

PREHNITE/CHLORITE AND ACTINOLITE/EPIDOTE  
BEARING MINERAL ASSEMBLAGES IN THE METAMORPHIC  
IGNEOUS ROCKS OF LA HELLE AND CHALLES,  
VENN-STAVELOT-MASSIF, BELGIUM<sup>1</sup>

by

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(4 figures, 4 tables and 2 plates)

**RESUME.**- De nouvelles analyses de roches et les premières analyses à la sonde électronique de leurs phases minérales sont données pour une métatonalite et un metabasalte observés dans des zones différentes du pré-Dévonien du Massif de Stavelot soumis ensuite à un métamorphisme faible d'âge hercynien.

Deux associations minérales ACF caractéristiques sont reconnues : 1) prehnite-chlorite-épidote dans la métatonalite ; 2) actinote-chlorite-épidote dans le metabasalte. Alors que la deuxième association, typique du faciès schistes verts, est propre à un métamorphisme relativement élevé dans la partie centrale du massif, l'association à prehnite, se rencontrant dans sa limite nord est, indique des températures plus basses entre environ 320° et 360°C et de basses pressions de confinement ( $P_{H_2O} < 2,5 \pm 1$  kb). Elle peut s'être formée aux dépens d'une pumpellyite préexistante, éventuellement stable dans des conditions de métamorphisme encore plus faibles.

Les épidotes observées dans le metabasalte ont des compositions qui suggèrent un domaine de non miscibilité entre un terme relativement pauvre en Fe (58 %  $Ca_2Al_2Fe^{3+}Si_3O_{12}OH$ ) et des termes plus riches variant entre 86 % (noyau) et 71 % (bordure) de cette composition théorique, en fonction du niveau croissant de métamorphisme. Des analyses à la microsonde sont également présentées pour la prehnite, l'actinote, la chlorite, la phengite, les feldspaths, le sphène et un minéral opaque résiduel avec une composition voisine de  $Fe_2Ti_3O_9$  (" pseudorutile ") formé à partir des lamelles d'ilménite d'une intercroissance primaire de magnétite-ilménite.

**ABSTRACT.**- New rock analyses and the first microprobe analyses of the constituent mineral phases are reported for a metatonalite and a metabasalt occurring in different zones of the pre-Devonian of the Venn-Stavelot-Massif that was later subjected to low-grade Hercynian metamorphism. Two characteristic ACF mineral assemblages are recognized : 1) prehnite-chlorite-epidote in the metatonalite; 2) actinolite-chlorite-epidote in the metabasalt. Whereas the latter assemblage typical for greenschists is representative for a relatively high grade of metamorphism in the central portion of the massif, the prehnite assemblage occurring near its north-eastern end indicates lower temperatures between about 320° and 360°C and low confining pressures ( $P_{H_2O} < 2.5 \pm 1$  kb). It may have formed at the expense of preexisting pumpellyite that should occur stably at a still lower grade of metamorphism.

The epidotes occurring in the metabasalt have compositions that suggest a miscibility gap between a relatively Fe-poor member (58 %  $Ca_2Al_2Fe^{3+}Si_3O_{12}OH$ ) and Fe-richer members varying from some 86 % (core) to 71 % (rim) of the above end member as a function of increasing metamorphic grade. Microprobe data are also presented for prehnite, actinolite, chlorite, phengite, feldspars, sphene, and a relic ore mineral with a composition near  $Fe_2Ti_3O_9$  (" pseudorutile ") that was formed from the ilmenite lamellae of a former magnetite/ilmenite intergrowth.

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## 1.- INTRODUCTION

The Rhenish Mass as part of the Hercynian Mountain Belt is relatively poor in rocks of igneous origin. Among those present by far the most common ones are Devonian volcanics of basaltic compositions such as the diabases of the Lahn-Dill area in Hesse and the "greenstones" of Sauerland. On the other hand, intrusive rocks, and especially plutonic types, are extremely seldom. Therefore, the tonalites and basic dykes occurring in the pre-Devonian parts of the Venn-Stavelot-Massif and their geologic and petrologic properties are of special interest to earth scientists. For rocks of this kind occurring in the German portion of the Massif SCHERP (1959) has presented a rather detailed description. In the Belgian literature similar studies exist by various authors, e.g. RONCHESNE (1934), VAN WAMBEKE (1955), and CORIN (1965).

Generally, these earlier publications have focused on the petrography and petrochemistry of the igneous rocks as well as on reconstructions of the original, magmatic mineralogy. The present study, on the other hand, was mainly aimed at characterizing those minerals and mineral equilibria that were formed subsequently to the igneous activity, that is mainly during the period of Hercynian metamorphism. Although these minerals usually make up the bulk of the rocks studied, they are generally finegrained so that microprobe analyses were required for adequate characterization. It was hoped that the new mineral data obtained might throw some additional light on the recently discussed problem of pressure-temperature conditions of Hercynian metamorphism (KRAMM, 1973; SCHREYER, 1975; FRANSOLETT *et al.*, 1977).

## 2.- PETROLOGIC DESCRIPTION AND ANALYTICAL RESULTS

### 2.1.- THE METATONALITE OF LA HELLE

This rock type which is known in the literature as tonalite forms a small intrusive mass within Early Paleozoic rocks (Revin) of the northeastern part of the Venn-Stavelot-Massif. Petrographic descriptions were given by DANNENBERG & HOLZAPFEL (1898), RONCHESNE (1930), VAN WAMBEKE (1955), and CORIN (1965). A new chemical analysis made on the very sample that was used for the microprobe studies (N<sup>o</sup> 7234) is listed in Table 1 in comparison to earlier analyses reported in the literature. The new analysis is very similar to the older ones and thus does not contribute to the nomenclature problem connected with

this rock. RONCHESNE (1930) had first called this granitoid material tonalite, because he could not find any K feldspar, and some cores of the plagioclase were as basic as An<sub>56</sub>. Nevertheless it is clear, that none of the analyses are rich enough in CaO and poor enough in SiO<sub>2</sub> for a tonalite, but would much rather correspond to the chemistry of a trondhjemite (TROGER, 1935). However, it is indeed possible that during metamorphism the original chemistry of the igneous rock was changed through loss of Ca and perhaps metasomatism of SiO<sub>2</sub> and alkalis. Therefore, in the present paper the rock is named metatonalite.

The rock specimen N<sup>o</sup> 7234 has a decidedly massive and typically plutonic fabric with an average grain size near 1 mm. It is of light grey color with a slightly greenish tint due to the presence of secondary mafic minerals. Under the microscope generally euhedral plagioclase and interstitial quartz are recognized as the dominant minerals, but there is also K feldspar amounting to some 10 %/o. The main mafic phase is coarse chlorite, probably in most cases pseudomorphous after biotite. White mica occurs both in coarse blades and in minute sericitic flakes, the latter mainly within plagioclase. That phase also contains small roundish secondary crystals of a mineral of the epidote group formed through saussuritization. An epidote mineral is also found as one of the constituents of a rather conspicuous mafic assemblage forming small aggregates together with calcite, pyrite, and often a finegrained chlorite. The most striking crystals within these aggregates (Pl.1 :1), however, have rectangular cross sections with straight extinction, negative elongation, medium birefringence, and two orthogonal cleavage planes paralleling the crystal outlines. The optical sign is positive. The axial angle of  $66 \pm 2^\circ$  suggests, and the microprobe work proved this phase to be prehnite which has previously not been described from this rock. The shape of these prehnite crystals may be described as thick plates after (001). There is a possibility that this mineral had earlier been misidentified optically as zoisite which is mentioned by both RONCHESNE (1930) and VAN WAMBEKE (1955), but was not found in the present study. A final mineral occurring both in the aggregates and throughout the rock in small anhedral masses often associated with chlorites is sphene (titanite).

The total number of microprobe analyses made is : 6 on plagioclase, 2 on K feldspar, 3 on chlorite, 1 on white mica, 9 on epidote, 4 on prehnite and 5 on sphene. The analytical results compiled in Table 2 were selected as extreme compositions thus demonstrating the relatively small variations in the chemistry of the phases; when only one analysis is reported, there was no significant variation.

Table 1.- Bulk chemical analyses of the metamorphic igneous rocks of La Helle and Challes as performed in this study and taken from the literature

	La Helle				Challes		
	No.7234	Dannenberg and Holzapfel (1898)	Ronchesne (1930)	Van Wambeke (1955)	No.9493	Chevron (1875)	Ronchesne (1934)
SiO <sub>2</sub>	71.2	70.28	70.06	68.28	46.7	48.26	49.23
TiO <sub>2</sub>	0.4	-	-	0.37	2.3	-	2.76
Al <sub>2</sub> O <sub>3</sub>	14.7	14.93	14.86	15.59	15.2	17.99	17.29
Fe <sub>2</sub> O <sub>3</sub>	0.8	1.42	1.64	0.20	4.9	8.41	2.78
FeO	1.2	-	0.63	2.90	7.9	4.56	8.39
MnO	0.02	0.06	0.06	0.18	0.22	0.39	0.18
MgO	1.1	0.76	1.02	1.37	6.5	5.38	2.73
CaO	2.3	3.29	3.45	2.52	9.9	8.58	10.16
Na <sub>2</sub> O	3.6	4.57	4.83	3.98	2.1	2.31	1.86
K <sub>2</sub> O	2.6	2.62	2.06	3.03	0.02	0.23	0.42
P <sub>2</sub> O <sub>5</sub>	0.04	-	-	trace	0.19	0.19	-
H <sub>2</sub> O	1.4	1.44	1.24	0.77	4.0	2.80	3.28
H <sub>2</sub> O <sup>-</sup>	0.1						
CO <sub>2</sub>	0.38				-		
S	0.80	FeS <sub>2</sub> 1.34	FeS <sub>2</sub> 1.28	0.44	0.49	-	FeS <sub>2</sub> 0.42
Total	100.64	100.71	101.13	99.63	100.88	99.11	99.50
-O*	-0.30				-0.18		
	100.34				100.70		

n.det. = not determined

\* The amount of oxygen subtracted is calculated assuming S to be present as FeS<sub>2</sub>.

Table 2.- Microprobe Analyses of Minerals of the Metatonalite of La Helle, Belgium (Sample 7234)

	Albi- te 1	Albi- te 2	K feld- spar	Chlori- te 1	Chlori- te 2	Phengite	Epido- te 1	Epido- te 2	Prehnite	Sphene 1	Sphene 2
SiO <sub>2</sub>	67.96	68.48	64.41	26.45	27.72	50.44	38.95	38.62	43.27	30.72	30.67
TiO <sub>2</sub>	-	-	0.30	0.03	0.10	-	-	-	-	35.28	32.80
Al <sub>2</sub> O <sub>3</sub>	19.01	19.49	18.10	19.07	17.44	29.83	29.90	27.69	24.13	3.38	5.38
Fe <sub>2</sub> O <sub>3</sub> 1)	0.08	0.10	0.32	-	-	-	4.70	7.19	0.27	-	-
FeO 2)	-	-	-	21.10	21.02	1.32	-	-	-	0.59	0.21
MnO	-	-	-	0.25	0.25	-	-	-	-	-	-
MgO	-	-	-	17.53	17.87	2.63	-	-	-	-	-
CaO	0.26	0.60	0.03	0.03	0.55	0.03	24.15	23.85	27.05	28.36	28.79
SrO	-	-	-	-	-	-	0.70	0.18	-	-	-
BaO	-	-	0.82	-	-	0.13	-	-	-	-	-
Na <sub>2</sub> O	11.46	11.58	0.35	-	-	0.12	-	-	-	-	-
K <sub>2</sub> O	0.05	0.06	15.84	-	-	11.14	-	-	-	-	-
	98.82	100.31	100.17	84.46	84.95	95.64	98.40	97.53	94.72	98.33	97.85
O-Basis	32	32	32	28	28	22	12.5	12.5	11	5	5
Si	12.01	11.95	11.95	5.67	5.90	6.69	3.00	3.02	3.00	1.01	1.01
Al <sup>IV</sup>	3.96	4.01	3.96	2.33	2.10	1.31	-	-	-	-	-
	15.97	15.96	15.91	8.00	8.00	8.00	3.00	3.02	3.00	1.01	1.01
Al <sup>VI</sup>	-	-	-	2.48	2.28	3.35	2.71	2.55	1.97	0.13	0.21
Ti	-	-	0.04	0.01	0.02	-	-	-	-	0.88	0.82
Fe <sup>3+</sup>	0.01	0.01	0.04	-	-	-	0.27	0.42	0.01	-	-
Fe <sup>2+</sup>	-	-	-	3.78	3.74	0.15	-	-	-	0.02	0.01
Mn <sup>2+</sup>	-	-	-	0.05	0.05	-	-	-	-	-	-
Mg	-	-	-	5.60	5.68	0.52	-	-	-	-	-
	0.01	0.01	0.08	11.92	11.77	4.02	2.98	2.97	1.98	1.03	1.04
Ca	0.05	0.11	0.01	0.01	0.13	0.00	1.99	2.00	2.01	1.00	1.02
Sr	-	-	-	-	-	-	0.03	0.01	-	-	-
Ba	-	-	0.06	-	-	0.01	-	-	-	-	-
Na	3.93	3.92	0.12	-	-	0.03	-	-	-	-	-
K	0.01	0.01	3.75	-	-	1.88	-	-	-	-	-
	3.99	4.04	3.94	0.01	0.13	1.92	2.02	2.01	2.01	1.00	1.02
Fe <sup>2+</sup>	-	-	-	0.40	0.40	0.22	-	-	-	-	-
Fe <sup>2+</sup> +Mg	-	-	-	-	-	-	-	-	-	-	-

1) Total iron as Fe<sub>2</sub>O<sub>3</sub>

2) Total iron as FeO

Plagioclase is relatively pure albite with end member ratios of  $Ab_{98.5}An_{1.3}Kf_{0.3}$  and  $Ab_{97.0}An_{2.7}Kf_{0.3}$  for analysis 1 and 2, respectively.

Potassium feldspar ( $KF_{96.7}Ab_{3.1}An_{0.2}$ ) is rather pure, too, which suggests very low temperatures of alkali feldspar equilibration. Noteworthy are its Ba, Ti, and Fe contents.

The two analyses of chlorite made in different portions of the interior of one flaky crystal are almost identical regarding their Mg/Fe-ratios, but they differ both in tetrahedral and octahedral Al. It seems possible that this property was inherited from the preexisting biotite of magmatic origin. The same may be true for the unusual Ca contents which are foreign to the chlorite structure and may have been preserved within the brucite layer as a relic of the mica interlayer.

The white mica composition is spectacular because of its high Si and Mg contents. It should, therefore, be named phengite. The typical substitution  $(Mg,Fe^{2+})Si \rightarrow AlAl$  is verified in a virtually ideal way.

The epidote group minerals are slightly inhomogeneous with regard to their  $Fe^{3+}/Al$  ratios. In terms of the ideal pistacite end member  $Ca_2Fe_3^{3+}Si_3O_{12}(OH)$  (= Ps) they range from  $Ps_9$  to  $Ps_{14}$ , which means they are partly clinzoisites, partly epidotes setting the limit at  $Ps_{11}$  as suggested by RAITH (1976). Notable are their strontium contents.

In contrast, the coexisting prehnite is very poor in iron and approaches the ideal formula  $Ca_2Al_2Si_3O_{10}(OH)_2$  very closely.

All the analyses of sphene (titanite) are characterized by low analytical totals of some 98 %/o. This is due to the additional presence of fluorine with estimated amounts near 1.5 weight %/o. A further deviation from the ideal formula  $CaTiSiO_5$  is caused by the appearance of Al which replaces up to 20 %/o of the Ti in octahedral coordination. It seems that the introduction of the Al follows a coupled substitution  $Al^{3+} + F^- \rightarrow Ti^{4+} + O^{2-}$ . On this basis the sphenes analyzed here might be called grothites (SAHAMA, 1946). COOMBS *et al.* (1976) report similarly Al-rich sphenes in low-grade schists of the Swiss Alps, but they tend to ascribe Al to the presence of a  $CaAlSiO_4(OH)$  component.

In summary all the minerals analyzed from the metatonalite are of secondary, post-igneous origin representing an assemblage formed during low-grade metamorphism.

## 2.2.- THE METABASALT OF CHALLES

This rock which was named diabase by RENARD (1878) occurs in the central part of the Venn-Stavelot-Massif. It forms a sill of about 5 m thickness in steeply dipping schists of the Revin. Petrographic descriptions were given by RENARD (1878) and RONCHESNE (1934). The locality is also of historic interest, because CESARO (1887) described large albite crystals occurring along joints of this rock and forming the "twins of Challes", i.e. following the Albite-Carlsbad law.

A chemical analysis of one of the rock samples ( $N^0$  9493) studied here is given in Table 1 and compared with the earlier analyses by CHEVRON (1875) and RONCHESNE (1934). Except for the lower oxidation ratio of iron the new analysis is rather similar to that of CHEVRON (1876), whereas RONCHESNE's analysis differs from both of these in its low MgO contents. This latter property would be most unusual for a basaltic rock and may, therefore, be due to some analytical error. The new analysis is suggestive for a derivation from a tholeiitic basalt or, assuming an original dike rock, from a quartz dolerite (YODER & TILLEY, 1962). The high  $H_2O^+$  content indicates strong hydrous alteration of the original magmatic mineral content. Since the original grain size of the rock which would be vital for a distinction between fine grained basalt and coarser grained dolerite is no longer preserved, the nomenclature has to rely strictly on chemistry. It is in this sense that the name metabasalt should be understood that is used throughout the present paper.

The metabasalt from Challes is a very dense, fine-grained, green rock. Its massive fabric without any signs of schistosity was undoubtedly inherited from the magmatic stage. It is transected by a number of joints filled by fibrous asbestos-like minerals grown perpendicular to the joint planes.

Under the microscope all the rock samples studied here were found to consist of an intimate intergrowth of the following minerals: sodic plagioclase, actinolite, chlorite, epidote, calcite, sulfides and quartz (Pl.1:2). Most spectacular within this fabric is the additional occurrence of large skeletal crystals of sphene exhibiting a relic lamellar texture reminiscent of a (111)-magnetite-ilmenite intergrowth (Pl.2:3). The asbestos-like veins consist of all the minerals mentioned except sphene, but in much coarser crystals (Pl.1:2). In contrast to the description given by RONCHESNE (1934) no relic augites and labradorites dating back to the magmatic stage

could be found in the present samples. This is probably due to the fact that they were taken from portions strongly dissected by the asbestos-like veins in order to ensure maximum equilibration during metamorphism. The skeletal crystals of sphene were already recognized by RENARD (1878) and RONCHESNE (1934) and explained as pseudomorphs of leucoxene after ilmenite.

The following numbers of microprobe analyses were performed on sample 9493 : 5 on plagioclase, 10 on actinolite, 6 on chlorite, 8 on epidote, and 7 on sphene (titanite). Table 3 gives a selection representative of the compositional variations of each mineral.

Although the sodic plagioclases may still be named **albites**, they are partly richer in Ca than those from La Helle : analysis 1 =  $Ab_{92.4}An_{7.6}$ ; analysis 2 =  $Ab_{97.7}An_{2.2}$ .

The feathery actinolites are variable in their Ca and Al contents as well as their Mg/Fe ratios. Analysis 1 is representative for crystals with the maximum Al and minimum Ca values. The structural formula shows that Al introduction follows partly a  $Al^{VI}Al^{IV} \rightarrow R^{2+}Si$  substitution. The spectacular Ca-deficiency in the M4 position is obviously balanced by excess  $R^{2+}$  attributed to octahedral coordination. This indicates that part of  $Fe^{2+}$ ,  $Mn^{2+}$  and perhaps Mg occupy M4, which can be seen as solid solution between actinolite and cummingtonite. However, it may well be that this is actually a submicroscopic intergrowth of two amphiboles. The anomalous Ca and Al values are characteristic for the total volume of the crystals analyzed and not only for certain zones as one might expect. - Analyses 2 and 3, on the other hand, are very low in Al and have normal Ca values for actinolites. Notable is the complete lack of Na in all three analyses which precludes the edenite substitution  $NaAl^{IV} \rightarrow Si$ . The  $Fe^{2+}/(Fe^{2+} + Mg)$  ratios of the 10 actinolites analyzed show a surprisingly wide range from 0.31 to 0.43 which, together with the other chemical variation, indicates disequilibrium within the area of a thin section although local mosaic equilibria may be present. In some cases even discrete bundles of actinolite show Mg/Fe zoning, but no systematic trends of Mg or Fe enrichment from the core towards the fringes of these bundles could be ascertained. The noteworthy enrichment of the actinolites and all other mafic phases of the rock in vanadium may be of geochemical interest.

The variation of the chlorite composition is mainly in the Mg/Fe distribution, whereas Al is rather constant. The chlorite analyses 1 and 2 are from the same crystal and indicate iron enrichment towards the grain boundary against a feathery actinolite crystal which is also

iron-enriched near this boundary again proving overall disequilibrium. Although the ranges of  $Fe^{2+}/(Fe^{2+} + Mg)$  values of actinolites and chlorites overlap it is clear that in each case the adjacent and coexisting chlorite is richer in  $Fe^{2+}$  than the actinolite. The chlorites from the Challes metabasalt are also generally more iron-rich than those of the metatonalite (cf. table 2).

The main compositional variation of the epidotes lies in their  $Fe^{3+}/Al$  ratios. Analysis 1 and 2 were made on a single crystal in which the pistacite content decreases gradually from  $Ps_{28.8}$  in a broad central area to  $Ps_{23.7}$  in a more or less narrow peripheral zone. Analysis 3 performed in the center of an unzoned crystal of a different portion of the rock has a still lower iron content ( $Ps_{19.3}$ ). Once again this seems to be evidence for disequilibrium. It is interesting to note, however, that the composition of epidote 3 lies within the low-temperature miscibility gap of the epidote series recently defined by RAITH (1976) for a series of progressively metamorphic rocks within the Alps. In this same picture the epidote 1-2 compositions would fall near the iron-rich limb of RAITH's solvus curve. All the epidotes from Challes are richer in iron than those from La Helle (cf. table 2). Among the mafic phases of the metabasalt the epidotes are by far the most vanadium-rich ones : One analysis not given in table 3 yielded 0.38 weight %  $V_2O_5$ .

The composition of the large skeletal sphene crystals is also somewhat variable but no systematic correlation between composition and location in the lamellar texture was found. In none of the analyses fluorine was detected. Analysis 2 approaches the more complicated sphene compositions determined from La Helle (table 2) the main impurity being Al. However, here at Challes, the iron content is even higher, and Mg appears as a component. The crystal chemical implications of these impurities for the sphene structure are not known, especially because no F for the grothite substitution is available. The analytical totals of sphene 1 and 2 allow only minor amounts of additional components, perhaps some  $H_2O^+$  from  $OH^-$ -groups.

Replacement of ilmenite by sphene is a rather common phenomenon in metabasic rocks (TROGER, 1969, p. 148). Regarding its intergrowth with titaniferous magnetite frequently present in igneous materials two quite different cases of alteration have been reported. TROGER (1969, p. 150) emphasizes the selective replacement of the magnetite phase by sphene with the ilmenite lamellae preserved, whereas KUNYOSHI & LIU (1976) found the ilmenite replaced by sphene and magnetite still present. For comparison, the relic

Table 3.- Microprobe Analyses of Minerals of the Metabasalt of Challes, Belgium

	Albite 1	Albite 2	Actinolite 1	Actinolite 2	Actinolite 3	Chlorite 1	Chlorite 2	Epidote 1	Epidote 2	Epidote 3	Sphene 1	Sphene 2
SiO <sub>2</sub>	66.37	67.91	51.06	54.42	54.94	25.28	26.10	37.44	38.04	38.48	30.01	30.63
TiO <sub>2</sub>	-	-	-	-	-	-	-	-	-	-	39.31	36.57
Al <sub>2</sub> O <sub>3</sub>	20.69	19.65	2.84	0.79	1.05	18.95	18.75	22.49	24.33	25.51	0.43	2.43
Fe <sub>2</sub> O <sub>3</sub> <sup>1)</sup>	0.17	0.17	-	-	-	-	-	14.22	11.83	9.53	-	-
V <sub>2</sub> O <sub>3</sub>	-	-	0.03	0.05	0.02	0.08	0.03	0.16	0.11	0.09	-	-
FeO <sup>2)</sup>	-	-	15.49	16.50	12.47	27.48	23.31	-	-	-	0.65	1.14
MnO	-	-	0.44	0.70	0.30	0.48	0.38	0.08	0.06	0.05	0.05	0.03
MgO	-	-	14.59	12.24	15.43	13.21	16.51	-	-	-	-	0.55
CaO	1.67	0.48	11.04	12.52	12.68	0.05	0.03	23.06	23.16	23.42	28.24	27.59
Na <sub>2</sub> O	11.03	11.46	-	-	-	-	-	-	-	-	-	-
K <sub>2</sub> O	-	-	0.04	0.02	-	-	-	-	-	-	0.01	0.02
	<u>99.93</u>	<u>99.67</u>	<u>95.53</u>	<u>97.24</u>	<u>96.89</u>	<u>85.53</u>	<u>85.11</u>	<u>97.45</u>	<u>97.53</u>	<u>97.08</u>	<u>98.70</u>	<u>98.96</u>
O-basis	32	32	23	23	23	28	28	12.5	12.5	12.5	5	5
Si	11.67	11.92	7.62	8.00	7.95	5.56	5.63	3.01	3.02	3.04	1.00	1.01
Al <sup>IV</sup>	<u>4.29</u>	<u>4.06</u>	<u>0.38</u>	-	<u>0.05</u>	<u>2.44</u>	<u>2.37</u>	-	-	-	-	-
	15.96	15.98	8.00	8.00	8.00	8.00	8.00	3.01	3.02	3.04	1.00	1.01
Al <sup>VI</sup>	-	-	0.12	0.14	0.12	2.47	2.39	2.13	2.28	2.38	0.02	0.09
Ti	-	-	-	-	-	-	-	-	-	-	0.98	0.91
Fe <sup>3+</sup>	0.02	0.02	-	-	-	-	-	0.86	0.71	0.57	-	-
V <sup>3+</sup>	-	-	0.004	0.006	0.002	0.01	0.005	0.01	0.007	0.006	-	-
Fe <sup>2+</sup>	-	-	1.93	2.03	1.51	5.06	4.20	-	-	-	0.02	0.03
Mn <sup>2+</sup>	-	-	0.06	0.09	0.04	0.09	0.07	0.01	0.004	0.003	-	-
Mg	-	-	3.24	2.68	3.33	4.33	5.31	-	-	-	-	0.03
	<u>0.02</u>	<u>0.02</u>	<u>5.35</u>	<u>4.95</u>	<u>5.00</u>	<u>11.96</u>	<u>11.98</u>	<u>3.01</u>	<u>3.02</u>	<u>2.96</u>	<u>1.02</u>	<u>1.06</u>
Ca	0.31	0.09	1.77	1.97	1.97	0.01	0.01	1.98	1.97	1.98	1.00	0.97
Na	<u>3.76</u>	<u>3.90</u>	-	-	-	-	-	-	-	-	-	-
K	-	-	<u>0.01</u>	<u>0.004</u>	-	-	-	-	-	-	-	-
	4.07	3.99	1.78	1.97	1.97	0.01	0.01	1.98	1.97	1.98	1.00	0.97
$\frac{Fe^{2+}}{Fe^{2+}+Mg}$	-	-	0.37	0.43	0.31	0.54	0.44	-	-	-	-	-

1) Total iron as Fe<sub>2</sub>O<sub>3</sub>

2) Total iron as FeO

Table 4.- Microprobe Analysis of Relic Ore Mineral in Sphene of Metabasalt, Challes, Belgium with Fe Taken in Different Oxidation States

	Molar Ratios					
			Oxygen basis = 3		Oxygen basis = 9	
	I	II	I	II	II	
TiO <sub>2</sub>	54.15	54.15	Ti	1.07	0.95	2.84
SiO <sub>2</sub>	0.35	0.35	Si	0.01	0.01	0.02
Fe <sub>2</sub> O <sub>3</sub>	-	38.88	Fe <sup>3+</sup>	-	0.68	2.04
FeO	34.99	-	Fe <sup>2+</sup>	0.77	-	-
MnO	2.61	2.61	Mn <sup>2+</sup>	0.06	0.05	0.15
MgO	0.05	0.05	Mg	0.00	0.00	0.01
CaO	<u>0.55</u>	<u>0.55</u>	Ca	<u>0.02</u>	<u>0.01</u>	<u>0.04</u>
	92.70	96.59		1.93	1.70	5.10

opaque phase included in the sphene of the Challes metabasalt (Pl.2:3) was analyzed by microprobe technique, too. The result is given in table 4 assuming total iron as FeO (I) or Fe<sub>2</sub>O<sub>3</sub> (II). In neither case the analytical total reaches 100 % so that probably some water or light elements are present in addition. Nevertheless the two extreme cases were plotted in the ternary system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (fig. 1) and a recalculation for the

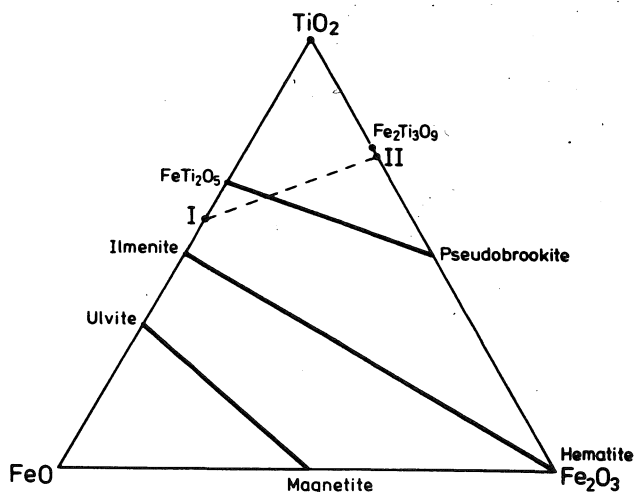


Figure 1.- Ternary system FeO-Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> showing the important binary series of mineral solid solutions as well as the extreme plots I and II of the analyzed opaque phase within the sphene of the Challes metabasalt (compare Pl.2:3 and table 4). For comparison the composition Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub> discussed in the literature as an alteration product of ilmenite (see text) is indicated also.

formula of ilmenite was attempted (table 4). It is clear that the ore mineral enclosed in sphene is very rich in Ti and can thus not be compared with the relic magnetite found by KUNYOSHI & LIOU (1976). On the other hand, it is also more titaniferous than any ilmenite-hematite solid solution, but approaches, or even surpasses, in its Ti content compositions of the pseudobrookite series (fig. 1). It is interesting to note that the composition given in terms of Fe<sub>2</sub>O<sub>3</sub> plots close to a compound Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub> and that a recalculation on the basis of nine oxygens (table 4) gives a cation content close to 5. Fe<sub>2</sub>Ti<sub>3</sub>O<sub>9</sub>, either named arizonite (PALMER, 1909) or pseudorutile (TEUFER & TEMPLE, 1966) is believed to be an intermediate product of the natural alteration of ilmenite which leads finally to rutile (GREY & REID, 1975). It is likely, therefore, that the relic ore mineral within the sphene of the metabasalt represents a former ilmenite

that was oxidized either during metamorphism or in the weathering stage. Further discussion would require the knowledge of the X-ray properties. Nevertheless, it is clear from the petrographic observations combined with the microprobe data that contrary to the explanation given by RONCHESNE (1934) the skeletal sphene crystals were not formed through replacement of single crystals of ilmenite with hexagonal morphology but at the expense of a former magnetite-ilmenite intergrowth of which magnetite was selectively replaced by sphene or other silicate minerals (Pl.2:3). Hexagonal outlines of magnetite octahedra are easily produced when sectioned parallel to (111).

### 3.- PETROLOGIC DISCUSSION

The mineral assemblages found and analyzed in the metamorphic igneous rocks of La Helle and Challes are plotted in fig. 5a-c in conventional AKF and ACF diagrams.

#### 3.1.- LA HELLE METATONALITE

The critical three-phase AKF-assemblage of the metatonalite is chlorite-K feldspar-phengite (fig. 2a) involving the highest silica phengite for these metamorphic conditions and a relatively aluminous chlorite. Chlorites or phengites that coexist with K feldspar only may have less extreme compositions. Based on the experimental study of VELDE (1965) the phengite composition analyzed (table 2) would indicate a temperature as low as about 250°C for an assumed water pressure of 2 kb. At higher water pressures the resulting temperatures would rise. The presence of prehnite in the metatonalite, however, yields an upper limit for the temperature of metamorphism in the order of 400°C on the basis of the experimental data of LIOU (1971). Temperatures below 400°C are also indicated by the compositions of the two coexisting alkali feldspars on the basis of the maximum microcline-low albite solvus (BACHINSKI & MÜLLER, 1971).

The ACF diagram of the metatonalite shows the characteristic three-phase silicate assemblage prehnite-chlorite-epidote which becomes a four-phase assemblage because of the presence of calcite. Most important is the conclusion to be drawn from the diagram that the three-phase silicate assemblage precludes the stability of the mineral pumpellyite in the presence of quartz. Although admittedly a simple ACF-plot may be deceiving for a multicomponent rock, it is clear that pumpellyite has never been reported from La Helle. On the basis of the experimental and theoretical results by NITSCH (1971) summarized in fig. 3 this paragenetic relationship

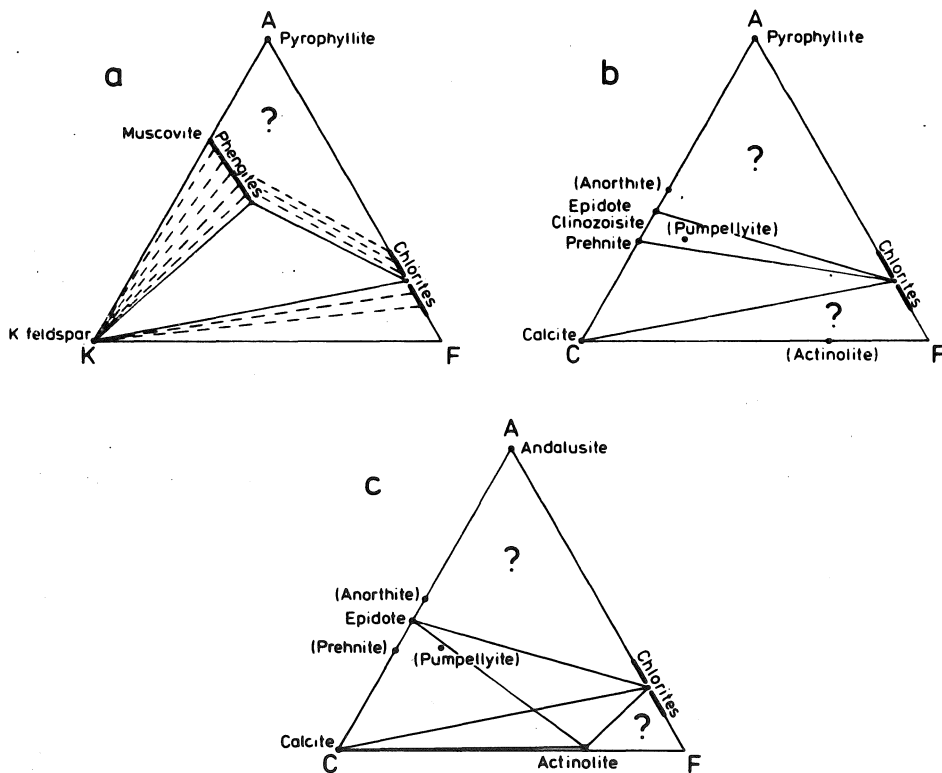


Figure 2.- a,b.- AKF- and ACF plots, respectively, of mineral assemblages characterizing the metamorphic grade of the metatonalite of La Helle. c.- ACF plot representing the mineral assemblage of the metabasalt of Challes. The appearance of calcite in b and c is due to the presence of some  $\text{CO}_2$  in the metamorphic fluids of both rocks and leads to additional, in c even intersecting, tie lines. Note that the silicate tie lines of b and c are interrelated by a simple reaction  $\text{prehnite} + \text{chlorite} = \text{epidote} + \text{actinolite}$ . Phases given in parentheses have not been found in the two rocks described nor in neighboring assemblages.

yields most valuable information concerning the pressure temperature conditions during metamorphism at La Helle : 1. The prehnite-chlorite-epidote assemblage is restricted to pressures below  $2.5 \pm 1$  kb. 2. Towards higher temperatures it is limited by the reaction  $\text{prehnite} + \text{chlorite} + \text{quartz} = \text{epidote} + \text{actinolite}$  which takes place near  $360^\circ\text{C}$ . 3. Towards lower temperatures this assemblage is bordered by the reaction  $\text{prehnite} + \text{chlorite} + \text{epidote} = \text{pumpellyite} + \text{quartz}$  for which a temperature of about  $320^\circ\text{--}330^\circ\text{C}$  is given. Thus metamorphism of the metatonalite and probably of the adjoining rocks in the northeastern part of the Venn-Stavelot-Massif has occurred within the narrow temperature range of about  $320^\circ\text{--}360^\circ\text{C}$  at low confining pressures. Considering the progressive metamorphic history of the metatonalite it seems possible that the development of the aggregates bearing the prehnite-chlorite-epidote assemblage (Pl.1:1) is actually caused by the breakdown of a preexisting pumpellyite-enriched zone through reaction with quartz.

It might be argued that the additional presence of sulfide in the aggregates of Pl.1:1 indicates that the latter were formed in the course of a hydrothermal activity that is well known for the La Helle igneous rock and has actually led to a complex association of rare sulfide and telluride minerals (VAN WAMBEKE, 1954). In the authors' opinion this does not contradict the concept submitted here, because it seems most likely that such hydrothermal activity has indeed taken place **during** the metamorphism through mobilization of rare elements from the neighboring black slates of Revin age. The sparse petrological data from other metamorphic rocks occurring in the northeastern part of the Massif are certainly not in disagreement with the metamorphic conditions derived here. Most important in this connection are the metamorphic igneous rocks of the German part of the Massif studied by SCHERP (1959). The main mafic phases found by him in tonalitic rocks and quartz diabases are chlorite and epidote or zoisite whereas prehnite is not mentioned, but actinolite does not occur either. It might



be interesting to search for prehnite in these rocks using modern techniques of phase analysis.

### 3.2.- CHALLES METABASALT

The ACF diagram constructed for the Challes metabasalt (fig. 2c) differs from that of the metatonalite in the coexistence of epidote and actinolite instead of prehnite and chlorite, although a direct comparison of the two chemically different rock types has to be taken with caution, especially because of the different Mg/Fe ratios. On the basis of NITSCH's (1971) data (fig. ) this comparison would indicate metamorphic temperatures in excess of about 350°C-380°C depending on pressure, but no estimate whatsoever concerning the latter variable can be given: The very common assemblage chlorite-epidote-actinolite is stable over the whole pressure range up to 10 kb. The absence of both prehnite and pumpellyite in the Challes rock suggests that it belongs to the greenschist facies of metamorphism.

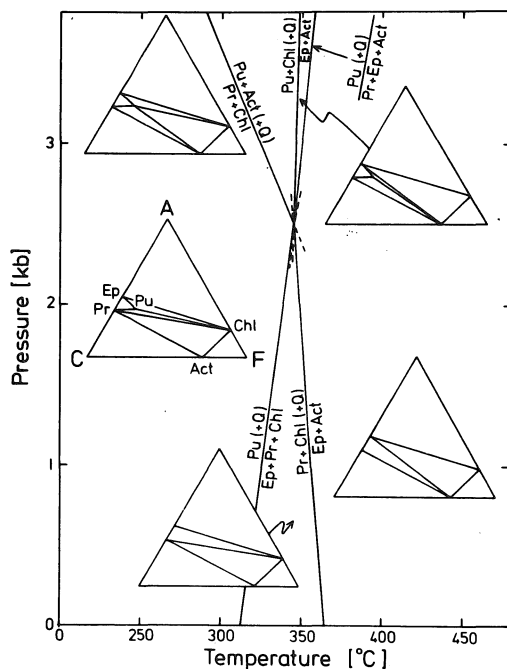


Figure 3.- Pressure temperature plot summarizing and simplifying experimental results by NITSCH (1971) on the mutual compatibilities of the metamorphic minerals prehnite (Pr), epidote (Ep), pumpellyite (Pu), chlorite (Chl), and actinolite (Act) in an ACF diagram, that is in the presence of excess quartz (Q).

It is interesting to compare the epidotes formed during these greenschist-type metamorphic conditions valid for the Challes metabasalt with the temperature-

composition-relations of the miscibility gap in the epidote series as deduced by RAITH (1976) for alpine greenschists. Although the confining pressures in the alpine area were certainly considerably higher than those obtained in the Venn-Stavelot-Massif, the phase relationships should be principally similar and a miscibility gap should occur under the low-temperature metamorphic conditions derived for the Challes rock as well. Of all 8 microprobe analyses of Challes epidotes described earlier (cf. table 3) none falls within the range between  $Ps_{19:3}$  and  $Ps_{23:7}$  (= 58 to 71  $Al_2FeEp$  following RAITH's (1976) nomenclature with  $Ca_2Al_2Fe_3/Si_3O_{12}(OH)$  as end member) which, therefore, is likely to represent the miscibility gap expected (fig. 4). This compares rather favorably with the miscibility gap between about 53 and 71-75  $Al_2FeEp$  established by RAITH (1976) for the middle greenschist facies of his area. Contrary to RAITH's finding, however, none of the epidotes of the Challes metabasalt exhibit this gap by virtue of a discontinuous Al/Fe-zonation of the epidote crystals, but here the homogeneous Fe-poor epidotes (e.g. analysis N<sup>o</sup>. 3 of table 3) form independent crystals coexisting with others characterized by a gradual Al/Fe-zonation with Fe-rich cores (86  $Al_2FeEp$ ) and Fe-poorer rims (71  $Al_2FeEp$ ). It has already been pointed out that these latter values lie approximately along the iron-rich limb of the unsymmetrical solvus curve derived by RAITH (1976) which is rather flat as compared to the iron-poor limb. Therefore, it seems

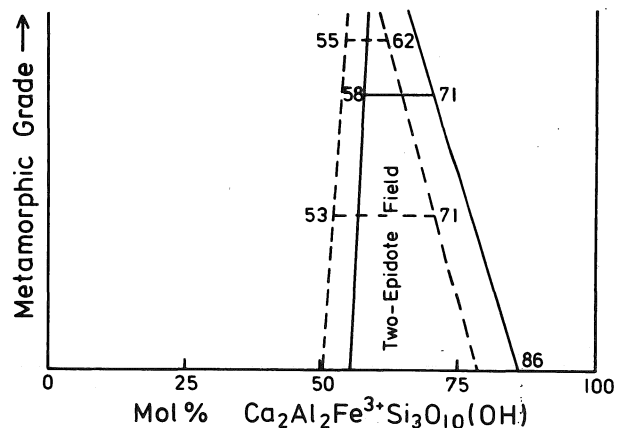


Figure 4.- Hypothetical diagram indicating, with solid lines, the possible extent of a miscibility gap in the epidote series as suggested here on the basis of microprobe data on the Challes metabasalt, in comparison with the gap derived by RAITH (1976) for alpine metamorphic rocks (broken lines).

that the Challes metabasalt actually contained two coexisting epidote phases through much of its metamorphic history, (1) a Fe-poor one near  $Ps_{19.3}(58 Al_2FeEp)$ , and a Fe-rich one with Fe-contents decreasing from  $Ps_{28.8}(86 Al_2FeEp)$  to  $Ps_{23.7}(71 Al_2FeEp)$  as a function of increasing metamorphic grade (fig. 4). This apparent epidote miscibility gap of Challes seems to be slightly offset towards higher Fe-contents as compared with that derived by RAITH (1976), but more detailed investigations on a larger number of samples would be necessary to prove this point.

#### 4.- CONCLUDING REMARKS

The presence of calcite and sulfides in the metamorphic assemblages of both the metatonalite and the metabasalt occurrences studied in the present paper indicates that the fluid phase present during metamorphism certainly contained some  $CO_2$  and sulfur in addition to water. Thus water pressures cannot have equalled total pressures, and the metamorphic temperatures could actually have been slightly lower than estimated above. Nevertheless, there is no reason to suspect vastly different  $X_{H_2O}$  values for the two localities so that the differences in the prevailing temperatures deduced in chapter 3 are probably realistic, at least regarding their direction.

Based on the most recent experimental data of HUNT & KERRICK (1977) the mere existence of sphe-ne in the two assemblages described indicates, for the low temperatures of metamorphism derived, partial pressures of  $CO_2$  below about 100 bars or fluid compositions with  $X_{CO_2}$  values below some 0.07.

Differences in metamorphic grade of the two rocks studied here that come from the southern central and the northeastern part of the Venn-Stavelot-Massif may well be significant regarding the temperature distribution during Hercynian metamorphism. The greenschist facies assemblage of the Challes metabasalt would, in agreement with the findings of NITSCH (1971), be compatible with the low-grade andalusite-producing metamorphism characteristic for the southwestern part of the Massif (FRANSOLET *et al.*, 1977). The temperatures derived for the metatonalite in the northeast, on the other hand, probably do not allow the formation of andalusite but would lie in the field of pyrophyllite (HAAS & HOLDAWAY, 1973). Unfortunately, no critical aluminosilicate assemblages have been found thus far in the vicinity of the metatonalite. Relatively low temperatures of metamorphism certainly prevailed in

rocks east of the Rhine as indicated by the occurrence of pyrophyllite in pre-Devonian strata (SCHERP & STADLER, 1968) and that of pumpellyite associated with prehnite and epidote in many Devonian metabasalts of the Sauerland (WEBER, 1972).

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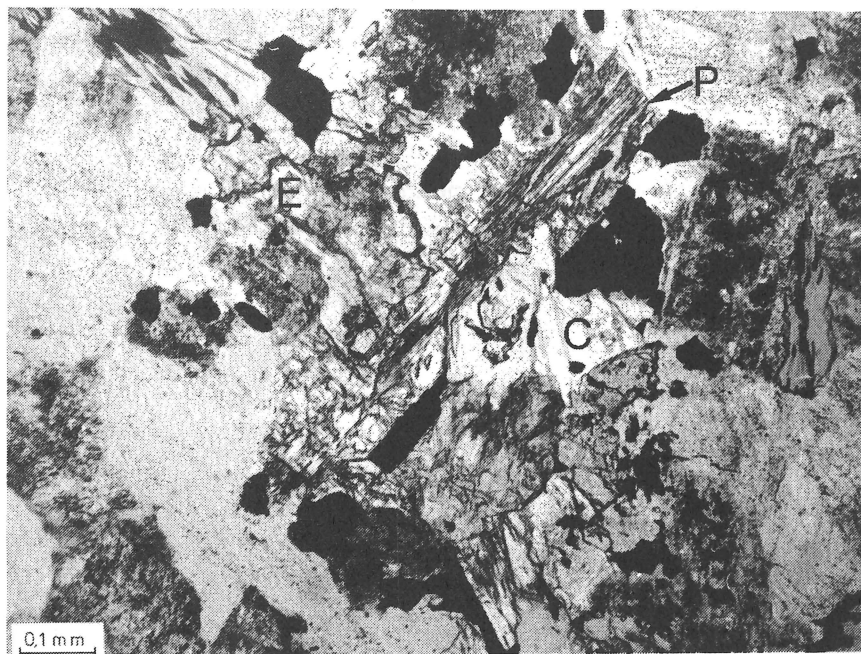
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## PLATE 1

1 : Lime silicate-bearing aggregates comprising prehnite (P), epidote (E), calcite (C), and pyrite (black) in the metatonalite of La Helle. Flakes of chlorite (near right rim and northwest corner) may contact both epidote and prehnite. - Ordinary light.

2 : Typical textures of the metabasalt of Challes. Upper portion : Finegrained fabric consisting mainly of albite, actinolite, chlorite, epidote, and calcite, formed after the earlier igneous texture, with larger skeletal, nearly opaque crystals of sphene. Lower portion : Coarse fabric of actinolite, epidote, chlorite, albite, and calcite in an asbestiform vein. - Ordinary light.

Plate 1



1



2

**PLATE 2**

Skeletal crystal of sphene embedded in finegrained matrix of metabasalt (see plate 2). Note the relic lamellar texture containing thin bands of opaque material. - Ordinary light.



