

ANNIBALE MOTTANA *, WILLIAM L. GRIFFIN **

PINK TITANITE (GREENOVITE) FROM ST. MARCEL, VALLE D'AOSTA, ITALY

RIASSUNTO. — Studi cristallografici sulla varietà rosa di titanite chiamata greenovite (A. DUFRÉNOY, 1840) presente nel giacimento metamorfico di manganese di Praborna, nel Valone di St. Marcel in Valle d'Aosta, e della normale titanite verde presente nella stessa località sono stati condotti nell'intento di spiegare il particolare colore di questa varietà unica per l'Italia e, probabilmente, per il mondo. La greenovite è presente in associazione con onfacite, piemontite, quarzo, braunite ed altri minerali e appare cristallizzata nella fase di alta pressione e bassa temperatura del metamorfismo alpino. Talora compare inoltre come prodotto dell'alterazione del violano e del rutilo, per cui risulta non solo stabile, ma anzi generata nella fase di scisti verdi successiva alla fase eoalpina. La composizione chimica è estremamente pura (meno del 5 % di sostituzioni vicarianti rispetto alla titanite teorica), mentre le dimensioni reticolari appaiono concordanti con quelle delle titaniti naturali più pure finora descritte, pur essendo decisamente minori delle dimensioni della titanite sintetica. La simmetria $A2/a$ risulta simile a quella della titanite disordinata, in contrasto con recenti osservazioni su campioni naturali particolarmente puri. Rispetto al 3,8 % MnO riscontrato per via umida dagli analisti del passato, le analisi in microsonda hanno dimostrato che il tenore di MnO è basso (0,34-0,99 %) e essenzialmente analogo a quello della titanite verde (0,42-0,52 %) presente nello stesso giacimento. Il colore rosa dipende da un rapporto Mn/Fe particolarmente elevato piuttosto che da un alto tenore assoluto di Mn. Considerazioni sull'equilibrio delle cariche e lo stesso colore suggeriscono che il Mn (e forse anche il Fe) sono presenti allo stato divalente, come vicarianti del Ca in coordinazione 7, in luogo che allo stato trivalente come vicarianti del Ti in coordinazione ottaedrica. Risulta pertanto confermato che la greenovite è una varietà « ex colore » della titanite, il cui colore rosa dipende da un inconsueto rapporto quantitativo tra i principali ioni cromofori.

ABSTRACT. — Pink titanite (greenovite) occurs in several assemblages within the Praborna manganese metamorphic orebody. It has a rather « clean » CaTiSiO_6 composition (< 5 mol% substitutions). Cell dimensions are very close to those of the purest natural titanites but slightly shorter than those of the synthetic end member. Old analyses show up to 3,8 % MnO but microprobe analyses show that the manganese content of greenovite is limited (0.34-0.99 wt% as MnO) and essentially similar to that of common green sphene (0.42-0.52 wt% as MnO) also present in the deposit. The pink colour appears to reflect higher Mn/Fe ratios rather than the absolute amount of Mn. Charge balance considerations and the colour itself suggest that Mn, and perhaps Fe, are present in these titanites as divalent ions, substituting for Ca in 7-fold coordination rather than Ti in octahedral coordination.

Introduction

The braunite ore body of Praborna, near St. Marcel (Val d'Aosta) is the foremost Alpine example of a metamorphic orebody derived from a manganese chert. It was metamorphosed during three alpine stages and assemblages of the alpine

* Istituto di Mineralogia e Petrografia, Città Universitaria, 00185 Roma (Italia).

** Mineralogisk-Geologisk Museum, Sars Gate 1, Oslo 5 (Norway).

eclogite facies, the greenschist facies and late hydrothermal stage may be recognized. The locality is famous for the occurrence of several manganiferous varieties of common rock-forming minerals. St. Marcel is in fact the type locality of two of these (pimontite and alurgite).

Systematic studies of St. Marcel have been undertaken not only to review a locality world-known in the past and now almost neglected by scientists, but also because it offers a unique opportunity to investigate the role of Mn in minerals. It also offers a rare opportunity to study phase equilibria in Mn-rich rocks metamorphosed under high-P, low-T conditions.

Two varieties of pyroxenes have already been studied (violan: MOTTANA et al., in press; schefferite: BONDI et al., in press). This investigation of the titanites was done because St. Marcel is the type-, and possibly the only known, locality for the alleged manganiferous variety, greenovite $(\text{Ca}, \text{Mn})\text{Ti}[\text{O}/\text{SiO}_4]$ (DUFRENOY, 1840).

The crystal chemistry of natural titanites has recently aroused considerable interest, after the discovery that the synthetic end-member $\text{CaTi}[\text{O}/\text{SiO}_4]$ has a primitive space-group symmetry $P2_1/a$ (ROBBINS, 1968; SPEER and GIBBS, 1976), whereas most natural specimens display side-centered symmetries. This had been described originally as $C2/c$ (ZACHARIASEN, 1930), but was transformed into the $A2/a$ space-group by MONGIORGI and RIVA DI SANSEVERINO (1968) who reinvestigated the structure. Moreover the synthetic titanite undergoes a non-quenchable, probably second order phase transition at $220^\circ \pm 20^\circ \text{C}$ (TAYLOR and BROWN, 1976), whereby the P cell transforms into the A cell. Systematic studies on 40-odd natural titanites (HIGGINS and RIBBE, 1976) showed that the same transition also occurs in nature, and is essentially related to the amount of solid solution. «Clean» titanites (containing less than 3-4 mol% Al+Fe substituting for Ti in the octahedral site) show sharp $k + l = \text{odd}$ reflections, typical of the primitive space group, whereas the very impure ones (with more than 20 mol% Al+Fe) show no odd $k + l$ and therefore an apparent side-centered symmetry. Samples with intermediate compositions show diffuse streaks in place of the $k + l = \text{odd}$ reflections. This suggests the composition-dependant presence of oppositely oriented domains of the $P2_1/a$ structure related by a half-turn parallel to b , so as to simulate the $A2/a$ total symmetry.

The interpretation of HIGGINS and RIBBE (1976) relies entirely on the composition of the octahedral chains; therefore they focussed their interest on the substitution of Al + Fe for Ti (leading to the variety *grothite*). They disregarded other possibilities, including those involving the 7-fold coordinated structural site, which they considered to be almost fully occupied by Ca, except for traces of rare earth elements. The presence of Mn substituting for Ca is, nevertheless, frequently mentioned in older and recent papers on titanites (HINTZE, 1897; SAHAMA, 1946; DEER et al., 1963). All of these are based, however, on wet chemical data, which are very old for just those samples with large MnO contents.

Literature survey

Greenovite, initially believed to be manganese titanate, was described by A. DUFRÉNOY (1840) on material collected by M. Bertrand de Lom at St. Marcel, at that time the largest manganese mine in Europe. PLATTNER (1843), on the basis of a qualitative analysis, suggested that it could be a manganiferous titanite, which was confirmed by two chemical analyses by DELESSE (1844; in DUFRÉNOY, 1847) and by a careful morphological investigation by DES CLOIZEAUX (1847; in DES CLOIZEAUX, 1862). Eventually the revision was accepted by DUFRÉNOY (1847), who also had a third chemical analysis made by Marignac.

The previously existing data on this mineral are collected in table 1. The best description is still that given by DES CLOIZEAUX (1862); later additions are restricted

TABLE 1
Published data on greenovite

	<u>1</u>	<u>2</u>	<u>3</u>	
SiO ₂	30.40	29.80	32.26	Density = 3.483 (anal.n.1)
TiO ₂	42.00	43.00	38.57	Powder: pale pink colour
Al ₂ O ₃	-	-	-	Cleavage: excellent (102)
Fe ₂ O ₃	-	-	0.76	good (221)
FeO	tr	tr	-	Twinning: (409)
MnO	3.80	2.90	-	Pyroelectric
Mn ₂ O ₃	-	-	0.76	AOP: //(010)
CaO	24.30	24.60	27.65	2E _{Na} = 51°06'
	100.50	99.30	100.00	Forms : (111), (221), (111), (205), (101)
Si	1.000	1.000	1.000	
Ti	1.039	1.085	0.899	
Fe	-	-	0.009	
Mn	0.106	0.078	0.009	
Ca	0.856	0.835	0.918	
anal.	Delesse	Delesse	Marignac	

to von RATH's (1882) mention of unusually large crystals (25 mm) and RONDOLINO's (1934) optical and morphological investigations. To the authors' knowledge, the name greenovite has been used outside the Alps only by FERMOR (1908) for a reddish titanite occurring in gondites of India.

Sample description

Detailed studies of the phase equilibria at St. Marcel are in progress. The mineralogy is often complex, due to metamorphic and hydrothermal overprinting. Early high-P assemblages are, however, recognizable in many rocks, and titanite is part of these assemblages as well as of the later greenschist facies and hydrothermal assemblages.

In SM-51, -52, -91 and -96, greenovite is intergrown with coarse-grained omphacite + albite. Quartz, K-feldspar, piemontite and braunite are possible minor phases. Omphacite shows varying degrees of breakdown to pyroxene + amphibole + albite symplectites. SM-5, SM-95 and SM-97 are late hydrothermal veins in which greenovite is intergrown with coarse-grained, unfoliated piemontite and minor quartz + albite + Kspars. SM-6 shows a similar assemblage, but here the greenovite is clearly surrounding and replacing primary rutile (0.6 % MnO, 0.5 % FeO). SM-99 are single crystals of almost red greenovite, kindly donated by C. GRAMACCIOLI.

The green titanite of SM-94 occurs in a medium-grained omphacite-albite-carbonate schist, and is thus considered part of the high-P assemblage. SM-14, by contrast, is from a foliated vein of albite amphibolite with abundant titanite and apatite. The large titanite crystals (up to 1 cm) occurring in coarser-grained pods have the same composition as the small grains in the greenschist, which cuts across brecciated spessartinefels in the wall rocks of the mine.

Experimental procedures

Electron microprobe analyses were done on a manual ARL-EMX probe at Sentralinstitutt for Industriell Forskning, Oslo. Standards were a series of natural and synthetic minerals, and the matrix corrections were carried out by the method of BENCE and ALBEE (1968).

The unit cell parameters were computed with the program of APPLEMAN and EVANS (1973) from the X-ray powder patterns recorded on two different Philips diffractometers, using filtered $\text{CuK}\alpha$ radiation, scanning speed 0.25 $2\theta/\text{min.}$, chart speed 300 mm/h, a flat glass slide as specimen holder and calibrated Si as the internal standard. Indexing was computer generated from the cell parameters given by HIGGINS and RIBBE (1976) for USNM B20360. The indices were checked and constrained against the structure factors for synthetic titanite listed by SPEER and GIBBS (1976).

Density was measured on two samples by equilibrating several grains in diluted Clerici solution, the density of which was estimated by measurement of the refractive index. Optical data were obtained by universal stage using the 1.647 hemisphere set; they are therefore considerably affected by errors due to the mismatch between the indices of the mineral and of the system.

Results

The microprobe analyses of titanites from Praborna are listed in table 2. The analysis of a USNM-B20360 (HIGGINS & RIBBE, 1976), which is also a greenovite from St. Marcel (P. DUNN, pers. comm.), is given for comparison.

Each analysis represents the average of 5-15 spots on each of two or more grains. The titanites are generally homogeneous within each sample, though minor zoning

does occur, in which Mn and Fe may either increase or decrease toward the rim of the grain. Large grains in SM-14 show patchy areas a few μm in diameter in which Al_2O_3 drops to $\frac{1}{2}$ the value reported here. The analytical sums are generally low, and the structural formulae indicate that this may be due to a deficiency (analytical error?) in CaO. However, the similarity to the analysis by HIGGINS and RIBBE of USNM-B20360 suggests that the low sums may be real, and may reflect the presence of 0.5-1.5 % H_2O , as OH^- . Mg, Ce and La are < 0.1 % in all samples.

TABLE 2
Microprobe analyses of St. Marcel titanites

	SM-5	SM-6	SM-51	SM-52	SM-95	SM-96	SM-97	SM-99	SM-14	SM-94	B20360
Colour	pink	pink	pink	pink	redbrown	palepink		reddish	green	green	pink(?)
No. grains	3	4	5	3	2	4	2	2			
SiO_2	30.6	29.6	30.3	29.9	30.8	30.9	29.6	31.1	30.7	30.5	29.99
TiO_2	38.5	39.5	38.5	39.0	38.5	38.2	38.7	38.7	38.7	38.8	38.10
Al_2O_3	1.1	1.1	1.3	1.4	0.72	1.3	0.94	1.1	1.3	1.1	1.19
Fe_2O_3	0.28	0.24	0.38	0.23	0.11	0.40	0.31	0.10	0.76	0.52	0.34
MnO	0.53	0.46	0.61	0.45	0.99	0.34	0.37	0.74	0.40	0.42	n.a.
CaO	26.8	27.4	26.7	27.1	26.9	28.4	27.2	27.0	27.7	27.2	28.4
Na_2O	0.07	0.07	0.14	0.0	0.09	n.a.	0.06	0.08	0.0	0.04	0.0
F	n.a.	0.0	0.2	0.2	n.a.	n.a.	0.1	n.a.	0.2	0.2	0.13
	97.88	98.35	98.13	98.28	98.11	99.44	97.38	98.87	98.76	98.78	98.15
Structural formulae (Si = 1.000)											
Si	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ti	0.946	1.003	0.956	0.981	0.939	0.930	0.983	0.935	0.945	0.922	0.955
Al	0.042	0.044	0.051	0.055	0.027	0.050	0.037	0.042	0.050	0.039	0.047
Fe	0.007	0.006	0.009	0.006	0.003	0.010	0.008	0.002	0.013	0.014	0.009
Mn	0.012	0.012	0.017	0.012	0.027	0.009	0.010	0.020	0.011	0.011	-
Ca	0.939	0.992	0.944	0.971	0.935	0.985	0.979	0.930	0.967	0.953	1.014
Na	0.004	0.004	0.009	-	0.006	-	0.004	0.005	-	0.004	-
Mn/Fe	1.71	2.00	1.89	2.00	9.00	0.90	1.25	10.0	0.85	0.89	?

The substitution of Al, Fe and Mn is < 5 % in all of the analyses. The only clear compositional difference between the pink and the green titanites is the slightly higher Fe content of the latter. The average Fe content of the greenovites is in fact lower than for any samples analyzed by HIGGINS and RIBBE (1976), except for USNM B20360, also a greenovite.

None of the pink greenovites contain large amounts (> 1 wt%) of Mn. This suggests that the older analyses by DELESSE (table 1) were contaminated with braunite or another Mn phase, while that of Marignac is more nearly correct. Nevertheless, the reported absence of Al_2O_3 , and the poor stoichiometry, require that this analysis also be rejected. HIGGINS and RIBBE (1976) unfortunately did not analyze their samples for Mn. Most titanite analyses in the literature show MnO

contents $< 0.1\%$, so the St. Marcel titanites are in fact relatively rich in MnO even though the absolute abundance is low.

The cell parameters for these samples are given in table 3. Greenovites of different assemblages are identical within two standard deviations; moreover they do not differ significantly from titanites from Praborna (our data) nor from the greenovite studied by HIGGINS and RIBBE (1976). The deviation of the cell parameters from those of pure synthetic titanite is larger (about 2 \AA^3), but it is in fact proportionally smaller than the deviation from the idealized formula. The cell volumes of greenovites are on the average 0.5% smaller than that of the synthetic titanite, while the amount of chemical substituents ranges from 2 to 4% mol.

TABLE 3
X-ray and physical data for St. Marcel titanites

Specimen	colour	$a_0(\text{\AA})$	$b_0(\text{\AA})$	$c_0(\text{\AA})$	β (deg)	$V(\text{\AA}^3)$	$2V(^{\circ})$	$G(\text{g/cm}^3)$
SM-5	pink	7.092(6)	8.699(7)	6.564(7)	$113^{\circ}23(8)$	372.1(1.3)	-	-
SM-6	pink	7.060(2)	8.706(2)	6.551(2)	$113^{\circ}85(1)$	368.3(0.3)	26	3.52
SM-14	green	7.061(1)	8.708(1)	6.553(1)	$113^{\circ}85(1)$	368.5(0.1)	27	3.51
SM-51	pink	7.061(2)	8.706(2)	6.552(2)	$113^{\circ}86(1)$	368.3(0.4)	-	-
SM-51bis	pink	7.065(3)	8.699(2)	6.546(2)	$113^{\circ}88(1)$	367.9(0.4)	-	-
SM-52	pink	7.061(1)	8.707(1)	6.552(1)	$113^{\circ}86(1)$	368.4(0.1)	-	-
SM-91	pink	7.061(2)	8.704(2)	6.550(2)	$113^{\circ}86(2)$	368.2(0.2)	27	3.52
SM-94	green	7.064(2)	8.703(3)	6.557(2)	$113^{\circ}80(3)$	368.8(0.4)	-	-
SM-94bis	green	7.057(3)	8.698(3)	6.554(2)	$113^{\circ}85(5)$	368.0(0.5)	-	-
SM-95	red-brown	7.059(1)	8.709(1)	6.553(1)	$113^{\circ}85(1)$	368.5(0.1)	28-29	3.49
SM-97	pale pink	7.063(2)	8.705(2)	6.555(2)	$113^{\circ}82(2)$	368.7(0.4)	-	-
SM-99bis	reddish	7.059(3)	8.698(4)	6.554(3)	$113^{\circ}80(5)$	368.2(1.2)	-	-
USNM B20360	pink	7.061(1)	8.708(1)	6.553(1)	$113^{\circ}86(1)$	368.5(0.1)	-	- (§)

N.B.: All cell data obtained by least squares fitting of powder diffractometer patterns, but those labeled « bis », which are the averages of the cells obtained on two grains for each sample, mounted directly on the single crystal Philips automatic diffractometer (courtesy of Dr. Luciano Ungaretti, Institute of Mineralogy of the University of Pavia, Italy). (§) Analysis and cell parameters after HIGGINS and RIBBE (1976).

This agrees with the normal behaviour of titanites. An inspection of HIGGINS and RIBBE's fig. 3 shows that the cell dimensions are significantly reduced relative to those of pure $\text{CaTi}[\text{O}/\text{SiO}_4]$ only when the amount of substitution becomes large (20-25 mol%); even in this case the reduction in volume barely reaches 2% . Otherwise, for fairly pure titanites, the observed deviations in the cell parameters are erratic, probably depending upon experimental error or upon structural damage due to metamictization.

Direct measurements on single grains performed with the PW 1100 Philips automated diffractometer at Pavia (courtesy of Dr. Luciano Ungaretti) agree with the cell parameters computed from the powder patterns within standard deviations for the cell volumes (table 3, cp. specimens labeled « bis »), but constantly show shorter b_0 , c_0 and larger β than the computed results. Moreover, within the same

sample, the two grains examined to detect systematical variations show a negative a_0 - c_0 relationship, whereby a large a_0 value corresponds to a small c_0 and vice versa, the volume thus remaining constant.

The space groups of two greenovites (SM-51 bis and SM-99) and one titanite (SM-94 bis) from Praborna, determined with the single crystal diffractometer (courtesy of Dr. L. Ungaretti) by scanning the $\bar{h}0l$ row, are always $A2/a$, irrespectively of their colour. No significant reflections exhibiting $(h+l) = \text{odd}$ were found. In particular, the $\bar{4}01$ and $\bar{6}01$ reflections specifically mentioned by HIGGINS and RIBBE (1976) as typical of the primitive lattice symmetry, are never present in the examined samples.

One greenovite (SM-5) appears to have an unusually large cell and erratic variations in certain peaks, including some strong ones, appearing in the X-ray powder diffraction pattern. Comparison with HIGGINS and RIBBE's (1976) data suggests it is in metamict state. However, the sample is megascopically and microscopically normal both in the colour and in the other properties, without the glossy or semiamorphous appearance that goes with metamictization according to several descriptions. The problem was not investigated further.

Interpretation of the colour

Titanites are an extreme example of an allochromatic mineral, ranging in tint from colourless to black. Reddish and brownish colours are fairly common, but pink is apparently limited to the St. Marcel greenovite.

Pink colour is characteristic only of idiochromatic minerals of Mn (rhodochrosite and rhodonite) and of some Li silicates. Mn, moreover, produces the pink colour only when divalent, while in the trivalent oxidation state it generates dark red to purple colours. The traditional interpretation of the colour of greenovite as due to Mn^{2+} thus seems to be correct, though based on erroneous data. In the old analyses by DELESSE (1844), Mn had to be considered as Mn^{2+} and allocated to Ca, to fit the titanite formula. However, since the actual Mn content of greenovites is shown here to be only 0.37-0.99 wt% as MnO , and similar to that of common green sphene (0.42-0.57 %), this interpretation needs qualification.

The analyses in table 2 show a range in Mn/Fe that correlates qualitatively with colour. The darkest analyzed titanite (SM-95) is red-brown rather than pink and has both the highest Mn and the lowest Fe (and Al). The normal bright greenovites have Mn/Fe ratios from 1.7 to 2.0, while two very pale pink samples have Mn/Fe of 0.96 and 1.25. The two green sphenes have still lower Mn/Fe, but this reflects higher Fe, rather than lower Mn. It thus appears that the pink colour is primarily dependent on the ratio of Mn to other chromatophoric elements, principally Fe. Where this ratio is unusually high, the colour will go toward reddish; with increasing Fe content the colour of Mn^{2+} will be masked, producing greenish tints.

The pink colour of greenovite may be enhanced, in crystals of mm-size, by another factor that was noticed during the selection of grains for single crystal X-ray work. These crystals, as all the macroscopic crystals of greenovite, are never transparent, but rather cloudy, a feature that persists until small splinters (less than 0.1 mm) are obtained. The splinters are then translucent, and still pink, although much fainter than before. The reason of the cloudiness (and darkening of the colour) may be due to the presence of inclusions in the major crystals consisting of a rose carbonate (turned out to be manganous calcite, according to the cell parameters) in rhombohedra as large as 0.2 mm across. Moreover, on the cleavage planes of certain samples (e.g. SM-51), reddish coatings were detected optically which did not produce an X-ray diffraction pattern. They may have the effect of diffusing the light, thus intensifying both the colour and the cloudiness.

Substitutions in greenovite

The valency states of Mn and Fe in titanites should be studied in more detail than has been done to date. For Fe, HIGGINS and RIBBE (1976) recognized the problem but assumed, given the absence of independent evidence such as Mössbauer determinations, that all Fe, even when chemically determined as FeO, could be computed as Fe^{3+} and grouped with Al as a substituent for Ti in the octahedral site. They do mention Mn, together with other ions such as Nb, Mg, Cr, V, etc., as potential octahedrally coordinated cations, but do not discuss its oxidation state. They do not, however, regard it as a possible substituent for Ca, in the 7-fold coordinated site.

As noted above, the pink colour of greenovite strongly suggests that Mn is in the divalent state; the green colour of the more Fe-rich sphenes suggests that Fe is also divalent. Most of the analyses in table 2 show an excess of Ti+Al relative to Ca+Na; this imbalance can be reduced in most cases, and the structural formulae brought closer to stoichiometry ($X = Y = 1$) if Mn and Fe are grouped with Ca + Na in the 7-coordinated site. However, this argument must be used with caution, since the amounts of Mn and Fe are small relative to the possible analytical errors (1-3 % relative) in Ca and Ti. For the same reason, the data do not allow evaluation of the substitution scheme $\text{Ti}^{4+} + \text{O}^{2-} \rightleftharpoons \text{Al}^{3+} + (\text{OH}, \text{F})^{-}$, suggested by several workers. This scheme is incompletely documented, due to the difficulties of measuring small amounts of OH and F by standard chemical techniques.

Conclusions

Greenovite is a «clean» titanite with less than 5 mol% substitutions in the formula. Cell parameters are indistinguishable from those of natural titanites, although slightly smaller than the synthetic end member. The colour is due to the relatively high Mn/Fe even though the total amount of Mn is less than 1 %.

Stoichiometry and charge balance considerations suggest that Mn, and possibly also Fe, occur as divalent ions, substituting for Ca in 7-fold coordination rather than for Ti in 6-fold coordination.

The name «greenovite» may be retained, but as the name of the pink «ex-colore» variety of titanite, related to a relatively high Mn/Fe ratio, rather than for a manganiferous «ex-compositione» variety as previously believed.

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