Zeitschrift: Schweizerische mineralogische und petrographische Mitteilungen = Bulletin suisse de minéralogie et pétrographie

Band: 67 (1987)

Heft: 1/2

Artikel: Braunite and red phengite from Vals, Grisons (Switzerland)

Autor: Plas, L. van der / Doesburg, J.D.J. van

DOI: https://doi.org/10.5169/seals-51589

SCHWEIZ. MINERAL. PETROGR. MITT. 67, 85-91, 1987

Braunite and red phengite from Vals, Grisons (Switzerland)*

by *L. van der Plas*[1] and *J. D. J. van Doesburg*[1]

Abstract

An occurrence of manganese-rich, red coloured $2M_1$ ferri phengite (tetrahedral Si/Al ratio near 7) associated with braunite is described for the first time of a phengite marble from the northern Adula region in Switzerland. The chemical composition of these micas as well as of the associated yellow-, green-, and white phengite and braunite are given together with the total rock analysis. The nature of the chromophore of the red phengite is discussed and ascribed to Mn^{3+}; the yellow phengites are manganese-rich also. The iron in the phengites is present in the ferric state. In addition optical properties of these phengites are listed as well as the length of the b-axis, measured from the $(060,\bar{3}31)$ reflection, and the approximate densities. A relation with the second phase of Alpine metamorphism is assumed.

Keywords: Phengite, braunite, alpine metamorphism, Adula nappe.

Introduction

Minerals of the Northern Adula region have been described by a number of authors since the end of the 18th century. Among those were VOM RATH (1862), SCHMIDT (1891), KÖNIGSBERGER (1917), JENNY, FRISCHKNECHT and KOPP (1923), PARKER (1954), MAISSEN (1955), VAN DER PLAS (1959) and STALDER (1966). During fieldwork between 1959 and 1973 numerous minerals were again collected. In the course of our work these minerals were analysed or reanalysed with modern methods; the red phengite of the "Ebene Runse" among them. Micas especially drew our attention as Professor Ernst Niggli established as early as the fifties, during a stay in Bern of the first author, the importance of micas as indicators of metamorphic zones, cf., NIGGLI (1986).

Geological setting

Approximately 3 km S of Vals, GR, in the northernmost crystalline rocks of the Adula Nappe, thin sheets of phengite-rich marbles and dolomite marbles alternate with mica-schists and schistose amphibolites. The minerals described in this paper are present in a fine-grained schistose marble. An outcrop is found in a stream gully running from the Selvasee in NE direction along Heinisch Stafel, through Aebni** at an altitude of 2010 m, coordinates 73344 / 16196, Landeskarte der Schweiz, Blatt Vals No. 1234 1:25000. A profile of the outcrop is shown in Fig. 1.

Red phengite and braunite are intimately intergrown in the schistose marble. The mica-rich bands (1 to 3 cm) give the rock a conspicuous reddish to pink and green striped appear-

* Dedicated to Professor Ernst Niggli on the occasion of his 70th birthday.

[1] Dept. of Soil Science and Geology, Agricultural University Wageningen, Netherlands, P.O. Box 37, 6700 AA Wageningen.

** due to a change in spelling of geographical names, "Aebni" is "Ebene" on maps prior to 1964.

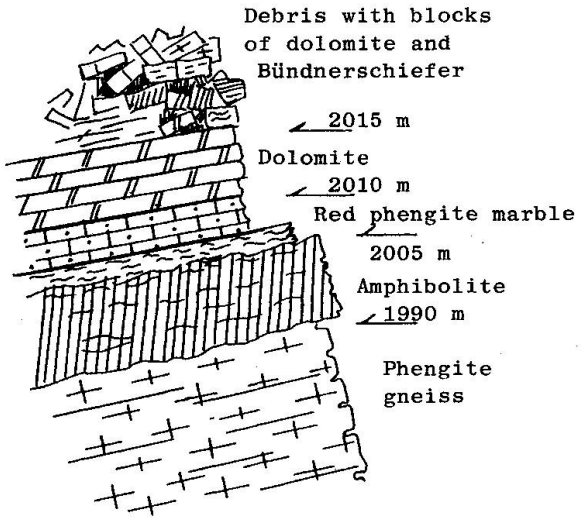

Fig. 1 Profile of the outcrop of red phengite marble in the Ebene Runse.

ance. Table 1 gives the quantitative mineralogical composition of a thin-section of 2.5 cm normal to the schistosity.

Microscopical description

The host rock is composed of calcite, dolomite, red-, yellowish-, colourless and greenish phengite, quartz, braunite and hematite with additional garnet, biotite, rutile and zircon. Virtually mica-free bands alternate with mica-bearing bands. Red mica and greenish mica do not occur in the same bands. The yellowish micas associate, but are not intergrown with red mica. Small hematite flakes seem to be found within the yellow and red micas only. Small rutile and zircon crystals are optically observed in all mica types. The average size of calcite and quartz is 0.05 mm; the micas vary between 0.05 and 0.15 mm. Braunite occurs as small flakes and irregular aggregates enclosed in or between the lamellae of the mica crystals; as aggregates of irregular grains in quartz and as slightly larger hypidiomorphic crystals in the calcite bands containing red mica. The micas, both the greenish and the reddish types, sometimes show fringes of yellowish brown biotite. This same biotite is only rarely seen isolated in the calcite matrix. Fig. 2 illustrates the relations between braunite, mica and quartz.

Tab. 1 Mode of red-phengite marble.

Calcite	66%	Additional minerals
Dolomite	11%	less than 1%, garnet,
Phengite	12%	zircon, rutile, very
Quartz	9%	small amount of bio-
Braunite	1%	tite.
Rest	1%	

Number of points counted: 473

Sample preparation

Because microscopical inspection of a small number of mica flakes showed a high amount of impurities within the mica crystals the following procedure for the isolation of micas and braunite was chosen:

A relatively large handspecimen was dissolved in diluted HCl. The residue was washed and dried. A first separation with bromoform (d = 2.87) produced a heavy and a light fraction, the heavy fraction holding the micas and the braunite. From this heavy fraction a virtually pure braunite sample was separated with methylene iodide (d = 3.32). Using methylene iodide diluted with increasing amounts of acetone the following fractions were produced: red mica with braunite and some hematite, red mica with a very small number of inclusions, red mica together with green and colourless mica. Afterwards microscopically clean micas were handpicked from these fractions and their density determined in diluted methylene iodide in which they just remain suspended, red mica having a density of ca. 2.89, green micas of ca. 2.87. The light fraction of the bromoform separation consisted of quartz and some mica.

The composition of the various fractions was checked with X-ray diffraction analysis showing the impurities within red mica to be mainly braunite and some hematite; the green and the "colourless" micas being rather free from inclusions of opaque minerals.

In order to avoid contamination microprobe analyses were preferred over X-ray fluorescence analysis of a bulk sample. Approximately 50 optically clean crystals of each category were handpicked under a microscope. Each group was again cleaned by magnetic separation producing a group of red-, of yellowish-, of green-, and of colourless mica. The braunite was handpicked from the heaviest

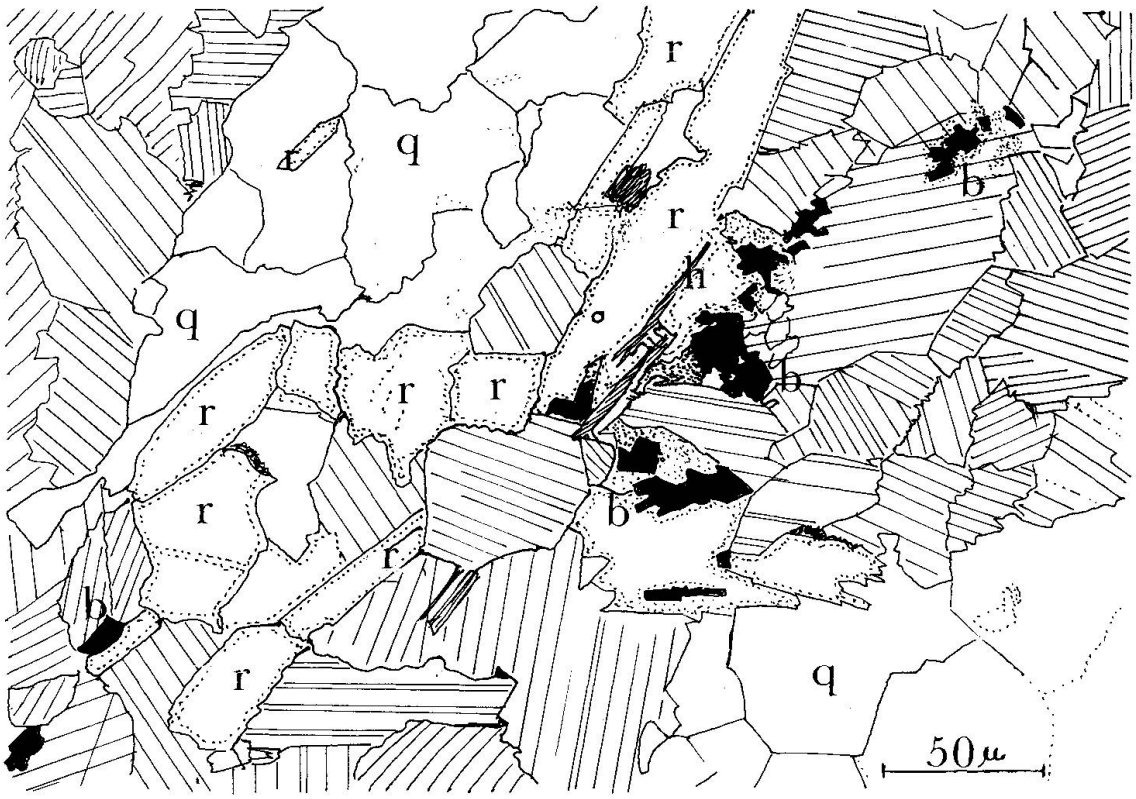

Fig. 2 Photomicrograph of thin section of red phengite marble, q is quartz, r is red phengite, b is braunite, h is hematite.

Tab. 2 Braunite analyses and calculation of structural formula.

No.	1	2	3	4	5	Mean	Cat%	Sum
SiO_2	9.86	9.22	9.97	9.96	10.33	9.81	0.99	0.99
Al_2O_3	0.13	0.61	0.24	0.28	0.17	0.29	0.03	
Fe_2O_3	8.18	8.80	8.56	9.56	7.94	8.60	0.65	6.00
Mn_2O_3	82.59	80.51	79.98	78.72	82.36	(80.83)		
						69.25	5.32	
MnO						10.42	0.89	
MgO	0.37	0.73	0.66	0.65	0.74	0.63	0.09	1.01
CaO	0.10	0.24	0.33	0.71	0.10	0.30	0.03	
Cr_2O_3	<.06	<.06	<.06	<.06	<.06	---		
TiO_2	<.06	<.07	0.11	<.06	<.06	---		
Tot	101.23	100.11	99.85	99.88	101.64	99.30		

fraction for microprobe analysis. Finally, a large rock fragment was crushed and ground for chemical analysis with X-ray fluorescence.

Chemical composition of braunite

The chemical analyses of 5 crystals of braunite are given in Table 2. Structurally the nature of these mineral was similar to a braunite pattern present as No. 33-904 in the JCPDS Powder Diffraction File, ruling out the presence of braunite II cf., DE VILLIERS (1980). The ideal formula is assumed to be

$$8(Mn^{2+}Mn^{3+})_6SiO_{12}$$

Possible substitutions are assumed to be given by the following formula:

$$(Mn^{3+},Fe^{3+},Al)_6 \times (Mn^{2+},Ca,Mg)SiO_{12}$$

Moreover, iron is assumed to be present in the ferric state. From these assumptions and a total of 6 trivalent cations and 12 oxygen atoms the formula of braunite present in these samples is:

$$(Mn_{5.32}Fe_{0.65}Al_{0.03})_{6.0}\cdots$$
$$\cdots(Mn_{0.89}Mg_{0.09}Ca_{0.03})_{1.01}Si_{0.99}O_{12}$$

Chemical composition of phengites

A number of crystals of each of the four phengite types were analyzed viz, red (14), yellowish (14), colourless (2) and green micas (13). Furthermore, the trace element content of a number of red and green crystals was measured separately, cf., Table 3. Finally, FeO was determined to be practically nil in a bulksample of red phengite not entirely free of inclusions of hematite and braunite with 1-10 o-phenantroline after BEGHEIJN (1979). Structurally these micas are $2M_1$ polymorphs without exception. Chemically, they are phengites without exception because the Si/Al ratio in tetrahedral sites approximates 7 as can be seen from table 4 in which the cation distribution of the various phengites is given. The amount of Cr in most samples is lower than the detection limit. Finally, the Li-content of these micas is rather low, suggesting that either Fe or Mn or both are responsible for the reported colours.

Optical properties of phengites

The red phengites under discussion are distinctively pleochroic, X is colourless, Y is yellowish-pink, Z is pink to reddish; nZ-nX is approximately 0.05; nZ and nY are between 1.60 and 1.63; $nZ > nY$. The axial angle varies, is never smaller than 20° and on the average 32°-43°, $r > v$. The mineral is slightly zonal.

The yellow phengites are slightly pleochroic $X < Y = Z$; the axial angle being approximately 35°, crystals with small axial angles have not been observed.

The green phengites are slightly pleochroic $X < Y \sim Z$; nZ-nX is approximately 0.04. The axial angle varies and is either small, or approximately 35°; crystals with small axial angles are extremely rare.

Discussion

A first publication of this red phengite, VAN DER PLAS (1959), failed to notice the assemblage braunite-red phengite. The opaque minerals were thought to be hematite. Moreover, the emphasis of that publication was on the presence of ferric iron, because all the iron present was determined to be Fe_2O_3. The present results, however, indicate the sample of the 1959 analysis to be contaminated by both braunite and hematite and by micas of the greenish type.

GRESENS and STENSRUD (1977) commented on the problem of red muscovite after a number of reports on these minerals since the publication of SCHALLER and HENDERSON (1926). They advocated the conclusion that both ferric iron and Mn^{3+} are predominantly octahedrally coordinated, a conclusion put forward by ANNERSTEN and HALENIUS (1976) also in their discussion of the paper by RICHARDSON (1976). They point to the fact, however, that the number of green muscovites from the same area have equal or even greater amounts of total Mn.

The analysis of Table 3 shows yellowish phengites with high total Mn. One crystal has a value as high as 1.97% Mn_2O_3, whereas the red phengites have high Mn but only one of the 14

Tab. 3 Chemical composition[1] of red-, yellow-, green-, and white phengites of the red phengite marble from the northern Adula region.

	Red n = 14	σ	Yellow n = 14	σ	Green n = 13	σ	White n = 2	Whole rock
SiO_2	50.85	0.39	50.82	0.39	51.95	0.52	51.16	14.07
Al_2O_3	18.80	0.21	19.09	0.55	19.45	0.40	21.59	2.94
Fe_2O_3	6.92	0.28	6.61	0.53	5.70	0.68	5.77	1.28
Mn_2O_3	1.58	0.22	1.44	0.27	0.25[7]	-	<0.14	1.05
MgO	4.74	0.16	4.87	0.26	5.40	0.25	4.30	2.94
CaO	0.09[2]	-	0.10[3]	-	0.10[8]	-	<0.10	40.92
K_2O	11.29	0.13	11.29	0.11	11.42	0.14	11.49	1.54
Na_2O	0.19[4]	-	0.22[5]	-	0.21[9]	-	<0.15	0.01
P_2O_5	n.d.	-	n.d.	-	n.d.	-	n.d.	0.17
TiO_2	0.78	0.11	0.76	0.15	0.83	0.14	0.86	0.35
Cr_2O_3	0.12[3]	-	0.12[6]	-	0.15[10]	-	<0.11	54 ppm
L.I.	n.d.	-	n.d.	-	n.d.	-	n.d.	34.81
Total	95.36		95.32		95.46		95.17	100.08

Trace elements in red and green mica in ppm are:

	Li	V	Ni	Cu	Zn	Cd	Co	Ba
Green	184	900	555	29	430	20	<d.l.	1669
Red	199	132	1068	78	239	6	11	1023

1 The reported values are the means of a number of n Microprobe analyses. "Whole rock" is an X-ray fluorescence analysis.
2 Average of 6, rest < detection limit 0.06
3 Average of 5, rest < detection limit 0.06
4 Average of 2, rest < detection limit 0.15
5 Average of 7, rest < detection limit 0.15
6 Average of 6, rest < detection limit 0.06
7 Average of 7, rest < detection limit 0.09
8 Average of 3, rest < detection limit 0.06
9 Average of 3, rest < detection limit 0.15
10 Average of 4, rest < detection limit 0.06

Tab. 4 Atomic proportions of red-, yellow-, green-, and white phengites on the basis of 44 negative charges and d(060,$\bar{3}$31) values.

	Red		Yellow		Green		White	
Si	6.98		6.97		7.06		6.93	
Al	1.02	8.00	1.03	8.00	0.94	8.00	1.07	8.00
Al	2.02		2.06		2.17		2.36	
Fe***	0.71		0.68		0.58		0.59	
Mg	0.97	3.94	0.99	3.96	1.09	3.95	0.87	3.92
Ti	0.08		0.08		0.08		0.09	
Mn***	0.16		0.15		0.03		0.01	
Na	0.05		0.06		0.05		0.00	
K	1.98	2.04	1.97	2.04	1.98	2.04	1.98	1.99
Ca	0.01		0.01		0.01		0.01	
d(060,$\bar{3}$31)	1.512		n.d.		1.510		n.d.	

analyses has a higher value than this 1.97%; the mean of the analyses of the red micas is 1.58%, that of the yellowish micas is 1.44%. In this case, however, the green micas are comparatively low in Mn, so are the two colourless specimens.

Both the extremely low FeO content of a red phengite sample not entirely free of hematite and braunite as well as the presence of hematite flakes in the red mica crystals indicate that the available iron is present as ferric iron. According to GUIDOTTI (1984), this ferric iron should be present in octahedral coordination. Analytical information on the oxidation state of Mn is not available. From the above literature and the data of Table 3 it is evident that the amount of Mn does not determine the colour of these micas. Therefore, our data strongly support the conclusion of both ANNERSTEN and HALENIUS (1976) and GRESENS and STENSRUD (1977) that the chromophore of red and pink muscovite as well as this red phengite is Mn^{3+} in distorted octahedral sites.

Finally, we did not succeed in finding references reporting the occurrence of red phengite or an association of hematite, braunite and red manganese-rich ferri phengite in a marble. Therefore, this seems a first report of such a mineral assemblage. The occurrence of braunite in Alpine metamorphic rocks has been discussed by E. NIGGLI (1974), information on associated micas, if present, has not been given. Moreover, the association under consideration occurs in a formation showing evidence of successive phases of Alpine metamorphism, of which the first phase produced glaucophane and sodium pyroxenes in amphibolites and greenschists nearby. VAN DER PLAS (1959) assumed the formation of phengite to coincide with the formation of blue-green amphibole of his second metamorphic phase on statistical evidence. FREY et al. (1983), showed 3T phengites next to $2M_1$ polymorphs to be associated with an Eo-Alpine metamorphic phase. They do not rule out, however, the prolonged existence and genesis of phengites in a second Meso-Alpine metamorphic event. The $2M_1$ character of the phengites under discussion is noteworthy. The cause of the presence of an association of 3T and $2M_1$ phengites in rocks nearby has apparently not been operative in these marbles. LOEW (1986) seems to assume phengite to belong to his second high pressure phase, the Zapport-phase, although he does not state this explicitly.

Acknowledgements

The authors are grateful to Prof. Olaf Schuiling of the University of Utrecht who made the ZWO-WACOM sponsored microprobe facility as well as the ICP-ES of the Institute of Earth Sciences available for the phengite and braunite analyses. Analyses with these instruments were made by Dr. M.J. van Bergen and Mr. P. Anten. Furthermore, we acknowledge the cooperation of A.J. Kuyper for X-ray fluorescence analyses and of L.Th. Begheijn for the wet-chemical analysis of the FeO content of red phengite.

References

ANNERSTEN, H. and HALENIUS, U. (1976): Ion distribution in pink muscovite, a discussion. Amer. Mineral., 61, 1045–1050.

BEGHEIJN, L.TH. (1979): Determination of iron (II) in rock, soil and clay. Analyst, 104, 1055–1061.

DE VILLIERS, J.P.R., (1980): The crystal structure of braunite II an its relation to bixbyite and braunite, Am. Mineral., 65, 756–765.

FREY, M., HUNZIKER, J.C., JÄGER, E. and STERN, W.B. (1983): Regional distribution of white K-mica polymorphs and their phengite content in the central Alps. Contrib. Mineral. Petrol., 83, 185–197.

Gresens, R.L. and STENSRUD, H.L. (1977): More data on red muscovite. Am. Miner., 62, 1245–1251.

GUIDOTTI, CH.V. (1984): Micas in metamorphic rocks. Reviews in Mineralogy, 13, S.W. Bailey Ed. Micas, 357–456.

HEINRICH, E.WM. and LEVINSON, A.A. (1953): Studies in the mica group, Mineralogy of the rose muscovites. Am. Mineral., 38, 25–50.

JENNY, H., FRISCHKNECHT, G. and KOPP, J. (1923): Geologie der Adula. Beitr. Geol. Karte Schweiz, N.F., 51, 123 p.

KÖNIGSBERGER, J. (1917–1919): Über alpine Mineral-lagerstätten. Abh. Kön. Bayr. Akad. Wiss., Math. Naturw. Kl., 18; 10 (1917), 25 p.; 11 (1919), 23 p.; 12 (1919), 108 p.

LOEW, S. (1986): Ein tektono-metamorphes Entwicklungsmodell der nördlichen Adula-Decke. Schweiz. mineral. petrogr. Mitt., 66, 129–134.

MAISSEN, P.F. (1955): Mineralklüfte und Strahler der Surselva. Universitätsverlag, Freiburg, Schweiz, 192 p.

NIGGLI, E. (1974): Alpine Metamorphose von Erzvorkommen der Schweizer Alpen. Schweiz. Mineral. petrogr. Mitt., 54, 595–608.

NIGGLI, E. (1986): Notizen zur Geschichte der Erforschung der Metamorphosen in den Zentralalpen. Schweiz. mineral. petrogr. Mitt., 66, 5–11.

PARKER, R.L. (1954): Die Mineralfunde der Schweizer Alpen. Wepf, Basel, 311 p.

PLAS, L. VAN DER (1959): Petrology of the Northern Adula Region, Switzerland (with particular refer-

ence to the glaucophane bearing rocks). Leidse Geol. Meded., 24, 416–586.

RATH, G. VOM (1862): Geognostisch-mineralogische Beobachtungen im Quellgebiet des Rheins. Zeitschr. Deutsch. Geol. Gesellsch., 369–770.

RICHARDSON, S.M. (1975): A pink muscovite with reverse pleochroism from Archer's Post, Kenya. Am. Mineral., 60, 73–78.

SCHALLER, W.T. and HENDERSON, E.P. (1926): Purple muscovite from New Mexico. Am. Mineral., 11, 5–16.

SCHMIDT, C. (1891): Beiträge zur Kenntnis der im Gebiet von Blatt XVI der geologischen Karte der Schweiz in 1:100000 auftretenden Gesteine. Anh. Beitr. Geol. Karte Schweiz, 25, 1–77.

STALDER, H.A. (1966): Mineralien aus den Schweizer Alpen. Lexi-Bildband Verlag, Vevey, 56 p.

STERN, W.B. (1979): Zur Strukturformelberechnung von Glimmermineralien. Schweiz. mineral. petrogr. Mitt., 59, 75–82.

Manuscript received April 4, 1987; revised manuscript accepted May 22, 1987.