Petrologic evidence for a rhodochrosite precursor of spessartine in coticules of the Venn-Stavelot Massif, Belgium

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Abstract

Minute CaMg-bearing rhodochrosite inclusions were discovered in spessartine crystals of small coticule globules enclosed within redschists that form the country rock of the famous coticule bands of Belgium. This points to a former metamorphic reaction relationship between the two minerals, such as rhodochrosite + pyrophyllite = spessartine + quartz + CO_2 + H_2O. The coexistence of spessartine with Mg-chlorite in the coticule globule could also indicate more complex reactions such as rhodochrosite + sudoite + quartz = spessartine + Mg-chlorite + CO_2 + H_2O. Our finding casts some doubt on the suggestion by Kramm (1976) that spessartine formed from Mn-montmorillonite in previously glassy volcanic tuffs.

KEYWORDS: rhodochrosite, spessartine, coticule, Venn-Stavelot Massif, Belgium.

Introduction

THE term coticule is applied world-wide to bands of essentially spessartine quartzites occurring in metamorphic sequences of sedimentary origin. Whereas in some cases the coticules are spatially related to stratiform metamorphosed hydrothermal ore deposits (e.g. Spry, 1990), in most others this is not so.

Perhaps the most famous coticules, to which the name meaning whetstone was originally applied, are those of the Venn-Stavelot Massif of Belgium (Renard, 1878; Lessuise, 1981). Their mode of origin is still a matter of considerable debate. They form centimetre- to decimetre-thick white to yellowish conformable bands within deeply purple redschists of Ordovician age. Not only is it problematic, how in an oxidizing sedimentary environment the elements Mn and Fe were most effectively fractionated in the Mn-rich, Fe-poor coticules versus the Mn-poor, Fe-rich redschists (for a discussion see Kramm, 1976), it is also controversial what the direct sedimentary or diagenetic precursor of the metamorphic mineral spessartine was. Spessartine is now part of a greenschists-facies assemblage with chlorite, quartz and white micas formed at some 400 °C and 2 kbar (Fransolet and Kramm, 1983). De Dycker (1939), Schreyer (1975), Lamens and Geukens (1984) as well as Lamens *et al.* (1986) favour carbonate-bearing protoliths as they are actually found in lower-grade portions of the massif. On the other hand, Kramm (1976) argued for a Mn-montmorillonite precursor that had formed diagenetically by diffusion of Mn into originally glassy tuff layers that were deposited intermittently within the shales subsequently transformed into red-schists. It is interesting to note in this connection that trace element studies of both coticules and red-schists yield virtually identical spectra for both rock types (Krosse, 1983; Krosse and Schreyer, in preparation) thus casting doubt on drastic changes in the material deposited.

Unfortunately, the petrography of the coticule bands with its equilibrated stable greenschists-facies assemblage does not lend unequivocal support to either hypothesis: While montmorillonite would not be expected to survive metamorphism, no indications were found thus far for any carbonate relics within the coticules. Therefore, it seems important to record here the first discovery of Mn-carbonate inclusions in spessartine within small coticule globules that occur as sedimentary fragments within redschists directly adjacent to coticule bands.

The locality of our samples are the dumps of the well-known former coticule mine Le Coreux

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situated between Vielsalm and Sâlmchateau in the southwestern portion of the Venn-Stavelot-Massif (locality 8a of Fransolet *et al.*, 1977). Some of the redschists present were found to be unusual, as they contain, in random distribution, numerous millimetre-sized round to ellipsoid globules exhibiting the distinct white to yellowish colour of the coticules. Apparently they are due to intraformational erosion and resedimentation processes. Thin sections confirm that all these globules contain the characteristic coticule mineral assemblage with spessartine, quartz and variable amounts of phyllosilicates. One redschist sample (No. 7288 of the Bochum collection) was chosen for more detailed study, because it contains the largest and most numerous carbonate inclusions. It is to be noted, however, that not all the globules observed do contain these inclusions, and that their nature was by no means clear initially, due to their minute crystal size.

Experimental results

Fig. 1 shows in thin section the entire globule studied here in detail. It is surrounded by the redschist made up of hematite, quartz, chlorite and white mica. The peripheral zone of the globule, especially thick in the upper left and lower right portion of the picture, consists virtually only of muscovite. Towards the centre, finer grained quartz becomes the dominant mineral, thus forming a matrix for the small euhedral to anhedral isometric spessartine crystals that contain the minute, highly birefringent crystals to be identified (Fig. 2). Their size turned out to be too small for quantitative electron microprobe analysis. Muscovite is spectacularly absent in the inner zone of the 'minicoticule'; however, there is some chlorite interspersed with quartz and garnet. Hematite is a rare accessory.

In Table 1 one selected microprobe analysis each of garnet, chlorite and muscovite are listed. *Garnet* is of nearly pure spessartine end-member composition with only little of the Ca-garnet and pyrope components. *Chlorite* is of nearly pure Mg end-member composition; however, it is more aluminous than ideal clinochlore, $Mg_5Al[AlSi_3O_{10}](OH)_8$, thus representing what was formerly called 'sheridanite', and it is also not ideally trioctahedral. Notable are the contents of F and in some analyses of Zn (up to 0.25 wt.% ZnO). The chlorites analysed by Kramm (1976) from coticules are still more aluminous than the ones found here. *Muscovite* contains some 19 mol.% of paragonite component. This is in fair agreement with the determination by Kramm (1976) from X-ray data (17 mol.%) and indicates minimum temperatures in the order of 400 °C (Chatterjee and Flux, 1986), in good agreement with other thermometers. Contrary to the assumption of Kramm (1976), however, the muscovite analysed is *not* phengitic but shows the ideal Si value of 3.0 per formula unit. Nevertheless, it does contain some Mg and Fe, the latter

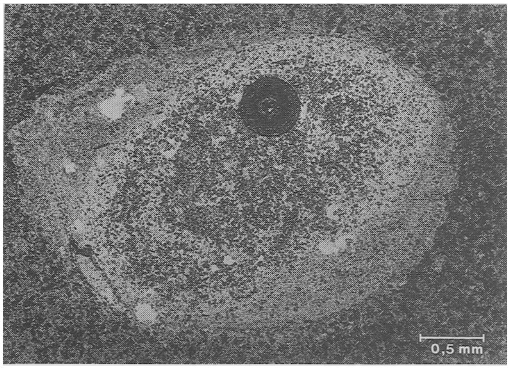

FIG. 1. Microphotograph of a globule of coticule enclosed within darker redschists. Its central portion consists essentially of garnet, quartz, and some chlorite. It is surrounded in the upper left and lower right by thick zones of muscovite. Dark circle at upper end of 'minicoticule' marks the location of drilling the thin section in order to obtain samples for optical measurements. The white patches in the muscovite zone are holes in the slide. Plane polarized light.

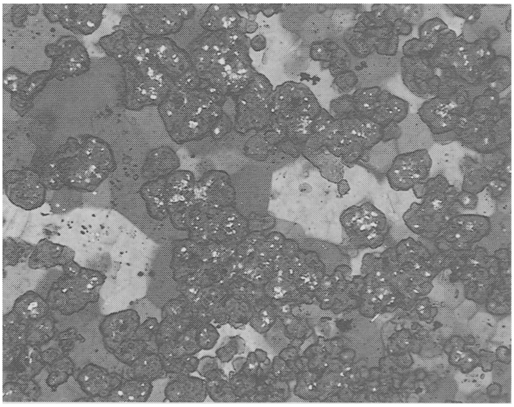

FIG. 2. Microphotograph of the typical coticule assemblage spessartine–quartz from the centre of the globule (Fig. 1). Note isometric garnet crystals carrying minute, highly birefringent inclusions (white). Matrix is formed by well recrystallized quartz. Nicols are not quite crossed in order to allow clearer distinction between garnet and inclusions. Long edge of picture equals 300 μm.

Table 1: Results of microprobe analyses of the constituent minerals of a coticule globule in redschist sample 7288 from Le Coreux, Belgium

	Analyses		
	Spessartine	Chlorite	Muscovite
SiO_2	36.36	28.21	45.29
TiO_2	.24	.03	.17
Al_2O_3	20.23	23.78	35.86
Cr_2O_3	.02	n.d.	.03
$Fe_2O_3$1)	.36	--	2.843)
FeO	.49	1.092)	--
MnO	40.04	1.55	.05
MgO	.59	30.20	.93
ZnO	n.d.	n.d.	.11
CaO	1.05	.02	n.d.
BaO	n.d.	n.d.	.22
Na_2O	n.d.	.01	1.40
K_2O	n.d.	.01	8.85
Cl	n.d.	.01	.02
F	n.d.	.40	.09
	99.38	85.31	95.86
O≡F,Cl	--	.17	.05
total	99.38	85.14	95.81

Structural Formulae					
	Spessartine		Chlorite		Muscovite
Valenc.	48.00		48.00		42.00
Si	5.99	Si	5.42	Si	6.00
Al	.01	Al	2.58	Al	2.00
$\Sigma^{[4]}$	6.00	$\Sigma^{[4]}$	8.00	$\Sigma^{[4]}$	8.00
Al	3.92	Al	2.80	Al	3.60
Cr	.00	Cr	--	Cr	.00
Fe^{3+}	.04	Fe^{3+}	--	Fe^{3+}	.28
Ti	.03	Ti	.00	Ti	.02
$\Sigma^{[6]}$	3.99	Mg	8.65	Mg	.18
		Fe^{2+}	.18	Zn	0.01
Mg	.15	Mn	.25	Fe^{2+}	--
Fe^{2+}	.07	Ca	.00	Mn	0.01
Mn	5.59	Na	.00	$\Sigma^{[6]}$	4.10
Ca	.19	K	.00		
$\Sigma^{[8]}$	6.00	$\Sigma^{[6]}$	11.88	Ca	.00
				Ba	.01
Spess.	93.90%	F	.24	Na	.36
Ca-Gt.	2.47%	Cl	.00	K	1.50
Pyr	2.45%			ΣInt	1.87
Alm	1.11%				
				F	.04
				Cl	.01

1)Calculated to make $\Sigma^{[6]}$ + Ti = 4.00
2)Total Fe as FeO
3)Total Fe as Fe_2O_3
n.d. = not detected

here computed as Fe^{3+} replacing Al. The fluorine content of the mica is considerably lower than in the chlorite.

In order to determine the nature of the strongly birefringent mineral inclusions within spessartine (Fig. 2), two independent methods were employed.

Firstly, using the spindle stage (Medenbach, 1985), it was found that the highest index of refraction of the minute inclusions happens to match exactly that of the garnet, which was determined as $n = 1.805$. This is the value of pure spessartine, in agreement with the chemical analysis. On the other hand, an n_o-value of 1.805 is close to, but lower than that of the ideal $MnCO_3$ end-member, the latter being 1.816. Thus, if the inclusions represent rhodochrosite, this phase is not of end-member composition. Lowering of the n_o could be caused, in particular, by some Ca replacing Mn.

Secondly, microprobe analyses were performed on the inclusions plus necessarily the enclosing garnet and compared with others of inclusion-free garnet. The results can best be judged from the energy dispersive spectra reproduced in Fig. 3. While the pure garnet exhibits only the peaks of Al, Si, and Mn with just a very small one for Ca, the 'mixed' spectrum shows a strong decrease in Si and Al connected with increases in Mn and Ca, and Mg appears in addition. No other elements were detected, but small amounts of iron cannot be seen here due to overlapping of Fe-$K\alpha$ and Mn-Kβ. Therefore, the inclusions must be poor in or free of Al and Si and contain Mn, Ca, and Mg as essential cations. Taking this in conjunction with the optical properties, we conclude that the problematic inclusions do represent a carbonate close to rhodochrosite, but contaminated by Ca and Mg causing solid solution towards kutnohorite, $CaMn(CO_3)_2$, and dolomite.

Discussion

The above results are considered as compelling chemical and textural evidence that the spessar-

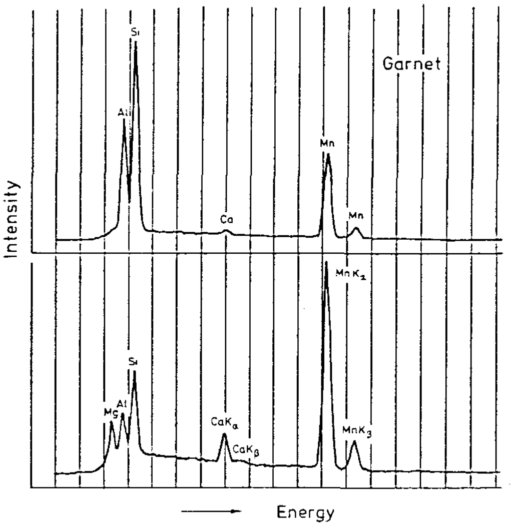

FIG. 3. Energy dispersive spectra measured with the electron microprobe on pure garnet (upper spectrum) and a portion of garnet rich in inclusions (see Fig. 2) below. The elements detected by their characteristic peaks are indicated.

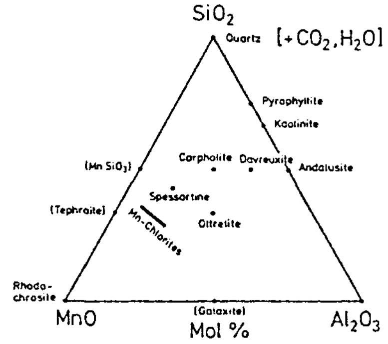

FIG. 4. Relevant phases of the system MnO–Al_2O_3–SiO_2–H_2O–CO_2 projected on the gas-free base plane. Phases in parentheses were not found in the Venn-Stavelot Massif. Carpholite (Fransolet, 1972) and davreuxite (Fransolet *et al.*, 1984) generally occur as nearly pure end members in the massif; virtually pure ottrelite, the Mn-end member of chloritoid, was only recently found by Theye and Reinecke (personal communication). For compositions of Mn-rich chlorites in the Massif see Schreyer *et al.* (1986). Hydrous Mn-silicates were neglected.

tine crystals of the 'minicoticule' grew by virtue of a metamorphic reaction, in which rhodochrosite was consumed. Note from Fig. 2 that the carbonate relics are exclusively located inside the garnet as the reaction product, whereas quartz is free of them, possibly because it was a reactant as well.

Like the normal, more voluminous coticule bands analysed by earlier workers (e.g. Kramm, 1976; Krosse, 1983), the bulk chemistry of the 'minicoticule' without the muscovite rim lies largely within the system MnO–Al_2O_3–SiO_2–H_2O. Fig. 4 shows, in a ternary projection, phases that are of interest for coticule formation and that were actually found in other manganiferous rocks of the Venn-Stavelot Massif. It is clear from this plot that spessartine formation at the expense of rhodochrosite requires an aluminous phase as a necessary reactant. Thus, one possible reaction might be

$$\text{rhodochrosite} + \text{kaolinite} + \text{quartz} \rightarrow \text{spessartine} + CO_2 + H_2O \qquad (1)$$

However, for conditions of water pressure equalling total pressure, the stability fields of kaolinite (Halbach and Chatterjee, 1982) and spessartine (Hsu, 1968) do not overlap. Therefore, pyrophyllite instead of kaolinite might seem a more likely reactant phase, except that in this case quartz is produced rather than consumed:

$$\text{rhodochrosite} + \text{pyrophyllite} \rightarrow \text{spessartine} + \text{quartz} + CO_2 + H_2O \qquad (2)$$

However, any other of the Al-bearing phases andalusite, carpholite, davreuxite, or even ottrelite may also have participated in the garnet-producing reaction. Unfortunately, no evidence whatsoever exists for any of all these potential reactants in our rock. It should also be borne in mind that with rhodochrosite as a reactant phase, water activity will certainly be well below unity, so that reaction curves will be generally shifted towards lower temperatures.

The presence of Mg-rich chlorite in the coticule globule studied is also of interest for the metamorphism of this small rock volume. It is well known that pure Mn-chlorites are stable at low temperatures only, and Hsu (1968) has found Mn-chlorite + quartz to represent the low-temperature assemblage equivalent of spessartine + H_2O below about 400 °C. In the Venn-Stavelot Massif, Schreyer *et al.* (1986) have discovered rather Mn-rich, Mg-bearing chlorites in those parts of the massif that are of lower metamorphic grade than the ones carrying the typical coticule bands, but that nevertheless contain spessartine. Considering the phase relations of garnet outlined by Hsu (1968), it is clear that, with increasing metamorphic grade, the chlorite phase becomes progressively more magnesian, while Mn is preferably incorporated in the garnet phase. The spessartine + Mg-chlorite assemblage found in the coticule globule studied here just as in normal coticule bands may thus indicate that originally Mn-rich chlorite was an additional reactant for spessartine formation besides rhodochrosite. The triangular plot of Fig. 5 shows these more complex phase relations in the multicomponent natural system. Thus the additional multivariant reaction envisaged would be

$$\text{MgMn-chlorite} + \text{quartz} \rightarrow \text{spessartine} + \text{Mg-chlorite} + H_2O. \qquad (3)$$

In recent years, the di/trioctahedral chlorite mineral sudoite (Fransolet and Bourguignon, 1978; Kramm, 1980) was found as an additional phase in some of the coticule bands of the Venn-Stavelot Massif (unpublished data of several workers of the Bochum Institute). Its presence opens up still another possibility for a spessartine-producing reaction at the expense of rhodochrosite (see Fig. 5)

$$\text{Rhodochrosite} + \text{sudoite} + \text{quartz} \rightarrow \text{spessartine} + \text{Mg-chlorite} + CO_2 + H_2O. \qquad (4)$$

The presence of Ca and Mg in the carbonate discovered in our sample obviously does not invalidate the above reactions but only renders them more complicated. Ca is incorporated in the garnet, while Mg enters the chlorite phase.

In summary, there is now petrologic evidence for a former reaction relationship between spessartine of the coticules and a former Mn-carbonate precursor. Our observations do not allow any conclusions, however, as to whether this Mn-carbonate was by itself a sedimentary product or formed—as suggested by Lamens *et al.* (1986)—by diagenetic replacement of initial calcite of marly sediments. Our observations cast some doubt on the hypothesis of Kramm (1976) that the coticule layers were originally volcanic tuffs altered to Mn-montmorillonite.

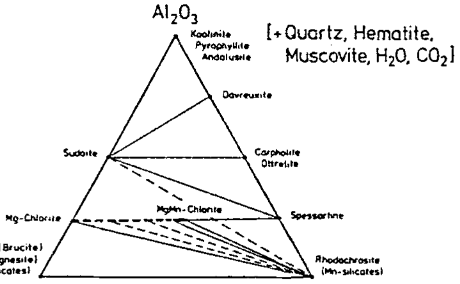

FIG. 5. Ternary projection of the multicomponent natural coticule system showing observed and possibly relevant phases for coticule metamorphism. Phases in parentheses were not found in the Venn-Stavelot Massif. Heavy dashed line indicates chlorite solid solutions found in the massif as summarized by Schreyer *et al.* (1986). Thin solid lines represent observed tie lines between coexisting phases in various rocks of the massif. Thin broken lines are inferred.

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