to purple schists occur that are devoid of chloritoid and rich in fine-grained haematite. Mesoscopically, these rocks are characterized by smooth and shiny foliation planes owing to very fine-grained, well-aligned sheet silicates. The monotonous mineral assemblage of this rock type is quartz, muscovite, paragonite, a mixed-layer

mineral muscovite–paragonite [see Frey (1969)], chlorite, haematite, and, in some cases, sudoite and spessartine (up to 0.03 mm in size).

Centimetre-sized white layers are occasionally present as intercalations within the red schists devoid of chloritoid. They are rich in spessartine associated with some quartz, muscovite, paragonite, chlorite and sudoite. These spessartine-rich layers are similar to the so-called coticles that are mined as whetstones in the Recht–Otré–Lierneux region. The petrological significance of these rocks will be the subject of a further paper.

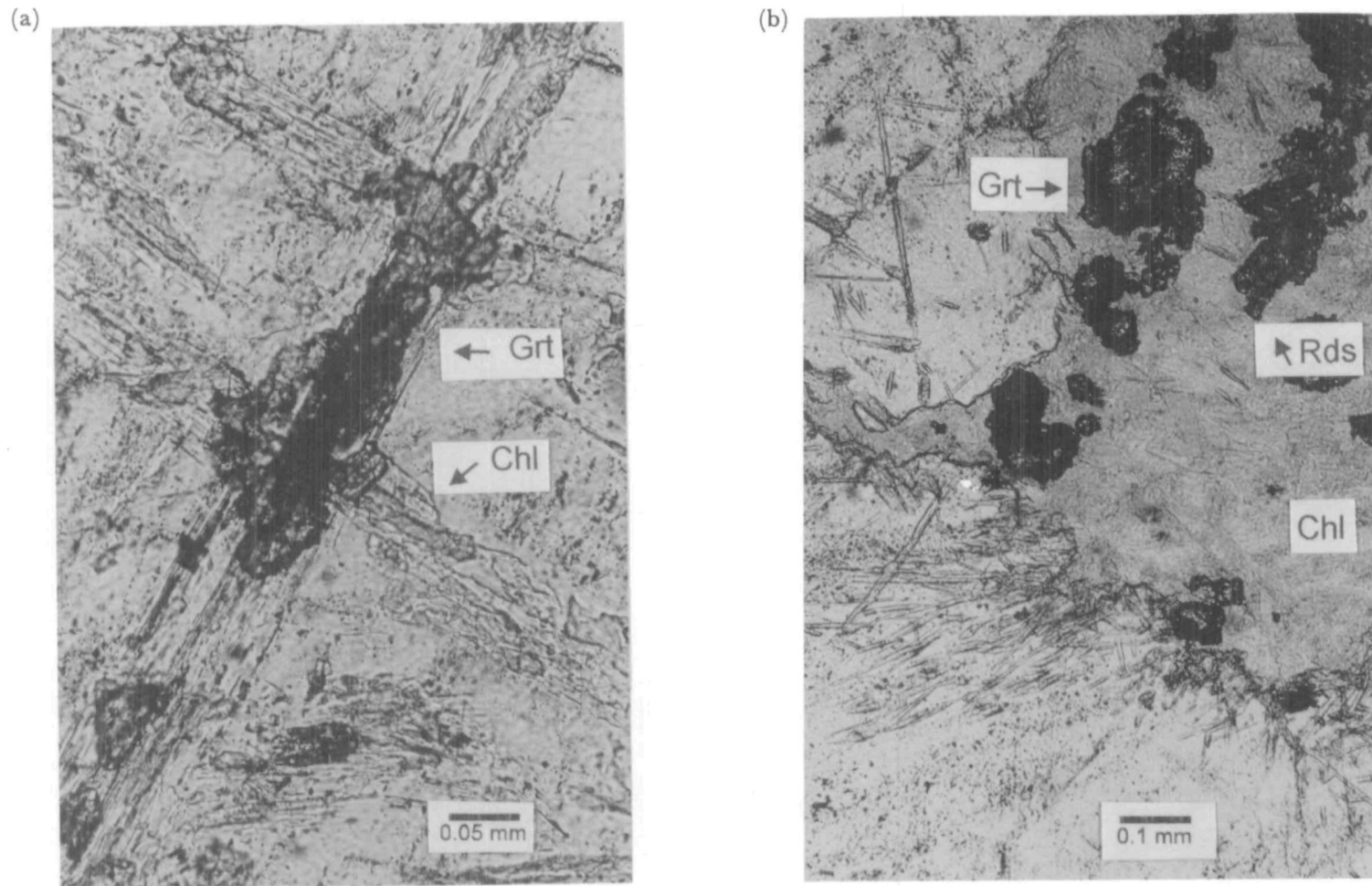
In contrast to the manganese- and haematite-rich schists of the Upper Salmian, metasediments of the Lower Salmian generally do not contain specific manganese minerals and are poor in haematite. These rocks contain the monotonous mineral assemblage quartz–muscovite–trioctahedral chlorite.

### Carpholite-bearing segregations

Carpholite in the Lienne area has been found only within quartz-rich segregations in the vicinity of Meuville and Bierleux. The carpholite segregations are, like the spessartine-rich layers, restricted to red or purple schists devoid of chloritoid. Mineralogically, the segregations consist of quartz, carpholite (and its alteration products; see below) and, in one specimen, rhodochrosite. In some cases, carpholite is in close contact with spessartine-rich layers of the country rocks without any microstructural indications of non-equilibrium between these minerals.

Needle-like crystals of carpholite (up to some millimetres long) occur within quartz-rich segregations which are, in most cases, developed parallel to the foliation of the country rock. Often, the carpholite needles are also orientated parallel to foliation. After the main crystallization stage of carpholite, many segregations are affected by crack-seal dominated extension processes. Cracks are mainly sealed with quartz, occasionally accompanied by minor carpholite indicating that this extension already began in the stability field of carpholite. However, in some cases, partly related to this extension, carpholite is replaced by various mixtures of chlorite, sudoite, paragonite and muscovite. Occasionally, small amounts of garnet are also present in these alteration products (see Fig. 1). All stages from completely fresh to completely pseudomorphed carpholite have been observed. Furthermore, as products of superficial weathering, carpholite may be altered into black, X-ray amorphous aggregates of Mn-oxides.

In one rock sample (22646), carpholite occurs



**Fig. 1.** Photomicrographs of carpholite-bearing segregations in Mn-ore. (a) Fibrous carpholite nearly completely replaced by garnet (dark, high relief) and chlorite. Thin fibres of fresh carpholite are included in quartz (light matrix). (b) Pseudomorphs, partly with fibrous outlines, of chlorite (grey) and garnet (dark, high relief) after carpholite. Rhodochrosite showing corroded outlines is present in the upper left. The light matrix is quartz.

associated with rhodochrosite. These two minerals seem to have been formed more or less contemporaneously. Minor amounts of muscovite are present, in this sample, along late shear planes.

### Manganese ore

A further rock type intercalated in red schists consists of layers of manganese ore which have been mined until 1934 (Fourmarier & Calembert, 1942; Berger, 1965). They are conformable sedimentary horizons rich in manganese carbonate minerals accompanied by quartz, white mica and haematite. However, intensive veining which includes deposition of quartz, haematite, rhodochrosite (up to some millimetres in size), kutnahorite, spessartine and Mn-rich chlorite also indicates significant mobilization of manganese during metamorphism. Rhodochrosite and kutnahorite are partly altered into Mn-oxides.

The vein mineralogy is of particular interest. The microstructure indicates simultaneous growth of quartz and carbonate minerals. Chlorite and spessartine, however, partly seem to replace the Mn-carbonates (Fig. 1b). Besides coarse chlorite-spessartine aggregates, these two minerals (partly accompanied by small amounts of muscovite) also occur in the form of columnar or fibrous pseudomorphs with rhombic cross-sections that are best interpreted as pseudomorphs after carpholite (Fig. 1a, b). This interpretation is corroborated by the presence of tiny fibres of carpholite which are preserved as inclusions in quartz.

## MINERAL CHEMISTRY

### Methods

Mineral analyses were obtained using a wavelength-dispersive Cameca electron microprobe. Measurement conditions were 15 kV, 10–15 nA, 10–20 s counting time. Standards were albite (Na), orthoclase (K), olivine (Si, Mg), anorthite (Ca, Al), Fe<sub>2</sub>O<sub>3</sub> (Fe), MnTiO<sub>3</sub> (Mn, Ti), BaSO<sub>4</sub> (Ba), ZnS (Zn), fluorite (F) and vanadinite (V), except for specimens 89/40a, 89/30x, 89/40z and 22646. For these specimens, we used andradite glass (Ca, Fe), pyrope (Si, Al, Mg), jadeite (Na), topaz (F), spessartine (Mn), K-silicate glass (K), Ba-glass (Ba), zincite (Zn), V-metal (V), and rutile (Ti). Some analyses show low oxide totals, which may be attributed to the small grain size of many of the analysed minerals.

### Carpholite

Carpholite present in quartz-rich segregations of

haematite-rich metapelites forms yellow crystals with needle-like habit (up to some millimetres long). The chemical composition of carpholite (Table 2a) is rather constant in terms of the divalent cations, which are mainly manganese and magnesium (Fig. 2a).  $X_{\text{Fe}^{2+}} = \text{Fe}^{2+}/(\text{Fe}^{2+} + \text{Mn} + \text{Mg})$  is generally <0.1,  $X_{\text{Mn}}$  varies between 0.9 and 0.8, and  $X_{\text{Mg}}$  varies between 0.1 and 0.2. Only one specimen (89/2c) tends to more Mg- and Fe-rich compositions. Fluorine varies between 0 and 0.5 wt%. Potassium does not occur in detectable amounts. The presence of significant vanadium in carpholite that coexists with V-rich ardennite is noteworthy [an analysis of ardennite coexisting with carpholite of specimen 89/95 has been given by Pasero *et al.* (1994)]. In specimen 89/85, carpholite contains up to 3.5 wt% V<sub>2</sub>O<sub>3</sub> corresponding to 8 mol% of the trivalent cations. Carpholite not coexisting with ardennite shows a low vanadium content (e.g. 89/81: 0.3 wt% V<sub>2</sub>O<sub>3</sub> corresponding to  $X_{\text{V}} = 0.007$ ). Fransolet (1972) analysed a V<sub>2</sub>O<sub>3</sub> content of 0.06 wt% in carpholite from Meuville. The low trivalent totals of some carpholite analyses in Table 2a, for which vanadium was not determined, may be due to a significant content of this element.

### Chloritoid

The mineral analyses show that chloritoid in metapelites and metapsammities is poor in magnesium end-member (<8 mol%; Table 2b; Fig. 2b; and Theye & Fransolet, 1994). Ferrous iron and manganese are present in nearly equal amounts.

### Chlorite

In contrast to chloritoid, coexisting chlorite is relatively poor in manganese. This chlorite contains ferrous iron and magnesium as major divalent cations (Table 2b). The divalent cations are regularly partitioned between chlorite and coexisting chloritoid (Fig. 2b). Chlorite replacing carpholite in quartz-rich segregations is poorer in ferrous iron and richer in manganese (Table 2a; Fig. 2a). As already described by Schreyer *et al.* (1986), two distinct populations of chlorite are present in the manganese ore (Table 2c; Fig. 2c). A relatively Mn-poor, Mg-rich chlorite occurs replacing carpholite, whereas Mn-rich chlorite is analysed in coarse chlorite-spessartine aggregates (Fig. 2c). Based on microstructural features of coexisting chlorites with different compositions, Schreyer *et al.* (1986) suggested a miscibility gap in Mn–Mg–Fe chlorites and, furthermore, a chemical evolution of vein minerals from Mn rich to Mn poorer and Mg rich.

Table 2: Representative mineral analyses from four different rock types in the Lienne area; average of *n* analyses (n.d., not determined; —, <0.05 wt %)

(a) Carpholite-bearing segregations (minerals replacing carpholite in parentheses)										
wt%:	Cph	Cph	Cph	Cph	Cph	Cph	Cph	Cph	Cph	Cph
No.:	89/2b	89/2c	89/3	89/40a	89/40x	89/40z	89/72c	89/81	89/95	22846
<i>n</i> :	6	5	5	8	3	2	3	2	5	6
SiO <sub>2</sub>	35.98	38.08	36.62	35.82	37.90	36.25	37.63	36.45	37.12	35.63
TiO <sub>2</sub>	0.22	0.23	0.28	0.15	0.17	0.18	0.41	0.24	0.17	0.21
Al <sub>2</sub> O <sub>3</sub>	27.20	30.76	28.94	28.98	30.60	29.40	29.10	29.70	27.94	28.62
V <sub>2</sub> O <sub>3</sub>	2.84	n.d.	n.d.	n.d.	n.d.	0.24	n.d.	0.32	3.49	0.05
FeO	0.91	2.55	1.02	1.66	0.97	1.21	2.89	0.79	1.19	2.98
MnO	19.13	14.00	17.54	17.93	17.39	18.30	16.50	17.45	18.62	17.79
MgO	1.27	3.14	1.68	1.64	1.84	1.49	1.72	2.09	1.14	1.24
ZnO	0.10	0.08	—	—	0.04	—	0.10	—	n.d.	n.d.
CaO	—	—	—	—	—	—	—	—	—	—
BaO	—	—	—	—	—	—	—	n.d.	n.d.	—
Na <sub>2</sub> O	—	—	—	—	—	—	—	—	n.d.	—
K <sub>2</sub> O	—	—	—	—	—	—	—	—	n.d.	—
F	0.10	0.30	0.20	0.20	0.50	0.30	0.30	0.20	n.d.	—
Σ	87.75	89.14	86.28	86.38	89.51	87.37	88.65	87.24	89.67	86.53
8 (O, OH)										
Si	2.016	2.034	2.044	2.007	2.038	2.011	2.049	2.011	2.023	2.001
Ti	0.009	0.009	0.012	0.006	0.007	0.008	0.017	0.010	0.007	0.009
Al	1.797	1.936	1.904	1.914	1.940	1.922	1.867	1.931	1.795	1.894
V	0.128	0.000	0.000	0.000	0.000	0.011	0.000	0.014	0.153	0.002
Fe <sup>3+</sup>	0.000	0.018	0.032	0.070	0.016	0.046	0.063	0.031	0.026	0.092
Fe <sup>2+</sup>	0.043	0.095	0.015	0.008	0.027	0.011	0.069	0.006	0.028	0.048
Mn	0.908	0.633	0.829	0.851	0.792	0.861	0.761	0.816	0.860	0.846
Mg	0.106	0.250	0.140	0.137	0.156	0.123	0.139	0.172	0.093	0.104
Zn	0.004	0.003	0.000	0.000	0.002	0.000	0.004	0.000	0.000	0.000
Σ	2.995	2.944	2.932	2.986	2.940	2.982	2.920	2.980	2.962	2.996
F	0.012	0.051	0.032	0.033	0.083	0.044	0.046	0.035	0.000	0.000

### Sudoite

The di/trioctahedral chlorite mineral sudoite has been detected using the intensity ratio of its basal X-ray peaks (Fransolet & Schreyer, 1984):

$$R = I_{(003)} / [I_{(002)} + I_{(004)}].$$

The *R* value of 'normal' trioctahedral chlorite is in the range 0.1–0.3, whereas *R* is 0.7–0.8 for sudoite (Fransolet & Schreyer, 1984; Theye *et al.*, 1992). Intermediate *R* values can be reasonably related to

mixtures of sudoite and chlorite. Most of the metapelites and metapsammities in the Lienne syncline area show *R* values of 0.12–0.27. However, intermediate *R* values of 0.35–0.64 indicating the presence of sudoite in addition to trioctahedral chlorite have also been measured in some red schists of this region. Microprobe analyses of sudoite occurring as rock-forming mineral in red schists as well as of sudoite replacing carpholite in quartz-rich segregations show that this mineral is always close to the magnesium end-member (Tables 2a, 2d; Fig. 2a).



Table 2: continued

(b) Chloritoid-bearing metapelites and metapsammities [compositions of chloritoid taken from Theye & Fransolet (1994)]									
wt%:	Cld	Cld	Cld	Chl	Chl	Chl	Ms	Ms	Rds
No.:	89/60	89/63a	89/70a	89/60	89/63a	89/70a	89/63a	89/70a	89/60
<i>n</i> :	5	3	3	4	3	3	1	1	1
SiO <sub>2</sub>	23.98	23.93	24.03	24.29	24.82	24.88	46.05	45.60	—
TiO <sub>2</sub>	—	—	—	0.05	—	—	0.11	—	—
Al <sub>2</sub> O <sub>3</sub>	38.98	39.33	39.33	24.65	25.29	25.64	34.41	30.83	—
FeO	12.80	12.63	12.00	18.05	18.85	17.34	2.67	4.40	3.21
MnO	13.88	13.13	13.93	5.82	5.61	4.71	0.07	0.63	50.02
MgO	1.08	1.17	1.30	12.98	12.76	12.94	0.62	1.70	1.90
ZnO	—	—	0.06	—	—	0.04	—	—	—
CaO	—	—	—	—	—	—	—	—	1.45
BaO	—	—	—	—	n.d.	—	n.d.	—	0.06
Na <sub>2</sub> O	—	—	—	—	—	—	0.94	0.39	—
K <sub>2</sub> O	—	—	—	0.08	—	0.30	9.20	10.01	—
Σ	90.72	90.19	90.65	85.92	87.23	85.85	94.07	93.56	56.64
	12 (O, OH)			14 (O, OH)			11 (O, OH)		1 cation
Si	2.035	2.037	2.036	2.582	2.597	2.627	3.093	3.141	
Al				1.418	1.403	1.383	0.907	0.859	
Σ				4.000	4.000	4.000	4.000	4.000	
Ti	0.000	0.000	0.000	0.004	0.000	0.000	0.006	0.000	
Al	3.899	3.946	3.928	1.670	1.714	1.796	1.817	1.644	
Fe <sup>3+</sup>	0.060	0.028	0.036						
Fe <sup>2+</sup>	0.848	0.873	0.815	1.605	1.650	1.528	0.150	0.253	0.054
Mn	0.997	0.947	1.000	0.525	0.488	0.419	0.004	0.037	0.858
Mg	0.139	0.148	0.164	2.057	1.991	2.029	0.062	0.175	0.057
Zn	0.000	0.000	0.004	0.000	0.000	0.003	0.000	0.000	0.000
Σ	5.943	5.940	5.947	5.861	5.843	5.773	2.039	2.109	
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.031
Ba	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Na	0.000	0.000	0.000	0.000	0.000	0.000	0.122	0.052	
K	0.000	0.000	0.000	0.010	0.000	0.040	0.788	0.880	
Σ	0.000	0.000	0.000	0.010	0.000	0.040	0.910	0.932	1.000

### Garnet

Garnet with composition close to spessartine has been observed as rock-forming mineral in metapelites and replacing carpholite in quartz-rich segregations. For the divalent cations, only minor amounts of Ca (CaO: 1.5–4.6 wt %) and Fe (FeO: 0.1–1.1 wt %) are present besides Mn. The MgO content is always below 0.1 wt % (Tables 2a, 2c, 2d). Normalizing the garnet analyses to 12 (O), the content of Si

per formula unit (p.f.u.) is significantly below 3.0 and the ratio of  $M^{2+}/M^{3+}$  deviates from 3/2. Moreover, the oxide totals are too low. This suggests that some hydrogarnet component is present in garnet from the Lienne syncline. Recalculating the garnet structural formulae to make  $Si + (H/4) = 3$  results in 0.09–0.17 (H/4) p.f.u. (corresponding to 0.7–1.2 wt % H<sub>2</sub>O). After this procedure, the ratio of  $M^{2+}/M^{3+}$  is satisfyingly close to 3/2. Further evidence for the presence of a hydrogarnet com-



Table 2: continued

(c) Segregation in manganese ore; carpholite replaced by garnet and the Mn-poorer chlorite of the two is present only as relics							
wt%:	Cph	Grt	Ms	Chl	Chl	Rds	Rds
No.:	93/7	93/7	93/7	93/7	93/7	93/7	93/7
n:	2	3	2	1	1	1	1
SiO <sub>2</sub>	35.73	34.60	47.29	25.27	27.73	—	—
TiO <sub>2</sub>	0.05	0.07	0.01	—	0.02	—	—
Al <sub>2</sub> O <sub>3</sub>	29.53	19.74	32.90	20.98	21.48	—	—
V <sub>2</sub> O <sub>3</sub>	0.06	0.08	0.06	—	—	—	—
FeO	0.63	0.06	2.44	5.41	9.46	—	1.93
MnO	19.29	39.05	0.47	21.90	7.65	55.53	48.95
MgO	1.36	0.00	1.00	12.80	19.92	0.35	0.92
ZnO	0.04	0.12	0.07	0.42	—	—	—
CaO	—	3.33	0.09	—	0.09	3.09	6.04
BaO	—	0.03	0.29	—	—	—	0.03
Na <sub>2</sub> O	—	—	0.28	0.23	0.14	—	—
K <sub>2</sub> O	—	—	9.66	—	—	—	—
F	0.10	—	0.10	—	—	—	—
Σ	86.79	97.08	94.66	87.01	86.49	58.97	57.87
	8	12	11	14 (O, OH)	1 cation		
Si	1.999	2.888	3.162	2.715	2.818		
Al			0.839	1.285	1.182		
H/4*		0.112					
Σ		3.000	4.000	4.000	4.000		
Ti	0.002	0.004	0.001	0.000	0.002		
Al	1.947	1.942	1.754	1.371	1.390		
V	0.003	0.005	0.003	0.000	0.000		
Fe <sup>3+</sup>	0.029	0.000	0.000	0.000	0.000		
Fe <sup>2+</sup>	0.000	0.004	0.137	0.486	0.804	0.000	0.032
Mn	0.914	2.760	0.027	1.993	0.658	0.925	0.814
Mg	0.114	0.000	0.100	2.050	3.017	0.010	0.027
Zn	0.002	0.007	0.003	0.033	0.000	0.000	0.000
Σ	3.011		2.025	5.933	5.871		
Ca	0.000	0.298	0.006	0.000	0.010	0.065	0.127
Ba	0.000	0.001	0.008	0.000	0.000	0.000	0.000
Na	0.000	0.000	0.037	0.048	0.028		
K	0.000	0.000	0.825	0.000	0.000		
Σ	0.000	5.021	0.876	0.048	0.038	1.000	1.000
F	0.018		0.021	0.000	0.000		

Table 2: continued

(d) Spessartine-bearing red schist			
wt%:	Ms	Grt	Sud
No.:	89/2b	89/2b	89/2b
n:	3	6	1
SiO <sub>2</sub>	45.73	34.26	32.84
TiO <sub>2</sub>	0.13	0.18	—
Al <sub>2</sub> O <sub>3</sub>	34.67	19.98	33.71
V <sub>2</sub> O <sub>3</sub>	—	—	—
FeO	1.52	0.14	2.05
MnO	0.04	38.63	1.36
MgO	0.53	—	13.16
ZnO	—	0.06	0.10
CaO	0.02	2.80	—
BaO	0.18	—	—
Na <sub>2</sub> O	1.57	—	—
K <sub>2</sub> O	8.34	—	0.13
F	—	—	—
Σ	92.73	96.05	83.35
	11	12	14
Si	3.106	2.876	3.108
Al	0.894		0.892
H/4*		0.124	
Σ	4.000	3.000	4.000
Ti	0.006	0.011	0.000
Al	1.880	1.977	2.868
V	0.000	0.000	0.000
Fe <sup>3+</sup>	0.000	0.000	0.000
Fe <sup>2+</sup>	0.086	0.010	0.162
Mn	0.002	2.747	0.109
Mg	0.054	0.000	1.857
Zn	0.000	0.004	0.007
Σ	2.028		5.003
Ca	0.002	0.252	0.000
Ba	0.005	0.000	0.000
Na	0.206	0.000	0.000
K	0.722	0.000	0.016
Σ	0.935	5.001	0.016
F	0.007		0.000

\*Calculated to make Si+(H/4) = 3.000.

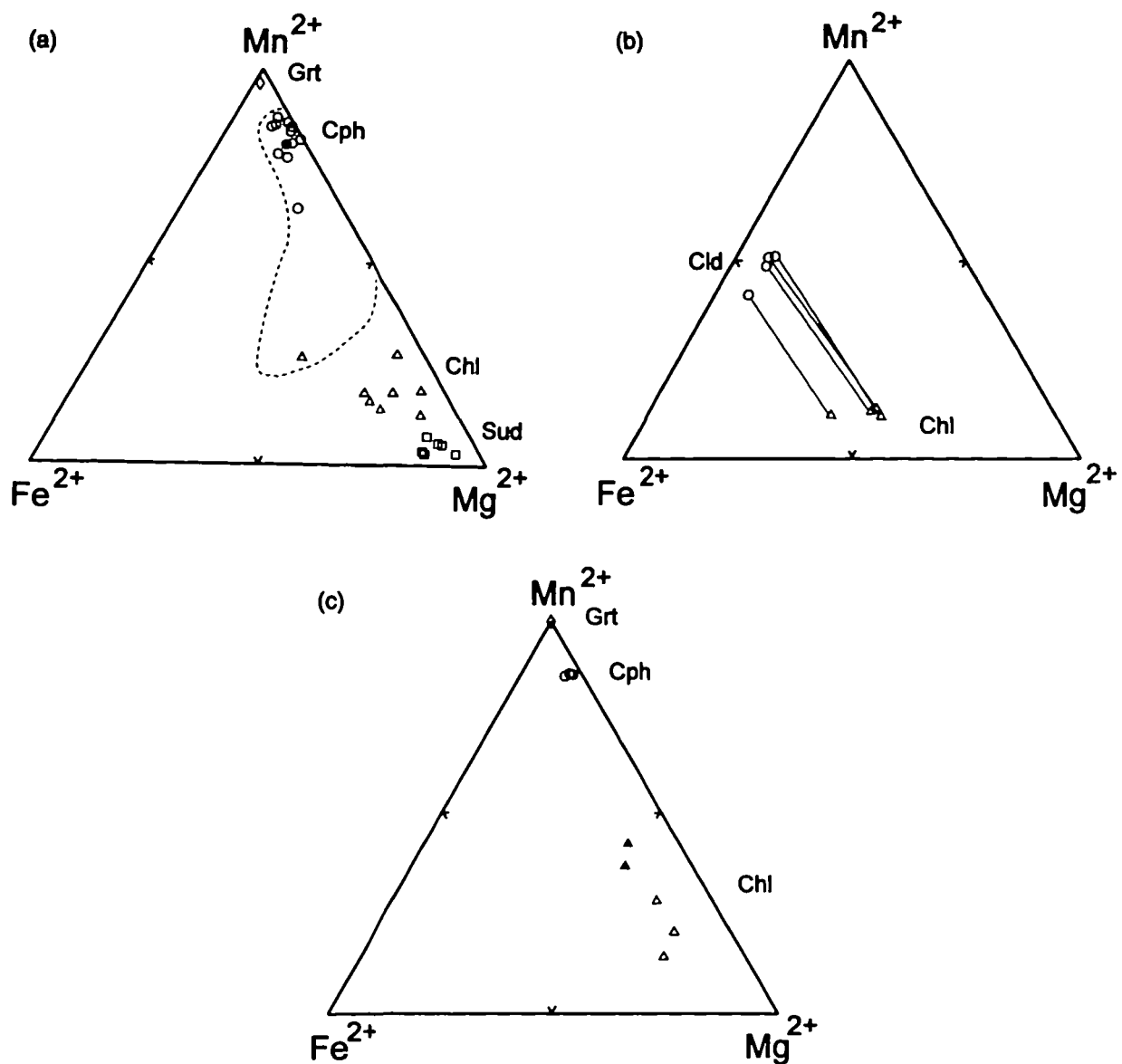


Fig. 2. Distribution of divalent cations  $Fe^{2+}$ ,  $Mn^{2+}$  and  $Mg^{2+}$  in minerals from the Lienne syncline. (a) Carpholite-bearing segregations with carpholite (circles) partly replaced by garnet (diamond), chlorite (triangles) and sudoite (squares). The black dot represents the carpholite from Meuville described by Franolet (1972). Dashed line encompasses the range of carpholite composition in rocks of the Wippra Zone, Harz (Theye & Siedel, 1993). (b) Chloritoid-chlorite-bearing metasediments. Coexisting minerals are connected by tie-lines. (c) Segregation in manganese ore (sample 93/7). Carpholite (open circles) is partly replaced by garnet (open diamond) and relatively Mn-poor chlorite (open triangles). Mn-rich chlorite (filled triangles) occurs as coarse aggregate microstructurally unrelated to carpholite.

ponent of the analysed garnets is indicated by their lattice constants. Four determined values for garnets from the Lienne syncline (93/7: 11.657 Å; 89/81: 11.569 Å; 89/2b: 11.648 Å; 89/3: 11.648 Å) are significantly higher than those of OH-free Mn-Ca garnet (Ito & Frondel, 1968; Fig. 3), which is in accordance with the behaviour of the grossular-

hydrogrossular series [Shoji, 1974; in Meagher (1982)]. Hsu (1968) observed that the lattice constants of spessartine synthesized below 500°C are significantly higher than those of spessartine produced at higher temperature. This is also attributed to the presence of a hydrosspessartine component in the low-temperature products (Hsu, 1968).

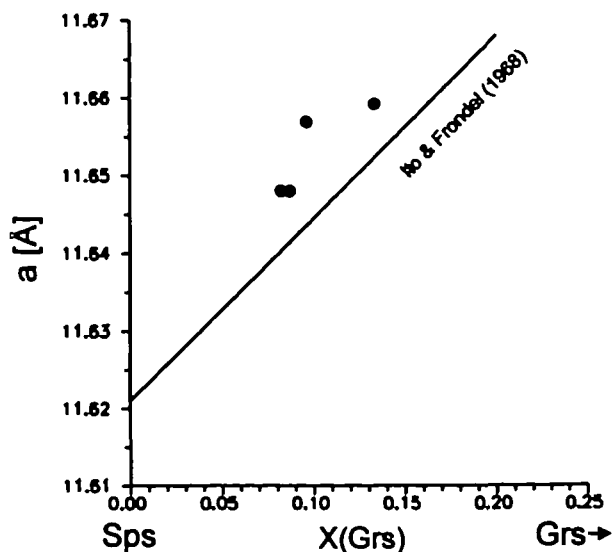


Fig. 3. Lattice constants of four spessartine samples from the Lienne syncline plotted against  $X_{\text{Grs}}$  of garnet. Compared with the lattice constants of OH-free spessartine-grossular garnet (Ito & Frondel, 1968), the determined values are significantly higher.

#### White mica

White mica minerals comprise muscovite, paragonite and a mixed-layer mineral muscovite-paragonite (see Frey, 1969; Kramm, 1980). These minerals occur either rock forming in metapelites or replacing carpholite in quartz-rich segregations. Analyses of muscovite show a low Si content of 3.0–3.1 Si p.f.u. (Tables 2a–2d).

#### Rhodochrosite

This mineral is present in the manganese ore (see below) and in segregations. It contains variable amounts of Ca, Fe and Mg (Tables 2a–2c).

### COMPARISON WITH Mn-RICH ROCKS OF THE WIPPRA ZONE, HARZ

Metasediments of similar sedimentation age, compositions and metamorphic assemblages to those of the Lienne syncline occur in the Wippa Zone (WZ) of the Harz, Germany (Siedel & Theye, 1993; Theye & Siedel, 1993). Temperature and pressure conditions were estimated by Theye & Siedel (1993) at  $\sim 320^\circ\text{C}$ , 3 kbar. Chloritoid compositions in the WZ are richer in iron. They show, however, a similar Mn/Mg to that in chloritoid schists of the Lienne syncline. In contrast to the Lienne syncline, the WZ carpholite also occurring within quartz-rich segregations shows a much more extensive compositional spread, ranging from almost pure carpholite to

magnesiocarpholite with  $X_{\text{Mg}}$  up to 0.52 (Fig. 2a). The most Mg-rich carpholite coexists with sudoite and chlorite without any microstructural sign of non-equilibrium. In contrast, sudoite in the Lienne rocks only occurs as breakdown product of carpholite, indicating that, in this case, the paragenesis carpholite + sudoite probably does not represent chemical equilibrium. These observations suggest that, during vein formation in the WZ, Mn/Mg of the vein-forming fluid has significantly decreased. Mn-rich carpholite formed at the beginning was followed by magnesiocarpholite + sudoite. In the Lienne area, the chemical evolution of carpholite-bearing veins is restricted to an Mn-rich episode. Rhodochrosite-bearing segregations occur both in the Lienne area and in the WZ.

### COMPARISON WITH HIGHER-GRADE ROCKS OF THE VENN-STAVELOT MASSIF IN THE RECHT-OTTRÉ-LIERNEUX AREA

*P-T* conditions of age-equivalent metasediments in the Recht-Ottré-Lierneux area are estimated to  $360\text{--}420^\circ\text{C}$ , 2 kbar (Kramm, 1982; Kramm *et al.*, 1985b). A major difference from those of the Lienne syncline is the grain size of metamorphic minerals. In particular, chloritoid and garnet occur as millimetre-sized blasts in the Recht-Ottré-Lierneux area, whereas these minerals are generally much more fine grained in the Lienne syncline. Differences of the chemical compositions of minerals are also striking. Garnet in the Lienne syncline is virtually pure spessartine containing some hydrogarnet component. In the Recht-Ottré-Lierneux area, however, garnet may contain significant amounts of ferrous iron (up to 14 wt%). Moreover, the stoichiometry of the published analyses does not indicate the presence of a hydrogarnet component (Kramm, 1982; Bossiroy, 1984; Schreyer *et al.*, 1992). Chloritoid in the Recht-Ottré-Lierneux area generally shows a higher Mg/Mn ratio (at widely varying  $X_{\text{Fe}}$ ) than in the Lienne syncline (Theye & Fransolet, 1994). A further mineralogical difference is the presence of andalusite in the Recht-Ottré-Lierneux area. This mineral is not known from the Lienne syncline. However, hydrous aluminosilicates such as kaolinite and pyrophyllite are also not observed in the Lienne syncline, indicating that these rocks are poorer in Al. Finally, carpholite has exclusively been described in the Lienne syncline but not in the Recht-Ottré-Lierneux area.

## P-T CONDITIONS OF METAMORPHISM IN THE LIENNE SYNCLINE

The mineralogical and microstructural differences clearly point to a lower temperature of metamorphism in the Lienne syncline compared with the Recht-Ottre-Lierneux area of the Ardennes. A minimum temperature of metamorphism for the Lienne syncline can be calculated from the equilibrium chlorite + kaolinite/pyrophyllite = chloritoid + quartz + H<sub>2</sub>O, using thermodynamic data presented below and mineral compositions of chloritoid schists in Table 2b. Four rock specimens yield minimum temperatures between 280 and 320°C (nearly independent of pressure). We estimate that temperature of metamorphism in the Lienne syncline is ~300°C, which is considerably lower than in the Recht-Ottre-Lierneux area. No indications for the metamorphic pressure are present in the Lienne syncline. We assume that it is in the same range as in the Recht-Ottre-Lierneux area, or slightly lower (1–2 kbar). These values are slightly lower than those estimated by Kramm (1982) for this region, but similar to those of the Wippra Zone.

## PHASE RELATIONSHIPS AND STABILITY OF CARPHOLITE BASED ON CALCULATED MINERAL EQUILIBRIA

The upper thermal breakdown of the high-pressure metamorphic minerals ferrocapholite and magnesiocapholite occurs according to the reactions carpholite *sensu lato* (s.l.) = chloritoid + quartz + H<sub>2</sub>O for Fe-rich compositions and carpholite *s.l.* = chlorite + kyanite + quartz + H<sub>2</sub>O for Mg-rich compositions (Vidal *et al.*, 1992). These reactions, which are continuous with respect to Fe or Mg, lead to parageneses involving carpholite *s.l.* + chloritoid or carpholite *s.l.* + chlorite + kyanite. Assemblages involving both carpholite *s.l.* and garnet, however, have never been observed in high-pressure metamorphic (Mn-poor) rocks. In contrast, in Mn-rich rocks of the Lienne syncline, we never observed carpholite + chloritoid or carpholite + chlorite + kyanite/andalusite (or hydrous Al-silicate) assemblages. Instead, we found the coexistence of carpholite (in segregations) with garnet (in adjacent layers) as well as the replacement of carpholite by spessartine and chlorite.

To semi-quantitatively evaluate the fundamental differences between phase relations of (1) Mn-poor high-pressure and (2) Mn-rich low-pressure car-

pholite-bearing assemblages, we calculated equilibrium curves using thermodynamic data. These equilibrium curves are essentially isopleths along which minerals with compositions as calculated or analysed may coexist under changing P-T conditions. In a first approximation, phase relationships of the Mn-rich rocks of the Lienne syncline in the Ardennes can be represented in terms of the chemical system MnO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O (MnMASH), involving the phases garnet, carpholite, chloritoid, chlorite, sudoite, pyrophyllite, kaolinite, quartz and H<sub>2</sub>O. Because a complete set of thermodynamic data is only available in the chemical system MASH, but not for Mn minerals, we confined our calculations to MASH equilibria, applying ideal mixing models to consider cations other than Mg in the divalent cation sites. The hydrogarnet component in garnet is not considered in the calculations. In the case of chlorite, ideal clinocllore, Mg<sub>3</sub>Al(AlSi<sub>3</sub>O<sub>10</sub>)(OH)<sub>8</sub>, is used to balance the equilibria. To account for the Tschermak substitution in natural chlorite, a constant activity correction factor of 0.7 calculated with the activity model of Vidal *et al.* (1992) from analyses in Table 2 is applied [see Berman (1988)].

We used the thermodynamic data set of Berman (1988) supplemented by data for magnesiocloritoid (B. E. Patrick & R. G. Berman, unpublished, 1990), sudoite and magnesiocarpholite (Vidal *et al.*, 1992). The calculations were performed with the PTAX and TWQ software (Brown *et al.*, 1988; Berman, 1991).

Constant Mn–Mg partition coefficients derived from references given in parentheses below were assumed:

$$K_D^{Mn/Mg}(Cph/Sud) = 35 \text{ (Harz; Theye \& Siedel, 1993)}$$

$$K_D^{Mn/Mg}(Cld/Sud) = 161 \text{ (Ottre; T. Theye, unpublished analyses, 1994)}$$

$$K_D^{Mn/Mg}(Cld/Grt) = 35 \text{ (Venn-Stavelot Massif; Theye \& Fransolet, 1994)}$$

$$K_D^{Mn/Mg}(Cld/Chl) = 26 \text{ (Venn-Stavelot Massif; Kramm, 1982; Bossiroy, 1984).}$$

In the MASH chemical system, the lower-pressure stability of magnesiocarpholite is defined at ~7 kbar (Fig. 4) by the reactions sudoite + quartz = carpholite, chlorite + kaolinite = carpholite + quartz + H<sub>2</sub>O, and chlorite + pyrophyllite + H<sub>2</sub>O = carpholite + quartz (Theye *et al.*, 1992; Vidal *et al.*, 1992). Because the Fe–Mg partition coefficients Cph/Chl and Cph/Sud are not very far from one, the lower-pressure limits of the ferro- and of the magnesiocarpholite stability fields are similar.

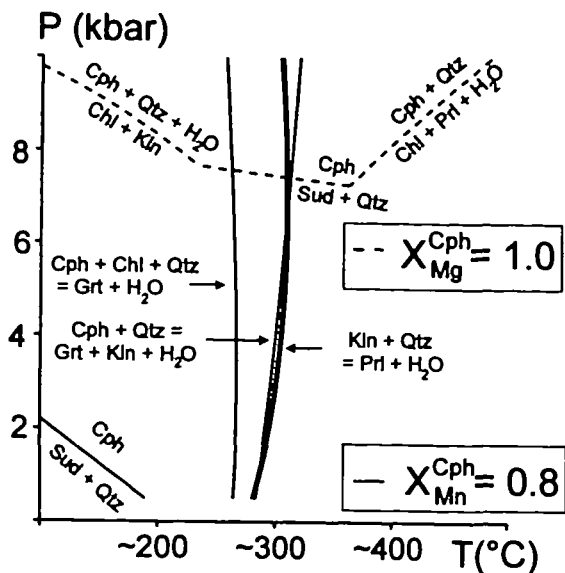
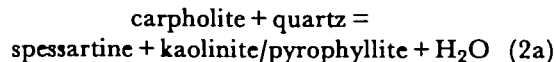
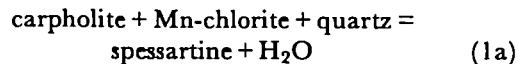


Fig. 4. Tentative  $P$ - $T$  diagram with calculated MnMASH equilibria. Thin lines are isopleths for  $X_{Mn}(Cph) = 0.8$  for the parageneses Cph + Sud, Cph + Chl + Grt and Cph + Kln + Grt ( $H_2O$  and quartz in excess); labels show the corresponding end-member equilibria. Dashed lines represent the lower-pressure stability of magnesiocarpholite. Thick line is ASH reaction as indicated. (For mineral abbreviations, see Table 1.)

In contrast, in the MnMASH system, these equilibria shift to lower pressure with increasing Mn/Mg of minerals owing to the high Mn-Mg partition coefficient between carpholite and sudoite or chlorite. In the limiting MnASH system, the stability fields of sudoite and of Mn-chlorite + kaolinite/pyrophyllite have completely disappeared, that is, carpholite is a stable mineral at very low pressure conditions (see Fig. 4). This result explains the presence of carpholite in the Lienne syncline as well as in natural low-pressure environments such as in hydrothermal formations.

The isopleth for the carpholite-sudoite equilibrium calculated from the mineral compositions as measured in the Lienne syncline [ $X_{Mn}(Cph) = 0.8$  in Fig. 4] is not meaningful, yielding negative pressures at  $T > 200^\circ\text{C}$ . Carpholite and sudoite of these rocks, consequently, probably do not represent chemical equilibrium as already inferred from microstructural features.

Another interesting result is that, in the MnMASH system, already at relatively low Mn/(Mn + Mg), equilibria involving chloritoid become metastable with respect to parageneses with both carpholite and garnet. At high Mn/(Mn + Mg), these parageneses are carpholite + chlorite + garnet and carpholite + garnet + kaolinite/pyrophyllite. The corresponding end-member equilibria are



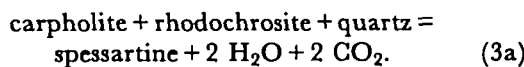
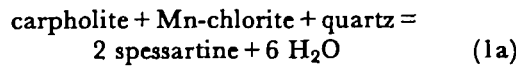
[the supplement (a) refers to equilibria of the end-member system MnASH(-CO<sub>2</sub>), whereas equilibrium numbers without supplement refer to the enlarged system MnMASH(-CO<sub>2</sub>) as discussed below]. The calculations indicate that pure carpholite would react, nearly independently of pressure, at  $\sim 240^\circ\text{C}$  according to equilibrium (1a), and at  $280^\circ\text{C}$  according to (2a). Concerning (1a), it should be noted that the composition of Mn-chlorite as analysed in the Lienne rocks is not sufficiently aluminous (see Fig. 6, below) to allow the simpler reaction Mn-chlorite + quartz to form spessartine + H<sub>2</sub>O, which was experimentally studied by Hsu (1968). To balance this simpler reaction, a chlorite with 2.33 Si p.f.u. is necessary. This value is far from chlorite compositions in the Lienne syncline (Table 2). Moreover, the calculated low-temperature limit of the spessartine stability field is considerably lower than according to the experimental data of Hsu (1968). [For a discussion of the work of Hsu (1968), see below.]

In Fig. 4, the calculated isopleths  $X_{Mn}(Cph) = 0.8$  as observed in the Lienne rocks are presented for equilibria (1) and (2). They indicate higher temperatures compared with the Mn end-member system:  $\sim 270^\circ\text{C}$  (paragenesis with Cph + Chl + Grt) and  $300^\circ\text{C}$  (Cph + Grt + Kln/Prl), respectively.

The calculated temperatures for  $X_{Mn}(Cph) = 0.8$  are not very far from the estimated metamorphic temperature range derived for the Lienne syncline. However, as described above, kaolinite or pyrophyllite have not been observed as decomposition products of carpholite, but muscovite and paragonite have been observed, in addition to chlorite and garnet. The formation of muscovite, paragonite and chlorite as alteration products of magnesiocarpholite was also described by Goffé & Vidal (1992) in high-pressure metamorphic pelites. These workers interpreted the appearance of white mica as due to a diminution of Na<sup>+</sup> and K<sup>+</sup> in the fluid phase if pressure drops or temperature increases. These processes lead to the formation of chlorite and of white mica (instead of pyrophyllite or kaolinite) at the expense of carpholite. The same reasoning can be applied to the rocks under consideration here.

Another environment that has to be discussed with respect to mineral reactions involving carpholite is rhodochrosite-bearing segregations in the manganese ore. In a first approximation, phase relationships of

these rocks can be represented in terms of the chemical system MnO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub>-H<sub>2</sub>O-CO<sub>2</sub> (MnASHC), involving the phases spessartine, carpholite, Mn-chlorite, rhodochrosite and quartz, as well as H<sub>2</sub>O and CO<sub>2</sub> in the fluid phase. A Schreinemakers analysis with the variables X<sub>CO<sub>2</sub></sub> and T (Fig. 5) shows that the upper thermal stability of carpholite in the presence of Mn-chlorite or rhodochrosite with quartz is defined by the reactions



Assuming the presence of all phases under consideration and buffering of the fluid phase by the mineral assemblage carpholite + chlorite + rhodochrosite + spessartine, the overall reaction corresponding to the MnASHC invariant point in Fig. 5 can be written

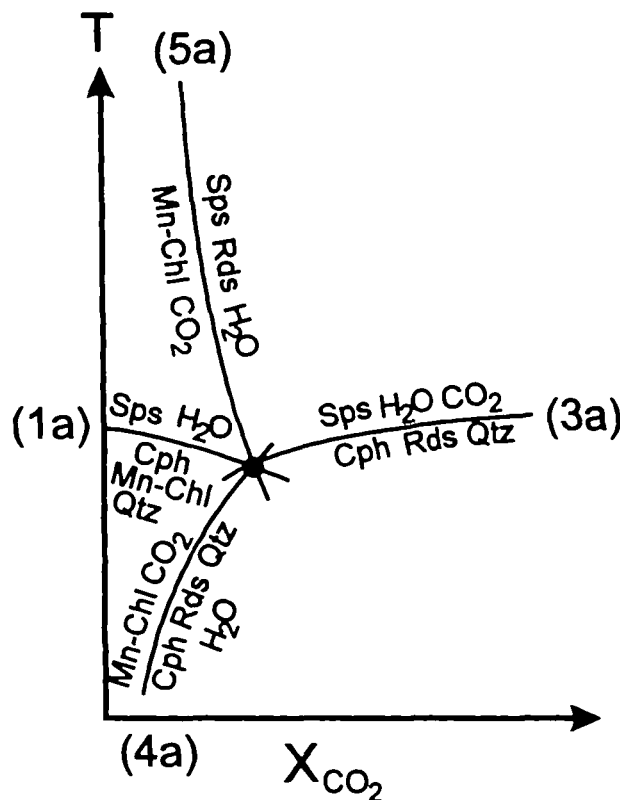
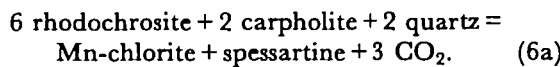
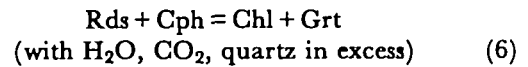


Fig. 5.  $T$ - $X_{\text{CO}_2}$  diagram showing a Schreinemakers analysis of equilibria in the chemical system MnASHC, involving the phases spessartine, Mn-chlorite, carpholite and rhodochrosite. H<sub>2</sub>O, CO<sub>2</sub> and quartz in excess. (For mineral abbreviations, see Table 1.)

This reaction corresponds to the observation that, in segregations of the Mn ore, pseudomorphs after carpholite consist of chlorite and garnet and that rhodochrosite shows corroded outlines (Fig. 1b).

The natural minerals of the Lienne syncline, however, cannot be represented within the simple chemical system MnASHC, and at least magnesium has to be considered in addition. In Fig. 6, phase compositions are represented in an A-Mg-(Mn+Fe) triangle (iron only plays a subordinate role). The mineral reaction which can be derived from the crossing tie-lines shown is similar to reaction (6a):



but now in the enlarged chemical system MnMASHC.

Also for this case, we calculated MnMASHC equilibria with the thermodynamic data mentioned above. The equations of state used for the fluid phase are from Haar *et al.* (1984) for H<sub>2</sub>O, Mäder & Berman (1991) for CO<sub>2</sub>, and Kerrick & Jacobs (1981) for H<sub>2</sub>O-CO<sub>2</sub> mixing. Because of the restricted validity of the Kerrick & Jacobs equations, equilibrium temperatures <350°C have been estimated using only reaction (1).

The result of the calculation performed for a pressure of 2 kbar is shown in Fig. 7. The univariant equilibrium (6) (thick line in Fig. 7) terminates in invariant points of the end-member systems

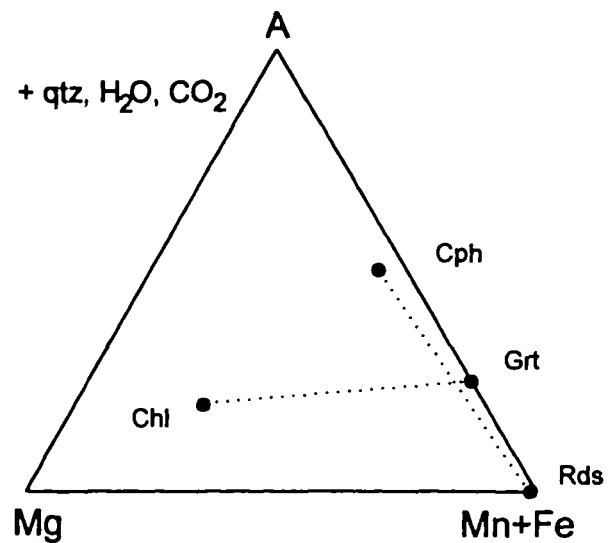


Fig. 6. A-Mg-(Mn+Fe) ternary plot presenting mineral compositions of coexisting garnet, carpholite, Mn-poor chlorite and rhodochrosite as measured in specimen 93/7 (Table 2c). Ferrous iron is present in significant amounts only in chlorite. The reaction  $\text{Cph} + \text{Rds} = \text{Grt} + \text{Chl}$  can be derived from the crossing tie-lines indicated. H<sub>2</sub>O, CO<sub>2</sub> and quartz in excess. (For mineral abbreviations, see Table 1.)

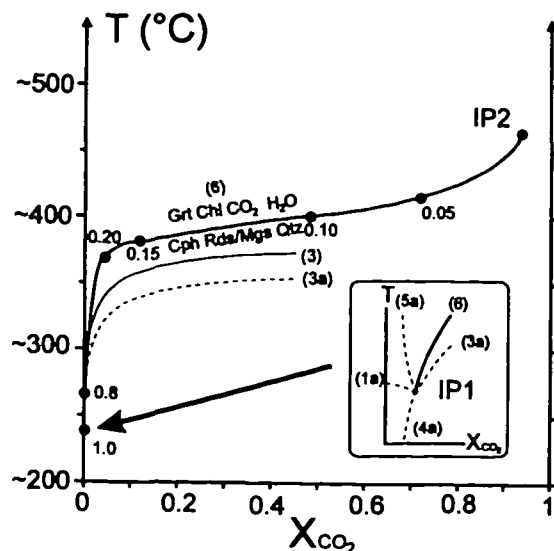
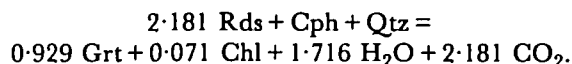


Fig. 7. Calculated tentative  $T$ - $X_{\text{CO}_2}$  section with phase equilibria in the chemical system MnMASHC at 2 kbar with  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and quartz in excess. Thick line: univariant MnMASHC equilibrium (6). The values given at the black dots along this curve indicate the changing  $X_{\text{Mn}}$  of carpholite. Thin line (3): isopleth  $X_{\text{Mn}}(\text{Cph})=0.8$  for the paragenesis  $\text{Cph} + \text{Rds} + \text{Grt}$ . Dashed lines emanating from invariant point IP1 are univariant equilibria for the end-member system MnASHC: (1a)  $\text{Cph} + \text{Chl} + \text{Qtz} = \text{Grt} + \text{H}_2\text{O}$ , (3a)  $\text{Cph} + \text{Rds}/\text{Mgs} + \text{Qtz} = \text{Grt} + \text{H}_2\text{O} + \text{CO}_2$ , (4a)  $\text{Cph} + \text{Rds}/\text{Mgs} + \text{Qtz} + \text{H}_2\text{O} = \text{Chl} + \text{CO}_2$ , (5a)  $\text{Chl} + \text{CO}_2 = \text{Rds}/\text{Mgs} + \text{Grt} + \text{H}_2\text{O}$ . IP2: invariant point for the MASHC system. Rds/Mgs: rhodochrosite-magnesite in solid solution (for other mineral abbreviations, see Table 1).

MnASHC (IP1) and MASHC (IP2), respectively. At each point of the univariant curve (6), the Mg/Mn of the minerals is fixed. The Mg-rich branch of the univariant curve is metastable with respect to minerals such as sudoite and pyrophyllite which are not considered in the calculations (Mg-rich carpholite is not stable at 2 kbar).

The calculated temperature for the invariant point involving the isopleths for  $X_{\text{Mn}}(\text{Cph})=0.8$  is also at  $\sim 250$ – $300^\circ\text{C}$  just as for the  $\text{CO}_2$ -free system. An important new result is that, for the mineral compositions under consideration, reaction (6), in the Lienne syncline, may take place in the presence of a very  $\text{CO}_2$ -poor fluid phase. The stable coexistence of carpholite and rhodochrosite as observed in one specimen (22646) can be attributed to a more  $\text{CO}_2$ -rich fluid phase. Breakdown of carpholite can be due to either increasing temperature or decreasing  $X_{\text{CO}_2}$ .

The stoichiometric coefficients of equilibrium (6) considering the composition of carpholite in the Lienne area [ $\text{Mn}/(\text{Mg} + \text{Mn})=0.8$ ; other minerals according to element partition coefficients] are



Thus, only small amounts of chlorite will be produced by the decomposition of Mn-rich carpholite and rhodochrosite. Because significant quantities of chlorite are present in the segregations of the Mn ore, this mineral is believed to have already been present associated with rhodochrosite and carpholite during the time of vein formation. A second generation of (Mn-poorer) chlorite was then formed through the decomposition of carpholite (see Fig. 2c). Possibly, this two-stage mineralogical evolution of the segregation can account for the presence of two distinct chlorite compositions as described by Schreyer *et al.* (1986).

In nature, carpholite exclusively occurs in low- $P$  environments. No natural examples and no information are available on the high- $P$  behaviour of this mineral, and calculations remain inconclusive as well.

The calculations performed here explain in a qualitative manner many natural observations in the Lienne syncline rocks such as the appearance of carpholite at low pressure and temperature and the reaction relations between carpholite and garnet. The quantitative values calculated above can only be considered as an approximation. Besides uncertainties in thermodynamic data, the assumption of  $P$ - $T$  independent element partition coefficients and of ideal mixing models, especially at low Mg/(Mg + Mn), introduces significant uncertainties. The temperature uncertainty of the calculations is estimated to be at least  $30^\circ\text{C}$ .

## APPEARANCE OF SPESSARTINE DURING PROGRADE METAMORPHISM

Experimental investigations on the lower thermal stability of spessartine were carried out by Hsu (1968). Hsu observed growth of spessartine at the expense of poorly defined 7 Å Mn-chlorite and quartz at  $488^\circ\text{C}$  and 3 kbar,  $415^\circ\text{C}$  and 2 kbar, and  $370^\circ\text{C}$  and 0.5 kbar under unbuffered oxygen fugacity conditions. No experiments, however, were reported showing the growth of Mn-chlorite and quartz at the expense of spessartine, but only the continued (metastable?) persistence of Mn-chlorite + quartz at low temperature. Moreover, the amount of the hydrospeessartine component in garnet and of the Tschermak substitution in chlorite were not determined in the run products of the equilibrium experiments. Therefore, the so-called equilibrium curve Mn-chlorite + quartz = spessartine + fluid drawn by Hsu (1968) was not really reversed and represents only the maximum lower thermal

stability of spessartine. The first appearance of spessartine (possibly containing some hydrogarnet component) during prograde metamorphism, possibly occurs as low as  $\sim 300^{\circ}\text{C}$  (at 1–2 kbar) as deduced from the reasoning presented here.

## CONCLUSIONS

The phase-petrological analysis of very low grade Mn-rich metasediments of the Ardennes shows that these rock types have the potential to sensitively characterize variables of metamorphism. At present, a full quantitative evaluation is hampered by the uncertainty or absence of thermodynamic data for Mn minerals. To improve this situation, it would be desirable to obtain more experimental data on Mn minerals, such as the upper thermal stabilities of otterelite, Mn-chlorite and carpholite, as well as further data on the lower thermal stability of spessartine.

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