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CRYSTAL CHEMISTRY AND GENESIS OF Nb-, V-, AND Al-RICH METAMORPHIC TITANITE FROM EGYPT AND GREECE

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ABSTRACT

Titanite $CaTiOSiO_4$ from calc-silicate rocks of Gebel Umm Shagir, Egypt, associated with garnet, pyroxene, scapolite, calcite and quartz, contains up to 11 wt.% Nb_2O_5, 6 wt.% Al_2O_3 and 2 wt.% V_2O_5. Other elements present in minor amounts are Fe, Ta, Sn, and F. The main substitutions are 2 Ti = Nb + Al, Ti + O = Al + (OH,F), and V for Ti. Up to 50 mol.% of Ti is substituted. The crystals show complex zoning, with Nb contents decreasing from core to rim. The growth of the crystals is correlated with different stages of metamorphism. Titanite from low-grade Mn-rich metasediments of Andros, Greece, contains up to 2 wt.% V_2O_5 in homogeneous crystals. The valence state of vanadium is uncertain; possible mechanisms of substitution are $Ti + O = V^{3+}$ + (OH,F), $Ti = V^{4+}$, and $2\ Ti = V^{5+} + (Al,Fe)^{3+}$.

Keywords: niobian titanite, vanadian titanite, calc-silicate rock, Mn-rich metasediment, chemical composition, Egypt, Greece.

SOMMAIRE

La titanite qui se trouve dans des calc-silicates à Gebel Umm Shagir, en Egypte, est associée à grenat, pyroxène, scapolite, calcite et quartz; elle contient jusqu'à 11% en poids de Nb_2O_5, 6% de Al_2O_3 et 2% de V_2O_5. Sont aussi présents en quantités moindres Fe, Ta, Sn et F. Les substitutions importantes sont Nb + Al pour 2Ti, Al + (OH,F) pour Ti + O, et V pour Ti. Ces couples mènent au remplacement de 50% du Ti. Les cristaux montrent une zonation complexe où le Nb diminue du coeur à la bordure. On établit le lien entre la croissance des cristaux et les différents stades de métamorphisme. La titanite dans les métasédiments riches en manganèse de Andros, en Grèce, faiblement métamorphisés, forme des cristaux homogènes qui peuvent contenir jusqu'à 2% de V_2O_5. La valence du vanadium n'est pas établie, et les couples de substitution possibles sont V^{3+} + (OH,F) pour Ti + O, V^{4+} pour Ti, et $V^{5+} + (Al,Fe)^{3+}$ pour 2Ti.

(Traduit par la Rédaction)

Mots-clés: titanite niobifère, titanite vanadifère, calc-silicates, métasédiments manganifères, composition chimique, Egypte, Grèce.

INTRODUCTION

The crystal chemistry of titanite $CaTiOSiO_4$ shows considerable variation in the octahedral sites normally occupied by Ti^{4+} (Ribbe 1980). Al^{3+} and Fe^{3+} may be incorporated by means of the substitution $Ti^{4+} + O^{2-} = M^{3+} + (OH,F)^-$, which has been found to replace up to 50% of the Ti in natural titanite (Franz & Spear 1985, and references therein). Charge balance for the exchange $Ti^{4+} \rightleftharpoons M^{3+}$ can also be maintained by a coupled substitution with a pentavalent cation, *e.g.*, Nb or Ta. Clark (1974) and Paul *et al.* (1981) described this type of substitution, $2\ Ti^{4+} = M^{5+} + M^{3+}$, in titanite of pegmatitic origin. In the present note, we describe an occurrence of an extremely (Nb,Al)-rich titanite from high-grade metamorphic calc-silicate rocks and an occurrence of V-enriched titanite in low-grade Mn-rich metasediments.

GEOLOGICAL SETTING AND PETROGRAPHY

Gebel Umm Shagir, Egypt

The (Nb,Al)-rich titanite comes from the Gebel Umm Shagir basement of southern Egypt. It is a Precambrian metamorphic complex consisting mainly of granitic gneiss and migmatite, minor calc-silicate rocks, marble and amphibolite, and small granitic intrusive bodies. Conditions of metamorphism were determined to be on the order of 8 kbar, 800°C for relics of the granulite facies. An amphibolite-facies overprint at approximately 6 kbar, 600 - 700°C, produced the main mineral assemblage of the rocks; a greenschist-facies overprint is also discernible (Bernau *et al.* 1987).

The (Nb,Al)-rich titanite occurs as an accessory mineral in a rock composed of garnet, clinopyroxene and scapolite, with small amounts of calcite and accessory quartz and opaque minerals. Other rock types from this area include different calc-silicate rocks, extremely coarse-grained marble with scapolite, clinopyroxene, zoisite and quartz, and gneisses of granitic composition. Lack of proper exposure did not allow the determination of the type of contact between calc-silicate rock and marble on one hand, and the migmatitic gneisses on the other, but from a comparison with other localities in this area, small irregular layers and lenses seem to be the typical mode of occurrence. There are no outcrops of pegmatite or granite in the immediate vicinity.

TABLE 1. REPRESENTATIVE COMPOSITION OF ACCOMPANYING MINERALS*

	garnet	garnet		scapolite	scapolite		pyroxene
SiO_2	37.86	38.66		41.69	44.79		50.76
TiO_2	0.43	0.36		-	-		0.06
Al_2O_3	15.60	18.15		29.02	27.12		1.46
Fe_2O_3	9.71	6.01		-	-		-
FeO	1.95	2.64		0.32	0.61		13.65
MgO	0.18	0.20		0.05	0.14		9.06
MnO	0.89	1.13		-	-		0.73
CaO	33.16	33.10		20.71	19.13		23.99
Na_2O	-	-		1.47	1.80		0.17
K_2O	-	-		0.18	0.31		-
Σ	99.78	100.25		93.44	93.90		99.88
Si	2.968	2.980	Si	6.591	7.027	Si	1.950
Al^{VI}	1.441	1.649	Al	5.408	4.997	Al^{IV}	0.050
Fe^{3+}	0.573	0.349	Fe^{3+}	0.042	0.080	Al^{VI}	0.016
Fe^{2+}	0.128	0.170	Ca	0.509	3.204	Fe^{3+}	0.042
Mg	0.021	0.023	Na	0.451	0.544	Fe^{2+}	0.397
Mn	0.059	0.074	K	0.036	0.061	Mg	0.519
Ca	2.785	2.734				Mn	0.024
Ti	0.025	0.021	Aneq	80.3	66.6	Ca	0.988
			Mar	12.0	15.4	Na	0.012
			Mei	88.0	84.6		
			Aneq = 100(Al-3)/3			En	25.9
Andr	28.7	17.5				Fs	19.9
Gross	64.3	73.8				Wo	45.8
Pyr	0.7	0.8	Mei = $\frac{100\,(Ca+Mg+Fe)}{(Na+K+Ca+Mg+Fe)}$			TS	4.8
Alm	4.3	5.5				Ac	1.2
Spess	2.0	2.5				Jo[1]	2.4

* Sample no. RU 05A, Umm Shagir; [1] Jo = Johannsenite

The main mineral assemblage of the titanite-bearing rock is garnet, clinopyroxene and scapolite. Representative compositions are compiled in Table 1. The garnet is a grossular-rich variety (62 - 74% gross), with subordinate (18 - 30 mol.%) andradite. Minor almandine, spessartine and pyrope components are rather constant in all grains. The garnet is anhedral, and no distinct zoning could be determined. The clinopyroxene is essentially a diopside--hedenbergite solid solution, with $Fe^{2+}/(Fe^{2+}+Mg)$ values between 0.34 and 0.44, and 44 - 46 mol.% $CaSiO_3$ component. Scapolite is an extremely Ca-rich variety, with 85 to 88% meionite component and ≤ 1 % of the K-bearing end member. Chlorine and sulfur could not be detected by microprobe analyses, and the mineral is assumed to be predominantly CO_3-scapolite. Opaque minerals are extremely rare; in the thin section analyzed, only three grains were found as inclusions in titanite. They are too small for a quantitative analysis; the data obtained (analyses recalculated to 100% after subtraction of Ca, Si and Ti of the surrounding titanite) indicate that it is a (Nb-Fe)-oxide mineral, probably of the wodginite–ixiolite type. The Nb/Ta ratio is very high, similar to that in the surrounding titanite. Calculation of the formulae on the basis of 8 negative charges, with the assumption that all the Fe is present as Fe^{3+}, yielded the average chemical formula $Nb_{1.05}Ta_{0.01}Fe^{3+}_{0.81}Mn_{0.13}O_4$, whereas calculation on the basis of 12 negative charges, with all Fe assumed to be present as Fe^{2+}, gave unsatisfactory results. Therefore, we conclude that the inclusions are not minerals of the columbite–tantalite or tapiolite groups, $(Fe^{2+},Mn)\,(Nb,Ta)_2O_6$.

Titanite occurs as oval-shaped inclusions (≤ 1 mm) in garnet, clinopyroxene and scapolite, as well as larger anhedral grains between the main silicate minerals (Fig. 1). It was also observed in contact with calcite and quartz. The crystals are pleochroic yellow-brown to brown. Optical extinction is not homogeneous over the grains, but reveals a zonation that matches the chemical zonation; three distinct zones can be distinguished (see below, in "Chemistry"). Furthermore, most of these crystals have many minute inclusions in the core. Somewhat larger inclusions, situated in the inner rim, are composed of clinopyroxene, scapolite and garnet. Their compositions do not differ from that of the matrix minerals (Table 1). Small round grains of zircon occur as inclusions in the titanite. In contrast to the core and the inner rim, the outer rim is free of inclusions.

Besides the zoned grains of titanite described above, smaller (≤ 0.05 mm) subhedral grains were observed on grain boundaries between the matrix minerals. Their composition is similar to that of the outer margin of the larger anhedral grains of titanite (see number 13, Table 2).

Vitali, Andros, Greece

Vanadium-bearing titanite was found in a piemontite–albite gneiss from Vitali, Andros Island, Greece. The gneiss belongs to the highly oxidized Mn-rich metasediments intercalated in a series of metapelitic quartzose schist, marble and basic metavolcanic rocks (Reinecke 1986). The metamorphic rocks on Andros form a part of the Eocene blueschist belt of the Hellenides and were affected by a high-P, low-T type of regional metamorphism (P ≥ 9 kbar, T 400 - 500°C) and a later Barrovian-type metamorphism (P 5 - 6 kbar, T 400 - 500°C), which generated widespread greenschist-facies assemblages (Matthews & Schliestedt 1984).

The accessory V-rich titanite coexists with piemontite, albite, muscovite or phengite, calcite, hematite and Mg-chlorite; small amounts of quartz, cymrite and apatite are also present (for more details, see Reinecke 1983). The titanite forms almost colorless, slightly brownish grey, euhedral crystals up to 1 mm across in contact with all other minerals (Fig. 2).

CHEMISTRY

The titanite grains were analyzed on a Camebax microprobe (WDS) using the following standards:

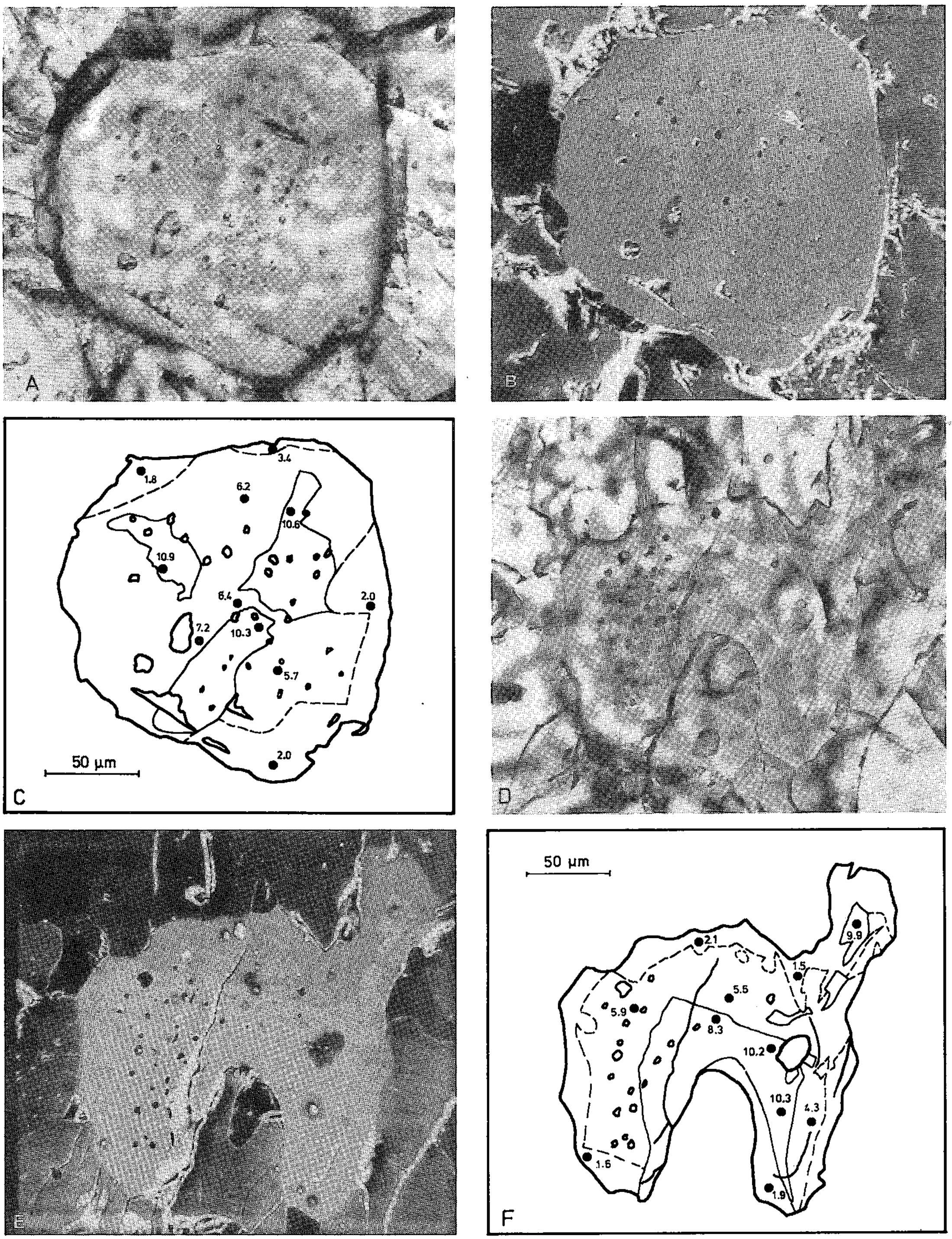

FIG. 1. Photomicrographs of zoned niobian titanite from Gebel Umm Shagir, Egypt. (A, D) plane-polarized light; secondary electron image (B, E) and chemical zoning of niobian titanite (C F). The continuous line in Figure 1C, F delimits the core, and the dashed line, the inner rim of zoned grains. Numbers refer to Nb_2O_5 contents in wt.%. Figure 1A shows niobian titanite as an inclusion in clinopyroxene. The large inclusion (black in Fig. 1B) is also clinopyroxene. Titanite in Figure 1E is surrounded by garnet and scapolite and has inclusions of garnet. Note the concentration of small inclusions in the inner rim and core of the titanite.

TABLE 2. COMPOSITION OF TITANITE AND STRUCTURAL FORMULAE

wt% oxide	ideal tit.	50 % Nb-Al	1^a	2^a	3^b	4^c	5^c	6^a	7^b	8^b
Nb_2O_5		16.44	10.94	10.40	6.41	3.39	1.96	11.18	6.17	5.79
Ta_2O_5			0.57	0.97	0.81	0.39	0.17	0.83	0.77	0.69
V_2O_5			1.29	1.31	1.64	1.78	2.02	1.11	1.68	1.52
SiO_2	30.65	29.73	29.32	29.72	29.62	29.84	29.90	29.02	29.64	29.69
TiO_2	40.75	19.77	21.40	21.84	27.42	31.08	32.36	21.71	26.97	28.49
SnO_2			0.34	0.33	0.63	0.87	0.76	0.34	0.70	0.56
Al_2O_3		6.13	5.89	6.04	4.41	3.47	3.15	5.62	4.54	4.36
$Fe_2O_3{}^{*1}$			1.55	1.42	1.24	1.12	0.91	1.52	1.22	1.12
CaO	28.60	27.75	27.90	27.50	28.19	28.42	27.98	27.54	27.99	28.36
MnO			0.02	-	0.05	0.03	-	-	-	-
Na_2O			0.08	0.01	0.02	-	-	0.01	-	-
F			0.63	0.72	0.68	0.56	-	0.22	0.77	0.13
Σ-F·16/38	100.00	100.00	99.66	99.96	101.83	100.71	99.21	99.01	100.13	100.66
Ca			1.00	0.98	0.99	1.00	0.99	1.00	0.99	1.00
Ti			0.54	0.55	0.68	0.76	0.80	0.55	0.67	0.70
Sn			-	-	0.01	0.01	0.01	-	0.01	0.01
Al			0.23	0.24	0.17	0.13	0.12	0.22	0.18	0.17
Fe^{3+}			0.04	0.04	0.03	0.03	0.02	0.04	0.03	0.03
Nb			0.17	0.16	0.10	0.05	0.03	0.17	0.09	0.09
Ta			0.01	0.01	0.01	-	-	0.01	0.01	0.01
V^{5+}			0.03	0.03	0.04	0.04	0.04	0.02	0.04	0.03
Σ oct			1.02	1.03	1.04	1.02	1.02	1.01	1.03	1.04
Si			0.98	0.99	0.98	0.98	0.98	0.98	0.98	0.97
F			0.07	0.08	0.07	0.06	-	0.02	0.08	0.01
OH^{*2}			0.01	-	-	0.01	0.07	0.04	-	0.06
O^{*3}			4.93	4.94	4.94	4.94	4.94	4.94	4.94	4.93
Σ O, OH, F			5.01	5.02	5.01	5.01	5.01	5.00	5.02	5.00

	9^c	10^a	11^b	12^c	13	14	15	16
Nb_2O_5	3.30	10.15	4.31	1.55	0.61	0.21	0.10	0.20
Ta_2O_5	0.45	0.90	0.28	0.17	-	0.09	-	0.09
V_2O_5	1.91	1.47	1.79	2.02	1.60	1.50	1.83	2.05
SiO_2	29.92	29.03	30.04	30.34	30.22	29.90	29.74	30.34
TiO_2	30.76	24.19	30.53	34.20	32.74	34.68	35.21	35.28
SnO_2	0.85	0.44	0.73	0.80	0.83	-	-	-
Al_2O_3	3.69	4.21	3.79	3.06	3.55	2.26	1.56	2.04
$Fe_2O_3{}^{*1}$	0.99	1.78	1.12	0.86	0.73	0.67	0.94	0.67
CaO	29.03	28.25	28.52	29.03	28.72	28.14	27.93	28.75
MnO	0.01	0.03	0.01	0.03	0.07	0.03	0.13	-
Na_2O	0.02	0.01	0.01	0.01	-	0.07	0.04	0.05
F	0.29	-	-	-	0.43	0.63	0.84	0.72
Σ-F·16/38	101.10	100.46	101.13	102.07	99.32	97.92	97.97	99.89
Ca	1.01	1.01	0.99	0.99	1.00	1.00	1.00	1.00
Ti	0.75	0.61	0.75	0.82	0.80	0.87	0.88	0.86
Sn	0.01	0.01	0.01	0.01	0.01	-	-	-
Al	0.14	0.17	0.15	0.12	0.14	0.09	0.06	0.08
Fe^{3+}	0.02	0.04	0.03	0.02	0.02	0.02	0.02	0.02
Nb	0.05	0.15	0.06	0.02	0.01	-	-	-
Ta	-	0.01	-	-	-	-	-	-
V^{5+}	0.04	0.03	0.04	0.04	0.03	0.03	0.04	0.04
Σ oct	1.01	1.02	1.04	1.03	1.01	1.01	1.00	1.00
Si	0.97	0.97	0.98	0.97	0.98	0.99	0.99	0.99
F	0.03	-	-	-	0.04	0.07	0.09	0.07
OH^{*2}	0.04	0.02	0.07	0.07	0.07	-	-	-
O^{*3}	4.92	4.97	4.94	4.94	4.89	4.93	4.92	4.95
Σ O, OH, F	4.99	4.99	5.01	5.01	5.00	5.00	5.01	5.02

Coefficients on the basis of Σ cat = 3.00 (1-13: sample RU 05A, Umm Shagir; 14-16: sample 80/179, Vitali Andros). ^{a} core; ^{b} inner rim; ^{c} outer rim; ^{*1} Fe_{tot} as Fe_2O_3; ^{*2} calculated : $(Al+Fe^{3+})-F-(Nb+Ta+V^{5+})$ = OH; ^{*3} calculated: {(Σ cation charges)-OH-F}/2.0.

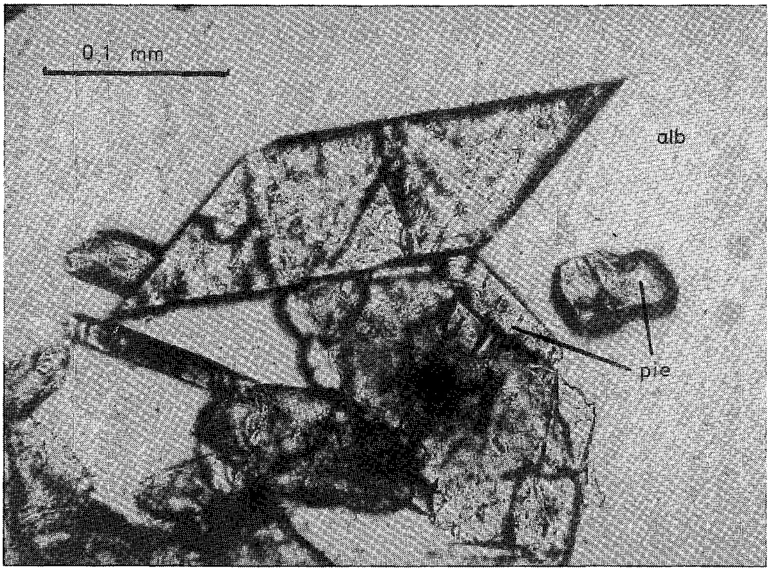

FIG. 2. Photomicrograph of euhedral vanadian titanite from Vitali, Andros Island, Greece, coexisting with albite (alb) and strongly zoned piemontite (pie); plane-polarized light.

wollastonite (Ca, Si), orthoclase (K) and albite (Na), synthetic F-phlogopite, TiO_2, $MgAl_2O_4$ and Fe_2O_3, and metallic Nb, Ta, Sn and Mn. The accelerating voltage was 15 kV; counting time was 20 seconds for F, Nb, Ta and Sn, and 10 seconds for the other elements. We used $L\alpha$ lines for Nb, Ta and Sn, and $K\alpha$ lines for all other elements. Raw data were reduced using the ZAF algorithm. All titanite grains were routinely checked for the presence of other elements such as *REE* with EDS (detection limit 0.5 - 1%). Representative compositions are presented in Table 2. Formulae were calculated on the basis of Σ cations = 3.00, since H_2O was not determined and there is no fixed number of oxygen atoms per formula unit. The chemistry of the (Nb,Al)-rich titanite from the calc-silicate rocks is described first.

The major oxide CaO shows only a slight variation, between 27.95 and 28.69 wt.%, which is close to the ideal value for pure titanite and for 50% of the hypothetical 2 Ti = Nb + Al substitution (Table 2). SiO_2 shows a slightly larger variation than CaO, especially toward lower values than the stoichiometric composition. Similar results were obtained by Franz & Spear (1985) for [Al + (F,OH)]-titanite; these are discussed below. TiO_2 is always lower than the ideal value of 40.75 wt.%, with a minimum recorded value of 20.9 wt.%. Al_2O_3 varies from 2.7 to 6.1 wt.%, and correlates negatively with TiO_2 (Fig. 3), positively with Nb_2O_5, and also positively with Fe_2O_3, which is always between 0.6 and 2.0

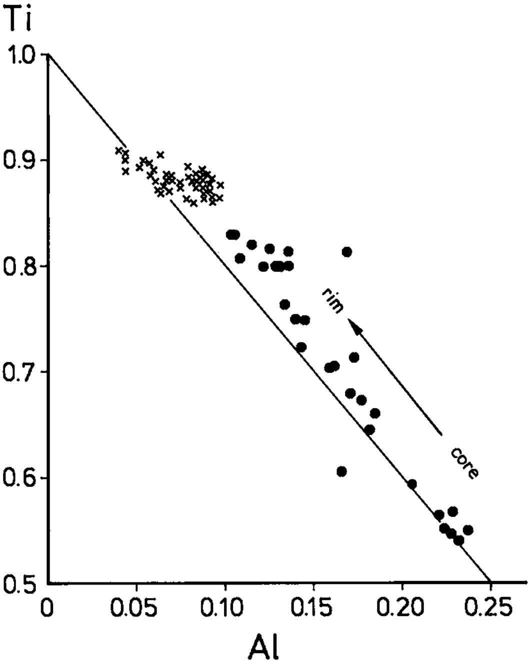

FIG. 3. Al *versus* Ti in titanite. Dots: niobian titanite from Gebel Umm Shagir, crosses: vanadian titanite from Greece. The straight line shows the ideal substitution 2 Ti = $M^{5+} + M^{3+}$. Cation coefficients calculated on the basis of 3 cations per formula.

wt.% (Fig. 4). Nb_2O_5 attains 11.3 wt.%, and Ta_2O_5 invariably is below 1 wt.%. Fluorine varies, but not systematically with Al_2O_3, as determined previously by Franz & Spear (1985); it invariably is below 1 wt.%. SnO_2 (0.3 to 0.9 wt.%), is positively correlated with V_2O_5 (1.0 to 2.1 wt.%) only (Fig. 5), and both oxides are negatively correlated with Nb_2O_5 (Fig. 6) and Ta_2O_5. Other elements, like Mg, Mn, K, Na and the *REE,* are mostly at concentrations below the detection limit of the microprobe.

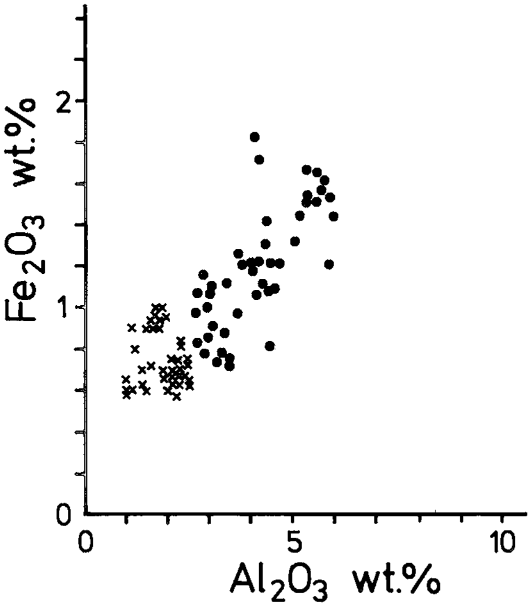

FIG. 4. Proportion of Al_2O_3 *versus* Fe_2O_3 (wt.%) in titanite. Dots: Gebel Umm Shagir, crosses: Greece.

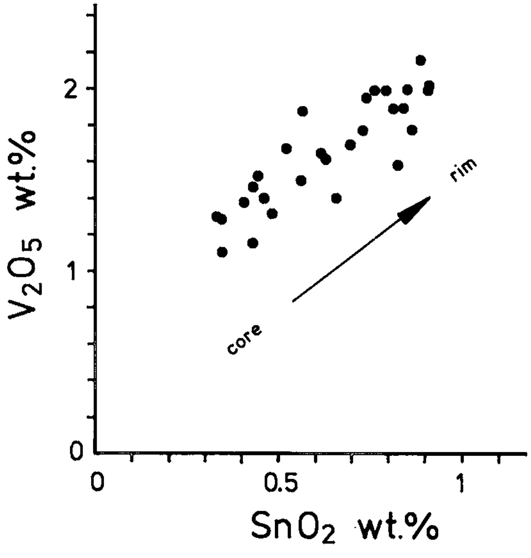

FIG. 5. Proportion of SnO_2 *versus* V_2O_5 (wt.%) in titanite from Gebel Umm Shagir.

The chemistry of the vanadian titanite from Greece is rather simple. V_2O_5 attains 2.3 wt.%. Fe_2O_3 is low ($\leq$ 1.1 wt.%) and is not correlated with Al_2O_3 (maximum 2.5 wt.%, see Fig. 4). All samples show decreasing TiO_2 contents with increasing V_2O_5 and Al_2O_3 contents (see Figs. 3, 7). Representative compositions are given in Table 2, numbers 14 - 16.

Figure 7 (Nb + Ta + V^{5+} *versus* Ti) shows the wide compositional range of the titanite, with TiO_2 values for the (Nb,Al)-rich grains approaching about 50% of 2 Ti = M^{5+} + M^{3+} substitution. However, the sum of M^{5+} is always lower than that for ideal (Nb,Ta,V,Al)-rich titanite, indicating that other substitutions occur as well. This is also evident from a plot of (Al + Fe^{3+}) *versus* (Nb + Ta + V^{5+}) (Fig. 8), which shows M^{3+} always higher than expected for an ideal (M^{5+} + M^{3+}) substitution. Additional elements that are present in minor amounts are responsible for these phenomena: Sn probably enters the Ti site by the simple substitution $Ti^{4+} \rightleftharpoons Sn^{4+}$, and F and OH replace O by the coupled substitution $Ti^{4+} + O^{2-} = Al^{3+} + (F, OH)^-$.

In contrast to the previously described (Nb,Ta)-rich titanite from granitic pegmatites (Clark 1974, Paul *et al.* 1981, Groat *et al.* 1985), the Nb/Ta value of the (Nb,Al)-rich titanite is extremely high (Figs. 9b, c). Both elements are positively correlated. The vanadian titanite shows a poor correlation between Nb and Ta (Fig. 9a) and a large scatter in the Nb/Ta values.

The calculation of formulae yielded cation coefficients for both Si and Ca near 1.00, and we assume that substitution for these elements is not important. On the other hand, substitution for Ti can be substantial, as has been shown above and also in Figure 10. The deviation from the 1:1 slope could reflect a systematic error in the microprobe data, but it might also be due to a slight substitution of Al for Si in tetrahedral positions. There is also the possibility that the titanite is not exactly stoichiometric.

Each crystal of (Nb,Al)-rich titanite can be subdivided into three separate regions, a core, an inner rim and an outer margin, with decreasing substitution for Ti from core to margin (Fig. 1). Nevertheless, there is an overlap of composition from all zones of different crystals, with no indications of a miscibility gap. The sharp, discontinuous zoning in individual crystals must therefore be due to changing P - T conditions or to changing activities of chemical species. The grains of vanadian titanite are rather homogeneous, with only a limited variation.

DISCUSSION

Crystal chemistry

The chemical data of the titanite samples analyzed allow some conclusions to be derived about possible substitutions. It is important to note that in the titanite from Gebel Umm Shagir, almost 50 mol.% of the Ti is replaced by other elements (Fig. 10). The most important substitution is 2 $Ti^{4+} = Nb^{5+} + Al^{3+}$; only small amounts of Ta are incorporated by 2 $Ti^{4+} = Ta^{5+} + Al^{3+}$. Instead of Al, these coupled substitutions may also operate with Fe^{3+}. There is a large surplus of $(Al+Fe^{3+})$ over the sum of pentavalent cations, and another substitution mechanism that is extensively involved is $Ti^{4+} + O^{2-} = (Al,Fe)^{3+} + (OH,F)^{-}$.

There is uncertainty concerning the valence state of V. It is common usage to list V in titanite compositions as V_2O_5 (*e.g.*, Sahama 1946, Deer *et al.* 1982, p. 449), but it might be present as V^{3+}, V^{4+} or V^{5+} (Evans 1969). That V is trivalent in kyanite is established experimentally (Langer 1976), and this seems also to be the case in the V-mica roscoelite (Heinrich & Levinson 1955) and in V-bearing garnet (Schmetzer & Otteman 1979). Staples *et al.* (1973) described two vanadian silicates (cavansite and pentagonite) with V^{4+}. Nevertheless, ionic radii in VI co-ordination (Shannon 1976) of V^{3+}, V^{4+} and V^{5+} are 0.64, 0.58 and 0.54 Å, respectively, and because Nb^{5+} (0.64 Å) and Al^{3+} (0.535 Å) both substitute for Ti^{4+} (0.605 A), all these valence states may be possible from a crystallochemical point of view.

There is also little information about dependence of oxidation state of V on $f(O_2)$. The data of Wakihara & Katsura (1970) show that complex oxides between V_2O_5 and VO_2 ($V_{2-x}O_3$, V_3O_5, V_4O_7) are stable over a limited range of T-$f(O_2)$ below the hematite - magnetite buffer, and the V_2O_3 - $V_{2-x}O_3$ stability limit is below the wüstite - magnetite buffer. Kosuge (1967) presented a phase diagram showing that up to 700°C, ten different non-stoichiometric oxides (magneli phases) are stable between V_2O_3 and V_2O_5. Therefore, it must be considered that V may be incorporated according to

i) $Ti^{4+} + O^{2-} = V^{3+} + (OH,F)^{-}$,
ii) $Ti^{4+} = V^{4+}$, or
iii) 2 $Ti^{4+} = V^{5+} + (Al,Fe)^{3+}$.

The oxidation state of the whole rock in which the vanadian titanite occurs is above the hematite - magnetite buffer (Reinecke 1986), and probably within the range of V_2O_5 stability. Moench & Meyrowitz (1964) and Wood (1982) have shown that V^{3+} is preferentially incorporated in garnet (goldmanite) and clinopyroxene. The calc-silicate rocks from Gebel Umm Shagir are composed essentially of these two minerals, and, if trivalent vanadium were present, it would have been a trace element in these minerals. Its concentration in the accessory

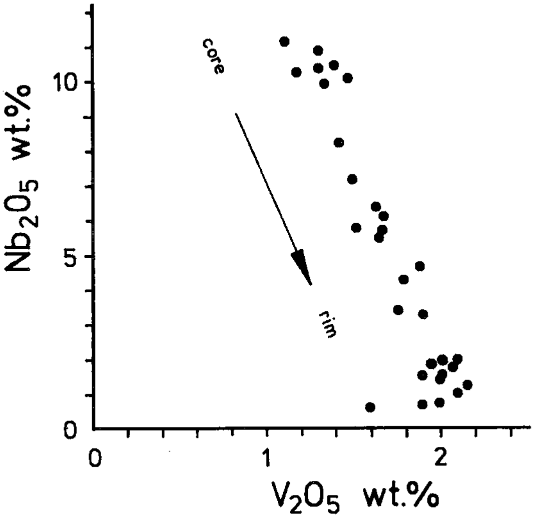

FIG. 6. Proportion of V_2O_5 *versus* Nb_2O_5 wt.% in titanite from Gebel Umm Shagir.

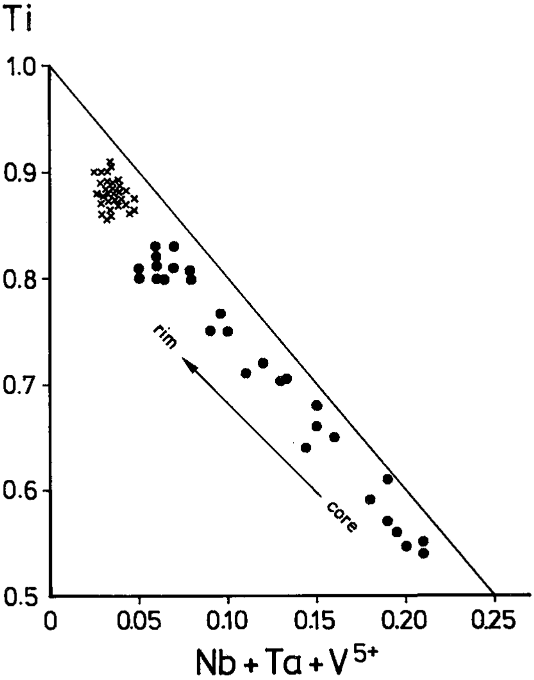

FIG. 7. Sum of pentavalent elements *versus* Ti (symbols as in Fig. 3). Note the deviation from the trend of the ideal substitution 2 Ti = $M^{5+} + M^{3+}$, which seems somewhat more pronounced at low contents of M^{5+}.

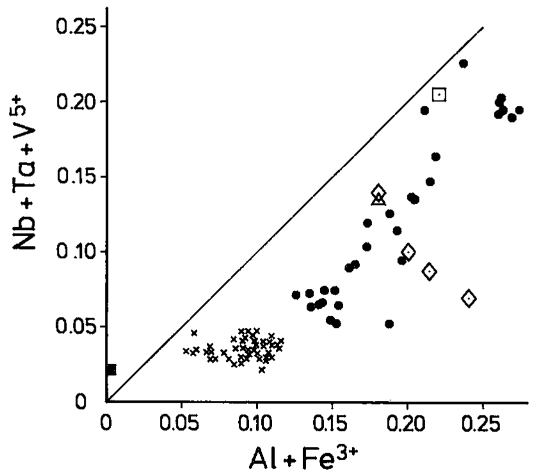

FIG. 8. Sum of trivalent elements *versus* sum of pentavalent elements. The straight line shows the ideal substitution 2 Ti = $M^{5+} + M^{3+}$. Symbols as in Figure 3; other symbols: square: Craveggia (Clark 1974), triangle: Huron claim (Paul *et al.* 1981), diamond: Irgon claim (Groat *et al.* 1985), filled square: Kola (Sahama 1946).

titanite indicates a different valence-state, unsuitable for substitution into garnet and clinopyroxene. Therefore, the compositions were calculated on the basis of V^{5+}. Another argument for pentavalent vanadium is its positive correlation with the pentavalent niobium (Fig. 6). However, it must be kept in mind that the other valence states are possible.

The end members (mol.%) of titanite were calculated in the following sequence: 1) Sn end member (malayaite), 2) Fe^{3+} + Nb, 3) Fe^{3+} + (OH,F), 4) Al + Nb, 5) Al + Ta, 6) Al + V^{5+}, 7) Al + (OH,F), and 8) Ti end member (titanite). For a graphic presentation of the non-Ti end members in a triangular plot (Fig. 11), the (Fe^{3+},Nb), (Al,Nb) and (Al,Ta) end members were grouped, and the [Fe^{3+} + (OH,F)] and [Al + (OH,F)] as well; malayaite is neglected since it represents only 0.5 (core) to 1.0 mol.% (rim).

The diagram thus shows the variation in these end members, and also the type of zoning. If V is calculated as V^{4+} or V^{3+} and plotted as vanadian titanite or [V^{3+} + (OH,F)]-titanite, the relative distribution would be different, of course, with a higher percentage of [(Al,Fe^{3+}) + (OH,F)]-titanite, but the general trend would be the same.

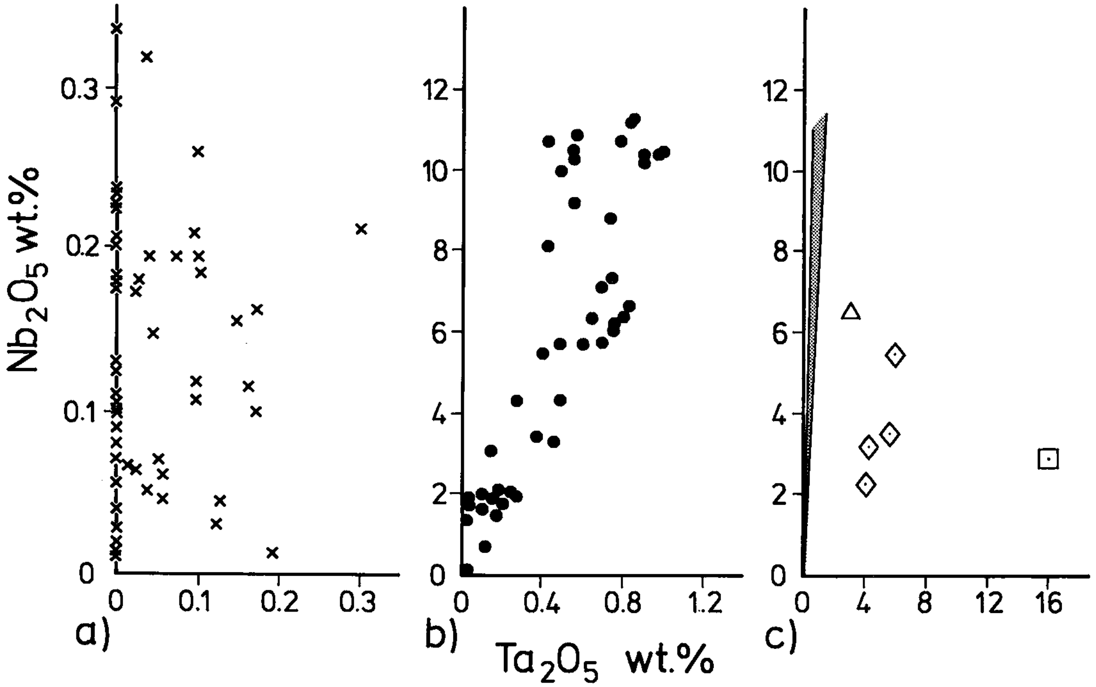

FIG. 9. Proportion of Ta_2O_5 *versus* Nb_2O_5 (wt.%) in titanite. Note the different scales. a. Greece, b. Gebel Umm Shagir, c. Gebel Umm Shagir (shaded area) compared with titanite from Craveggia (square), Huron claim (triangle), and Irgon claim (diamond).

The vanadian titanite from Greece shows a wider range of $(Al+Fe^{3+})$ and V contents, no regular type of zoning, and low contents of (Nb + Ta). The (Nb,Al)-rich titanite shows a large variation in (Nb + Ta), but only a very limited variation in V. The core of grains of (Nb,Al)-rich titanite is highly enriched in the $[(Al,Fe^{3+})+(Nb,Ta)]$ component. The inner margin is characterized by a large variation in $[(Al,Fe^{3+})+(Nb,Ta)]$, with a constant ratio of $(Al+V)/[(Al,Fe^{3+})+(OH,F)]$. In the outer margin, the content of the (Al + V) end member is rather constant, and only the ratio $[(Al,Fe^{3+})+(Nb,Ta)]/[(Al,Fe^{3+})+(OH,F)]$ decreases. This type of zoning is interpreted as growth zoning, with relatively sharp discontinuities between the different zones. The shape of the zones is irregular, as observed earlier in natural [Al + (OH,F)]-titanite (Franz & Spear 1985). The Nb-rich core typically is embayed (Fig. 1) and therefore probably corroded as a result of a reaction with a new Al-rich titanite component. The outer rim is partly an overgrowth on euhedral crystal shapes, partly an overgrowth on embayed crystals. The formation of the zones can be correlated with different metamorphic stages (see below).

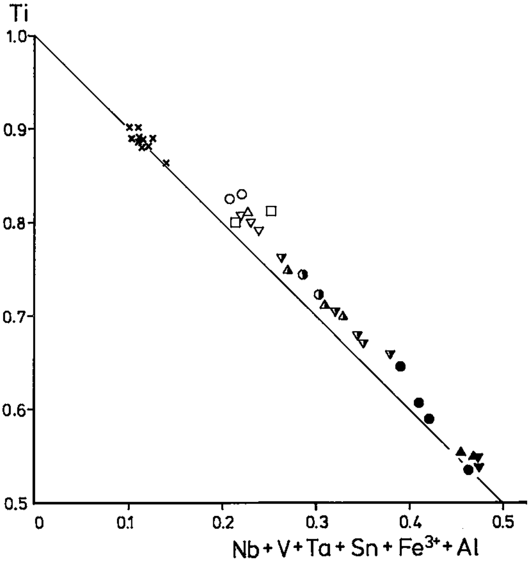

FIG. 10. Substitution for Ti by other cations in titanite. Dots, triangles and squares represent different crystals from Gebel Umm Shagir (filled: core, half-filled: inner margin, open: outer margin). Crosses represent titanite crystals from Greece.

Paragenetic and geochemical considerations

The calc-silicate marble association at Gebel Umm Shagir probably represents the high-grade equivalent of a marly limestone. The possibility of a metamorphosed carbonatite cannot be ruled out, but there is no other supporting evidence for this hypothesis except the high Nb-contents in titanite. However, a granitic origin of the Nb is improbable because of the geological setting.

The mineral assemblages possibly developed in the following way. A carbonate–marl sediment was deposited, together with heavy minerals such as zircon, apatite, rutile and those that provided the Nb. These could have been, for example, complex oxides of the pyrochlore–microlite group, the euxenite–aeschynite group, the tantalite or the ixiolite–wodginite group. The only other Nb-mineral besides titanite present now in the sample is an oxide, probably of the ixiolite–wodginite type, in the core of the titanite, where Nb contents are extremely high. Therefore the core of the titanite can be interpreted as a product of the first metamorphism, and the ixiolite–wodginite inclusions are either relics or have formed during this metamorphism from other complex oxides. The Al content of the rock is rather high, as documented by the presence of garnet and scapolite, and the Al necessary for the coupled substitution was supplied by this assemblage. The high Ca-content of the scapolite indicates peak temperatures of metamorphism on the order of 800°C (*cf.* Oterdoom & Gunter 1983), but the (Nb,Al)-rich titanite could have been formed also in a prograde stage of this metamorphism. However, we suppose that the high Nb-content of the titanite is rather due to unusual chemical conditions than to unusual P – T conditions.

The development of the titanite continued with the formation of an inner rim, with increasing proportion of [Al + (OH,F)] and decreasing proportion of $[(Nb,Ta)+(Al,Fe^{3+})]$ end members. The inner rim is considered to be the product of mineral reactions involving the previously formed (Nb,Al)-rich cores (in part) and the matrix minerals, *e.g.*, breakdown of scapolite, leading to titanite compositions more enriched in the $CaAl(OH,F)SiO_4$ component. This second stage of titanite growth is tentatively correlated with the amphibolite-facies metamorphism that produced the main mineral assemblages in the gneisses, and also led to the emplacement of small granitic stocks. The generally sharp and straight boundaries between the core and the inner rim of the crystals (Fig. 1) may suggest that migmatite formation did not follow immediately after granulite-facies metamorphism. The small syntectonic granitic stocks could not have provided the Nb, because the core zone of the titanite was already formed at the granulite-facies stage. The outer rim is mainly enriched in the [Al + (OH,F)] component; the (Al + V) component does not increase further, and the boundary between inner and outer rim is less sharp. This stage of mineral formation is correlated

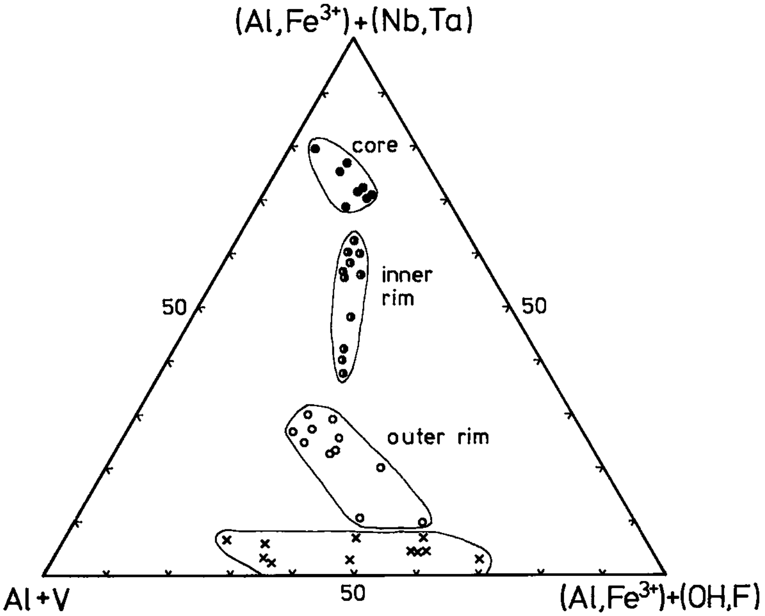

FIG. 11. Relative distribution of [(Al,Fe^{3+}) + (Nb,Ta)], (Al,V) and [(Al,Fe^{3+}) + (OH,F)] end members in the Gebel Umm Shagir (dots) and Vitali (crosses) titanite crystals.

with the retrograde greenschist-facies overprint. At rather low temperatures, incorporation of the $CaAl(OH,F)SiO_4$ component continues, but there is only minor Nb available. The small grains of titanite in the matrix (number 13, Table 2) have the same composition as the outer rim and were probably formed at this stage as well.

The rocks from Greece come from a completely different tectonic environment. An early high-pressure, low-temperature event with a later overprint at greenschist-facies conditions is well documented (Reinecke 1986). The vanadian titanite in the piemontite–albite gneiss could have been formed on the prograde path of metamorphism. Alternatively, the vanadian titanite could have been formed by the greenschist-facies overprint of a high-P assemblage containing, *e.g.*, V-bearing jadeitic clinopyroxene. V-bearing clinopyroxene fom high-P metamorphic rocks was described by Wood (1982). A late titanite-forming reaction resulting from the breakdown of piemontite and rutile was described by Reinecke (1986) for spessartine-bearing rocks from the same locality.

The variable Nb and Ta contents, shown in Figures 9a, b and c, clearly demonstrate that titanite has no preference for either one of these elements. The extent to which it incorporates Nb and Ta may only be a question of the geochemical environment.

CONCLUSIONS

The importance of titanite as a mineral that incorporates many other elements is documented by the occurrence of a complex (Nb,Al)-rich variety and an (Al,V)-rich variety. Geochemical studies of metamorphic rocks must consider titanite as a sink for Nb, Ta and V, in addition to the well-known incorporation of Sn and the *REE*.

The substitutions of Nb, Ta and V for Ti are complex. Therefore, they cannot be completely interpreted without knowledge of the hydrogen content and the valence state of V and Fe. Nevertheless, this study shows that the most important substitutions are:

1) $2Ti^{4+} = Nb^{5+} + (Al,Fe)^{3+}$,
2) $2Ti^{4+} = V^{5+} + (Al,Fe)^{3+}$, and
3) $2Ti^{4+} + O^{2-} = Al^{3+} + (OH,F)^{-}$.

Zoning is very strong and irregular, and reflects growth conditions at different stages of metamorphism.

Vanadium is probably pentavalent in titanite because of the high oxidation state of the rocks. If vanadium were trivalent, it would have been incorporated also in garnet and clinopyroxene.

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