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Compositional variation of metasomatic titanite from Adamello (Italy)

by *Reto Gieré*[1]

Abstract

Metasomatic titanite is an abundant phase in titanium-rich ($TiO_2 = 2.1$–4.5 wt%) veins found in dolomite marbles of the Adamello contact aureole (northern Italy). Titanite is generally idiomorphic and exhibits within individual crystals a pronounced compositional variation which is due to discontinuous zoning. The occurrence of titanite in parageneses containing graphite and pyrrhotite suggests that iron is present mainly in the bivalent oxidation state. From the analytical data it is inferred that ferrous iron substitutes for titanium rather than for calcium. The crystal chemical data further suggest that the total hydroxide content of the studied titanites consists of two components involved in two different substitutions which may be expressed by the exchange vectors $Al(OH,F)Ti_{-1}O_{-1}$ and $Fe^{2+}(OH)_2Ti_{-1}O_{-2}$.

Keywords: Titanite, compositional zoning, crystal chemistry, substitution, contact metamorphism, Adamello.

Introduction

Hydrothermal veins rich in titanium have been found in dolomite marbles of the Adamello contact aureole (northern Italy; GIERÉ, 1990a). These veins contain metasomatically formed titanite with a widely variable composition which was studied in order to elucidate the principal substitution mechanisms.

Numerous investigations have shown that titanite may contain high amounts of aluminum and iron, as well as fluorine and water (for reviews, see RIBBE, 1980, and DEER et al., 1982). It was therefore suggested that in titanite the substitution of primary importance is

$$(Al,Fe)^{3+} + (OH,F)^{-} <==> Ti^{4+} + O^{2-} \quad (1)$$

(HIGGINS and RIBBE, 1976). These authors also found the replacement of titanium by aluminum and iron to be directly related to a variation of the titanite lattice parameters (see also ČERNÝ and RIVA DI SANSEVERINO, 1972). This result was recently confirmed by OBERTI et al. (1991) who demonstrated in a study on highly Al-rich titanites that the unit-cell volume decreases linearly with increasing Al content.

Al-rich titanite is quite often found in eclogites (SMITH, 1977; FRANZ and SPEAR, 1985; OBERTI et al., 1991). This observation has led SMITH (1981) to investigate experimentally a possible pressure dependence of substitution (1); his experiments demonstrate that in the Fe- and OH-free system the accommodation of Al is favored by increasing pressure at constant temperature.

Many investigations have focussed on reporting data for unusually Al-rich titanites (see review in OBERTI et al., 1991) rather than for the more common Al-poor varieties (1–3 wt% Al_2O_3). Therefore, substitution (1) is well characterized by crystal chemical data at high concentrations of both Al and F (FRANZ and SPEAR, 1985; see also PAN and FLEET, 1992). Reliable electron microprobe data, however, are quite rare for titanites with low Al contents and particularly for those

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with low concentrations of F (e.g. Higgins and Ribbe, 1976; Zabavnikova, 1957). This is mainly due to the lack of F data in many published titanite analyses, but also to the generally encountered difficulties in analyzing for fluorine at low levels. Today, the use of multilayer crystal spectrometers allows for significantly improved, relatively precise electron microprobe determinations of fluorine even at low concentrations.

The principle aim of this paper is to report analytical data for titanites with relatively low contents of F and Al, and to characterize the possible chemical substitutions. The results presented here have been obtained from the study of two mineralogically different samples from a single Ti-rich vein.

Geological setting

The Adamello batholith is the largest igneous complex of Tertiary age in the Alps. It is composed of several petrographically and isotopically distinct plutons (Bianchi and Dal Piaz, 1948; Bianchi et al., 1970) which were intruded into the Southern Alpine basement and its sedimentary cover between 42 and 30 Ma (Del Moro et al., 1985). The southernmost and oldest pluton (Hansmann et al., 1985), the Re di Castello massif, is a composite intrusion of predominantly gabbroic, tonalitic and granodioritic rocks, and is bordered by small mafic and ultramafic bodies (Ulmer et al., 1985).

The Ti-rich veins occur in contact metamorphic, pure dolomite marbles of middle to upper Triassic age (Brack, 1984) at the contact with a tonalite intrusion of the Re di Castello massif (near Malga Trivena[1], Valle di Breguzzo, Provincia di Trento). The veins are commonly folded and concordant with the folded bedding produced in the dolomite marble by syn-intrusive (Brack, 1985), ductile deformation; occasionally, however, the veins are discordant to the structural elements in the host rock. Furthermore, the vein minerals do not show evidence of deformation. These observations suggest that the Ti-rich veins were formed contemporaneously with and outlasted the syn-intrusive deformational event (Gieré, 1990b).

Thermodynamic analysis of the phase assemblages indicates that the vein minerals were formed at 500–600 °C ($P_{total} \approx 2$ kbar) from a relatively water- and fluorine-rich ($X_{CO_2} \approx 0.2$; $f_{HF} = 10^{-2.1}$ bar), reducing ($f_{O_2} = 10^{-20}$ bar) and H_2S-dominated ($f_{H_2S} : f_{S_2} : f_{SO_2} \approx 10^6 : 0.6 : 1$) fluid which originated from the nearby tonalite intrusion (for details, see Gieré, 1990b).

Vein mineralogy

The Ti-rich veins are characterized by four distinct mineral zones, comprising (from margin to center) 1) forsterite + calcite, 2) pargasite + calcite + titanite + pyrrhotite, 3) phlogopite + calcite + titanite + pyrrhotite, and 4) titanian clinohumite + spinel + calcite + pyrrhotite. This geometry reflects the temporal sequence of vein formation, as indicated by textural relationships observed in thin section.

Titanium is concentrated along with rare earth elements (REE) and other high-field-strength elements in the three central assemblages (TiO_2 = 2.1–4.5 wt%; see Gieré, 1990b). These elements are mainly incorporated in titanian clinohumite, phlogopite, pargasite, titanite, and the accessory minerals zirconolite (ideally $CaZrTi_2O_7$), geikielite ($MgTiO_3$), rutile, and aeschynite-(Ce), a complex REE–Th–Ti–Nb oxide. The three central zones also contain abundant sulfides, mainly pyrrhotite and minor chalcopyrite, as well as accessory galena and pyrite (as secondary mineral only). Fluor-apatite is very abundant in all three Ti-rich central zones, and is invariably present as euhedral crystals commonly associated with the Ti-, Zr- and REE-bearing minerals.

Titanite is abundant in both the pargasite and phlogopite zones (3–4 vol.%), and commonly occurs as euhedral crystals up to approximately 1.0 mm in size. Titanite is texturally closely associated with F-bearing pargasite and phlogopite (Figs 1a, 1b), as well as with fluor-apatite (Fig. 2; see also Fig. 10 in Gieré and Williams, 1992).

Details on the vein mineralogy and on the crystal chemistry of all major phases may be found in Gieré (1990b). The composition of the REE-bearing minerals is reported by Gieré and Williams (1992).

Analytical procedure

Titanite analyses were performed using a CAMECA SX-50 electron microprobe at the Institut für Mineralogie und Petrographie, ETH Zürich. The microprobe is equipped with five wavelength dispersive spectrometers and was operated at an acceleration potential of 15 kV and a beam current of 20 nA measured on a Faraday cage (beam size ≈ 2 μ). Samples and standards were coated with 200 Å of carbon. Natural and synthetic minerals,

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[1] Exact location: 10°36'47"E/46°03'05"N.

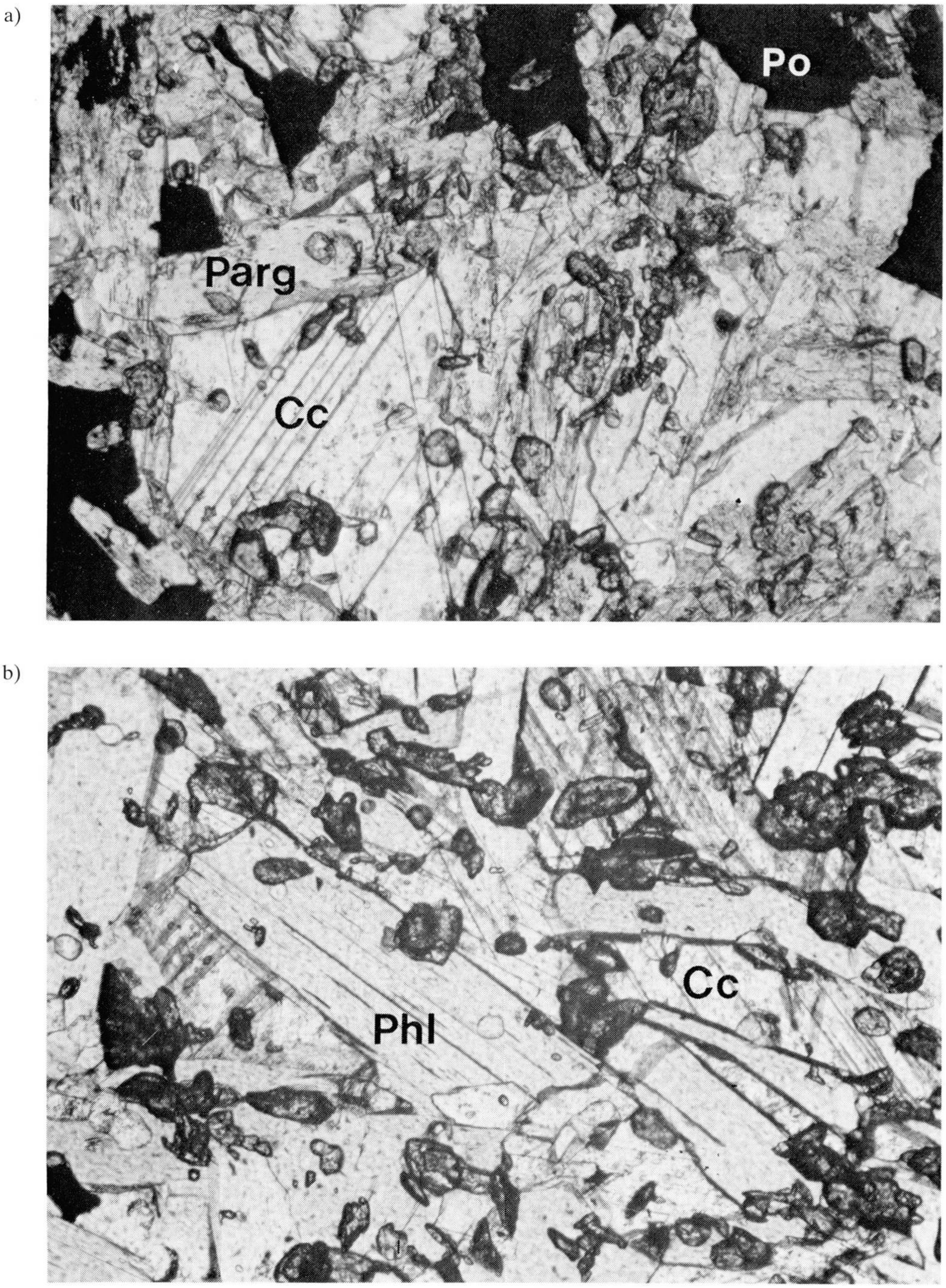

Fig. 1 Photomicrographs of the titanite assemblages in the described Ti-rich vein from the Adamello contact aureole. Both pictures: 1.4 × 0.9 mm.
a) Pargasite zone (sample Br193), *b)* phlogopite zone (sample Br194). Titanite appears as relatively dark crystals with high refractive index. Note the tendency towards euhedral morphology. Abbreviations: Cc = calcite; Parg = pargasite; Phl = phlogopite; Po = pyrrhotite.

synthetic oxides and glasses were used as standards; the standard for F was a synthetic F-phlogopite containing 9.02 wt% F, for Cl it was a natural scapolite containing 1.83 wt% Cl. Data collection time was 20 s for most major elements, 30–40 s for F and some trace elements including Cl. Fluorine was analyzed on a multilayer PC1-crystal spectrometer (2d = 60.0 Å) with background positions and analysis mode chosen in such a way as to avoid interference with the characteristic Fe–L_α and Al–$K_\alpha^{2nd\ order}$ lines. Data collection on background positions above and below the peaks was half the time of data collection on respective peak position. The raw data were corrected on-line by the PAP correction procedure (Pouchou and Pichoir, 1984).

Slight systematic differences exist between the titanite analyses of sample Br193 and sample Br194 (cf. Tab. 1; totals and data for SiO_2, CaO, and the calculated sum of octahedral cations). These differences are most probably due to the fact that the electron microprobe analyses of the two samples were performed in two different runs, during which, however, the analytical conditions and the standards used were identical.

Regression analysis

Regression data for the discussed correlations were obtained by a computer program (written by the author) using standard procedures for an unweighted linear regression of *y* on *x* ($y = b \cdot x + a$). Uncertainties in the *slope* (s_b) of a regression line were calculated from the sample standard deviation from regression ($s_{y/x}$), the *n* data points for x (x_i), and the average of all x values ($\bar{x}$) according to the equation: $s_b = s_{y/x} \cdot [\Sigma\ (x_i - \bar{x})^2]^{-0.5}$. Uncertainties in the y-intercept (s_a) of a regression line were calculated from the relation $s_a = s_{y/x} \cdot [\Sigma\ x_i^2/(n \cdot \Sigma\ (x_i - \bar{x})^2)]^{0.5}$. All confidence limits are given on a 95% level. Details on procedures may be found in Miller and Miller (1988).

Composition of titanite

Average compositions of titanite from the pargasite (sample Br193) and phlogopite zones (sample Br194) have been reported by Gieré and Williams (1992). These authors have shown that titanite exhibits in both assemblages a relatively large variation in the concentrations of several components, particularly of TiO_2, Al_2O_3, FeO and F (see Tab. 1 for a selection of representative titanite analyses). As demonstrated by Gieré and Williams (1992), this scattering can be accounted for by compositional variations within individual crystals. Backscattered electron images reveal that titanite exhibits discontinuous zoning with very complex patterns (Fig. 3; see also Fig. 10 in Gieré and Williams, 1992) which are similar to those described by Paterson et al. (1989) and Nakada (1991) for titanites from igneous rocks. A review of zoning patterns in many different crystals shows that titanite often possesses a high-$\bar{Z}$[2] core (cf. Fig. 2) rich in U and total Ree, and a low-$\bar{Z}$ rim, which is significantly lower in U and Ree and commonly displays itself a complex internal zoning (for analytical data on zoning, see Tab. 5 in Gieré and Williams, 1992). The high-$\bar{Z}$ areas further correspond to Al-poor compositions, a feature described also by Franz and Spear (1985).

The Adamello titanites contain small amounts of iron which only rarely exceed 0.4 elemental wt% (maximum value: Fe = 1.06 wt%). Most analyses of natural titanite report all iron as Fe_2O_3, but several wet chemical analyses point to the presence of ferrous iron as well (see Deer et al., 1982). Furthermore, Muir et al. (1984) and Holényi and Annersten (1987) showed by means of ^{57}Fe Mössbauer spectroscopy that natural titanite may indeed incorporate both ferric and ferrous iron. The paragenetic association of titanite in the Adamello veins (presence of graphite and pyrrhotite) strongly suggests that iron is present mainly in the bivalent oxidation state. Therefore, all Fe was treated as ferrous iron[3] in this study (see Tab. 1).

The concentration of aluminum (Al_2O_3 ranging from 0.80 to 2.84 wt%) is generally higher than in titanites from similar metasomatic rocks in the Bergell contact aureole (Gieré, 1986). The highest aluminum content in the Adamello titanites, however, is distinctly lower than the maximum values yet reported for titanite (in eclogitic

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[2] $\bar{Z}$ = mean atomic number.

[3] Because of the pronounced discontinuous zoning, no attempt has been made to determine by wet chemical analysis the concentrations of ferric and ferrous iron in mineral separates of titanite. As demonstrated by Gieré (1990b), pargasite which coexists with titanite in sample Br193 contains only small amounts of Fe_2O_3 (0.35 ± 0.1 wt%) as compared to FeO (3.3 ± 0.1 wt%; both are colorimetric determinations). These data indicate that some ferric iron might be present also in titanite. If the Fe^{2+}/Fe^{3+} ratio in titanite, however, would be identical to the ratio in pargasite, only 8.7% of the total iron would be trivalent. Furthermore, whole-rock analyses of three samples from the phlogopite zone revealed the presence of ferrous iron only (colorimetric determinations; see Gieré, 1990b).

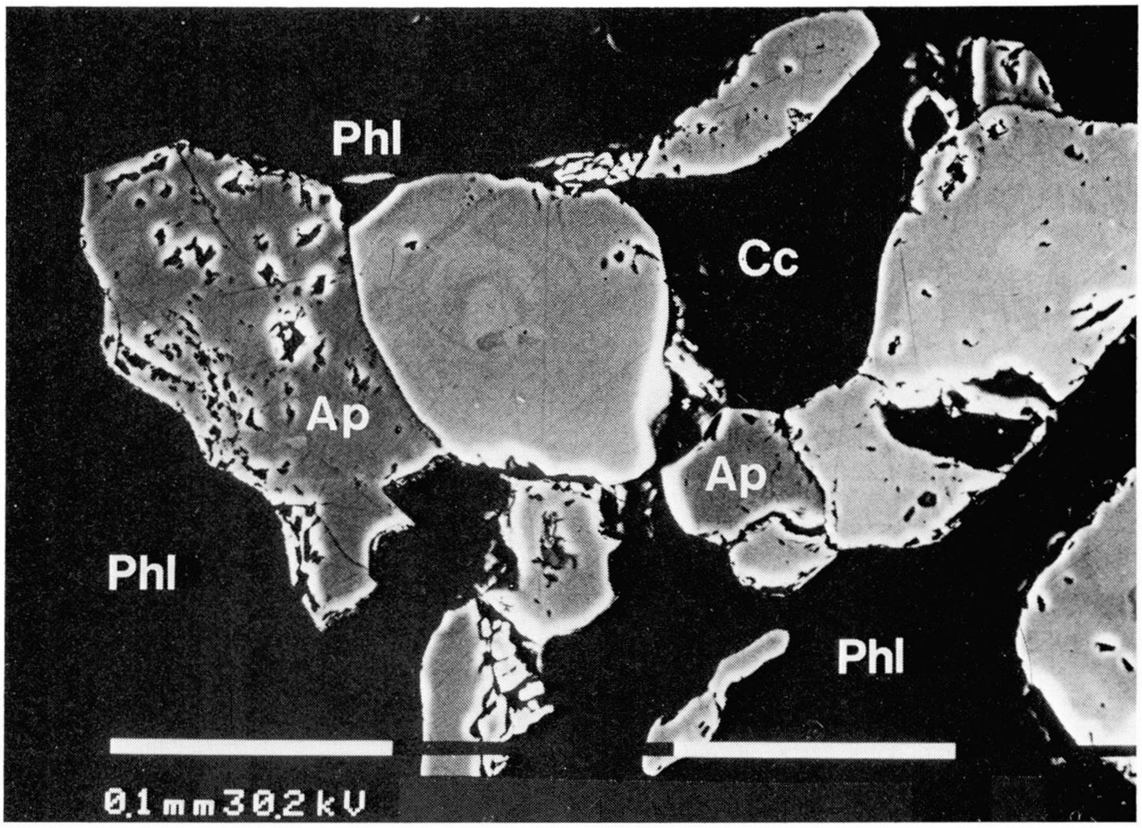

Fig. 2 Backscattered electron image of titanite crystals (bright grains with smooth surface) associated with apatite (*Ap*), phlogopite and calcite (phlogopite zone, sample Br194). Note zoning in titanite. For abbreviations, see figure 1. Photograph: SEM Laboratory, University of Basel.

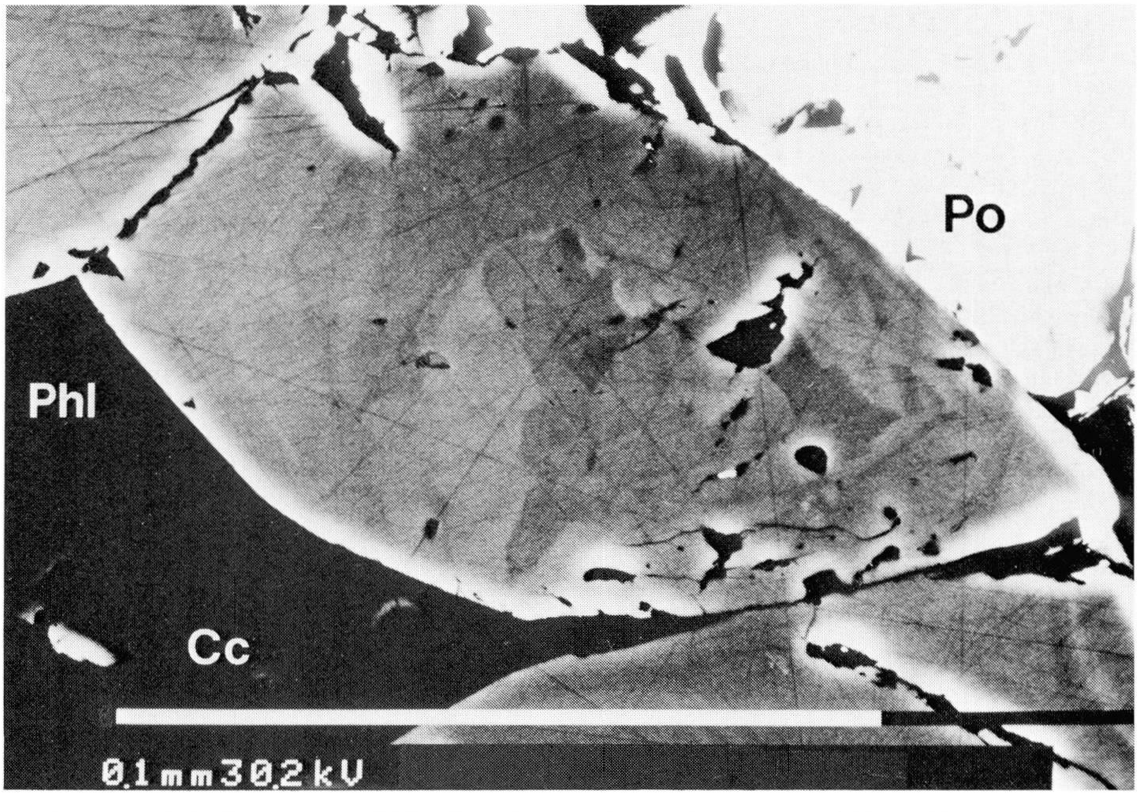

Fig. 3 Backscattered electron image of titanite with complex zoning pattern (phlogopite zone, sample Br194). Note euhedral morphology of titanite. For abbreviations, see figure 1.
Photograph: SEM Laboratory, University of Basel.

Tab. 1 Representative selection of single-spot electron microprobe analyses of titanite from the Ti-rich vein.

	pargasite zone					*phlogopite zone*				
[wt%]	Br193-1	Br193-2	Br193-3	Br193-4	Br193-5	Br194-6	Br194-7	Br194-8	Br194-9	Br194-10
SiO_2	30.2	30.3	30.3	30.5	30.4	30.7	30.8	30.9	30.6	30.8
TiO_2	38.4	38.0	38.1	37.7	37.5	38.0	38.4	37.3	38.9	36.2
Cr_2O_3	0.09	0.17	0.05	0.03	0.05	0.38	0.22	0.08	0.03	0.04
Al_2O_3	2.16	2.05	1.84	2.13	2.48	0.99	0.80	1.43	0.87	2.12
FeO 1)	0.04	0.14	0.32	0.50	0.32	0.22	0.29	0.46	0.11	0.52
CaO	28.9	28.7	28.6	28.9	28.8	28.8	28.5	28.6	28.5	28.8
F	0.45	0.41	0.24	0.30	0.53	0.19	0.16	0.32	0.19	0.59
H_2O_{calc} 2)	0.42	0.44	0.58	0.76	0.50	0.52	0.34	0.47	0.18	0.59
O=F	0.19	0.17	0.10	0.13	0.22	0.08	0.07	0.14	0.08	0.25
Total 3)	100.5	100.1	100.0	100.7	100.4	99.6	99.4	99.4	99.3	99.5
Number of ions on the basis of Σ(cations) = 3.000										
Si	0.976	0.986	0.987	0.986	0.985	1.004	1.009	1.010	1.005	1.007
Ti	0.936	0.928	0.934	0.917	0.913	0.934	0.946	0.918	0.959	0.889
Cr	0.002	0.004	0.001	0.001	0.001	0.010	0.006	0.002	0.001	0.001
Al	0.082	0.078	0.071	0.081	0.094	0.038	0.031	0.055	0.034	0.082
Fe^{2+}	0.001	0.004	0.009	0.014	0.009	0.006	0.008	0.012	0.003	0.014
Ca	1.002	1.000	0.999	1.002	0.998	1.008	1.001	1.001	0.999	1.007
F	0.046	0.042	0.025	0.031	0.054	0.020	0.016	0.033	0.020	0.061
OH_{tot} 2)	0.046	0.048	0.062	0.082	0.054	0.056	0.037	0.052	0.019	0.064
$OH_{M^{3+}}$ 4)	0.039	0.041	0.047	0.051	0.042	0.028	0.020	0.024	0.015	0.022
$OH_{Fe^{2+}}$ 5)	0.007	0.007	0.015	0.030	0.013	0.028	0.017	0.028	0.004	0.042
Σ(oct. cations)	1.022	1.014	1.014	1.012	1.017	0.988	0.990	0.988	0.996	0.986

Note: Average relative errors (2σ-level) resulting from counting statistics are as follows (in %, for high/low concentrations): SiO_2: 0.9/1.0; TiO_2: 0.8/0.8; Cr_2O_3: 4.2/16.6; Al_2O_3: 2.6/3.3; FeO: 8.5/17.1; CaO: 0.7/1.0; F: 5.2/9.4; H_2O: 18.5/39.0.

Error for H_2O is a cumulative error, calculated by Gaussian error propagation (see e.g. MILLER and MILLER, 1988) from 2σ-erros for F and for the cations (for calculation of H_2O content, see below).

[1] Total Fe as FeO.

[2] Calculated assuming charge-balance and stoichiometry, i.e. $OH_{tot} = 10 - \sum(\text{cation charges}) - F$.

[3] For average rare earth and other trace element concentrations, see GIERÉ and WILLIAMS (1992); Na_2O, K_2O, MgO and MnO < 0.05 wt%; Cl < 0.01 wt%.

[4] $OH_{M^{3+}} = Al + Cr - F$ (see text for discussion).

[5] $OH_{Fe^{2+}} = OH_{tot} - OH_{M^{3+}}$ (see text for discussion).

marbles up to 14 wt% Al_2O_3; see FRANZ and SPEAR, 1985). Very high aluminum contents have further been found by ČERNÝ and POVONDRA (1972), SMITH (1977), TULLOCH (1979), MRÁZEK and VRÁNA (1984), and by OBERTI et al. (1991).

The Adamello titanites always contain significant amounts of fluorine (F = 0.16–0.59 wt%), and thus document, like all other hydrous minerals in the vein, the presence of fluorine in the metasomatic fluid. As already predicted by ZACHARIASEN (1930), fluorine is a very common constituent of natural titanites, and fluorine contents up to 5.5 wt% have been reported (FRANZ and SPEAR, 1985).

In contrast to fluorine, chlorine could not be detected in the studied titanites (Cl < 0.01 wt%) although the fugacity of HCl in the fluid was inferred to be one order of magnitude higher than the fugacity of HF (GIERÉ, 1990b). This observation shows that titanite does not exhibit a strong affinity for chlorine which has a considerably larger ionic radius than fluorine (AHRENS, 1952; WHITTAKER and MUNTUS, 1970). It should be noted, however, that SAHAMA (1946) reported a chlorine content of 0.10 wt% for a F-poor titanite from the Urals.

Crystal chemistry of titanite

In order to unravel the crystal chemical relationships, the following discussion and associated diagrams include the data for all (n = 42) analyses of titanite from the two vein zones.

Titanite can be described by the general formula $CaTiSiO_4(O,OH,F)$ as suggested already by ZACHARIASEN (1930) and SAHAMA (1946). Aluminum, ferric iron and chromium are commonly assigned to the octahedrally coordinated Ti-site (SAHAMA, 1946; ZABAVNIKOVA, 1957; RIBBE, 1980). In natural titanites little or no substitution occurs in the tetrahedrally coordinated Si-site (HIGGINS and RIBBE, 1976), whereas in synthetic titanite some Si may be replaced by Ti (HOLLABAUGH and ROSENBERG, 1983) or by ferric iron (MUIR et al., 1984). Substituents for the seven-coordinated calcium include alkaline earth and alkali elements, as well as other large ions such as REE, U and Th (e.g. DEER et al., 1982)

There is some dispute in the literature regarding the position of ferrous iron in the titanite structure. MUIR et al. (1984) and HOLÉNYI and ANNERSTEN (1987) have demonstrated by Mössbauer spectroscopy that ferrous iron can substitute for titanium in the octahedral position, whereas most other authors (e.g. COOMBS et al., 1976; DEER et al., 1982; NAKADA, 1991; OBERTI et al., 1991) consider it to be incorporated into the sevenfold Ca-site. The following evidence from the chemical composition of the Adamello titanites strongly suggests that Fe^{2+} is accommodated in the octahedral site:

a) There is no correlation between the total iron and the CaO contents in the Adamello titanites (Fig. 4).

b) When normalized to Σ(cations) = 3.0, the Ca-site is always filled with Ca for more than 99.4% (average value: 100%) of the theoretical value of 1.0, and, when normalized to one silicon per formula unit (HIGGINS and RIBBE, 1976), for more than 98.4% (average value: > 99.8%). Furthermore, when REE, U and Th are included in the total of the Ca-site cations (data from GIERÉ and WILLIAMS, 1992), the site is in all cases occupied by more than 99.9%, thus leaving no space for the accommodation of ferrous iron.

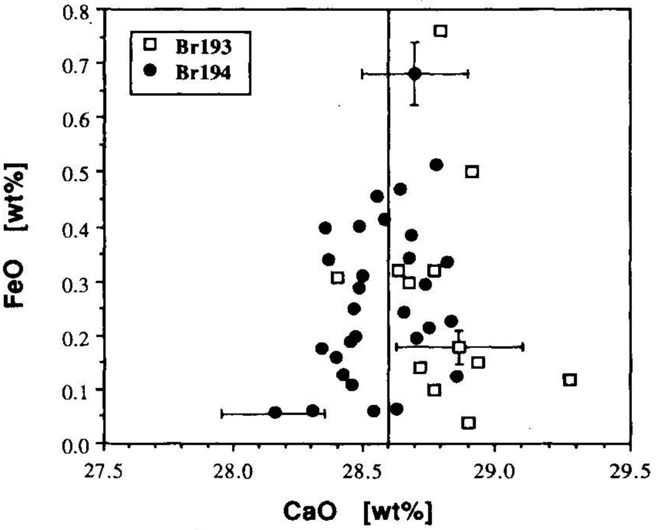

Fig. 4 Variation of FeO and CaO in titanites from the pargasite (Br193) and the phlogopite (Br194) zones. Total iron as FeO. Vertical line at 28.6 wt% CaO displays the theoretical CaO content of stoichiometric, pure titanite. Error bars represent 2σ-errors resulting from counting statistics.

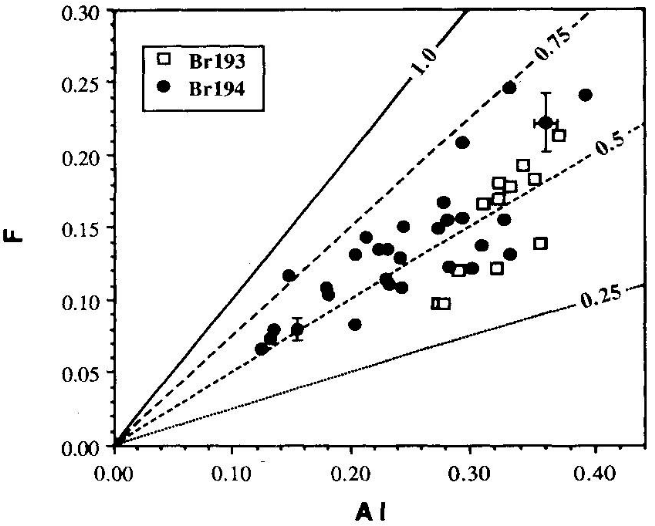

Fig. 5 Variation of F and Al in titanites from the pargasite (Br193) and the phlogopite (Br194) zones. The data are based on Σ(octahedrally coordinated cations) = $\Sigma(Ti + Al + Fe_{tot} + Cr) = 4.0$. Error bars represent 2σ-errors resulting from counting statistics. Numbered lines illustrate constant F/(F + OH) ratios (see text for discussion). The calculated regression line (not shown) for the data has a slope of 0.485 ± 0.127, an intercept of 0.012 ± 0.035, and a correlation coefficient of 0.777.

Figure 5 displays a F vs Al diagram for the Adamello titanites and shows that the concentration of fluorine increases with increasing aluminum content, indicating that incorporation of Al is bound to incorporation of F. The calculated linear regression line has a slope of 0.485 ± 0.127 and an intercept of 0.012 ± 0.035, implying that Al-free titanite should not contain any fluorine. For a given Al content, however, there are several data points with different F contents, resulting in a relatively large scattering. As outlined below, this scattering may be explained by the observed compositional zoning.

Because Al substitutes for Ti in the octahedral sites and probably not for Si in the tetrahedral sites (HIGGINS and RIBBE, 1976), an antipathetic relationship must exist between Al and Ti. This is displayed in figure 6, where (Al + F) correlates negatively with Ti (slope = –1.405 ± 0.174, r_{cor} = –0.934). Two data points are suspect (arrows in Fig. 6) because they exhibit very large deviations from the regression: their residuals[4] with values of –0.115 and –0.096 are outside the 95%-confidence interval of the unweighted linear regression which has a sample standard deviation of ± 0.081. A statistical outlier test[5] was performed on the residuals of the data and revealed that both suspect data points may be rejected as outliers at the 1%-significance level. Therefore, a new linear regression was calculated without these data points yielding a better correlation (r_{cor} = –0.963) along a line with a steeper slope (–1.557) and a smaller uncertainty (± 0.145). This good correlation for the titanites from the two vein zones confirms that the coupled substitution

$$Al^{3+} + F^{-} <==> Ti^{4+} + O^{2-} \qquad (2)$$

proposed by ZABAVNIKOVA (1957) is important in the studied titanites. As shown by the regression analysis of the data in figure 5, however, the amount of fluorine corresponds on an average to approximately 0.5 · [Al], which means that only half of the aluminum is compensated by fluorine and that substitution (2) is not charge-balanced. Thus, an alternative substitution accounting for the remaining Al must be found.

ZABAVNIKOVA (1957) suggested that the substitution of Ti by Al in REE-rich titanites may also be accompanied by simultaneous replacement of Ca by REE, according to the equation

$$Al^{3+} + REE^{3+} <==> Ti^{4+} + Ca^{2+}. \qquad (3)$$

In the Adamello titanites, however, the total REE contents are too low to compensate the remaining ≈ 0.5 · [Al]: from the data given by GIERÉ and WILLIAMS (1992) it can be calculated that the cation contents of trivalent REE account for at most 34%, but sometimes for less than 10% of the remaining aluminum. Thus, a combination of substitutions (2) and (3) still does not completely describe the incorporation of aluminum. Furthermore, substitution (3) cannot be proven to be effective in the Adamello titanites, because only six REE analyses are available (four electron microprobe analyses, two instrumental neutron activation analyses of mineral separates).

As shown in table 1, the Adamello titanites contain significant amounts of water (average contents: 0.58 wt% [Br193] and 0.50 wt% [Br194]). The amount of water was not analyzed, but calculated from the analytical data assuming stoichiometry and charge-balance (see Tab. 1). The calculated H_2O contents are relatively high, suggesting that the substitution

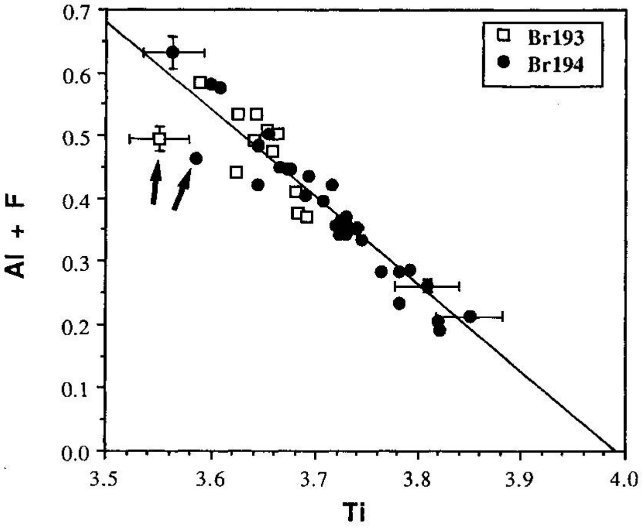

Fig. 6 Variation of (Al + F) and Ti in titanites from the pargasite (Br193) and the phlogopite (Br194) zones. The data are based on Σ(octahedrally coordinated cations) = Σ(Ti + Al + Fe_{tot} + Cr) = 4.0. Error bars represent 2σ-errors resulting from counting statistics. The plotted regression line has a slope of –1.405 ± 0.174, and a correlation coefficient of –0.934. Arrows point to outliers (see text for discussion).

$$Al^{3+} + OH^{-} <==> Ti^{4+} + O^{2-} \qquad (4)$$

recognized by SAHAMA (1946) might be of similar importance as substitution (2). The data, thus, indicate that incorporation of aluminum into the Adamello titanites can be attributed to the combined coupled substitution

$$Al^{3+} + (OH,F)^{-} <==> Ti^{4+} + O^{2-}. \qquad (5)$$

Substitution (5) is usually written in a more general form as

$$M^{3+} + (OH,F)^{-} <==> Ti^{4+} + O^{2-} \qquad (6)$$

and is regarded as the main mechanism for incorporation of aluminum and ferric iron into natural titanites (HIGGINS and RIBBE, 1976). Similarly, substitution (6) also describes the accommodation of Cr^{3+} in titanite which may contain up to 1 wt% Cr_2O_3 (DEER et al., 1982).

If substitution (5) completely describes the accommodation of Al in the Adamello samples, the relatively large scattering of the data in figure 5

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[4] Defined as: $r_i = y_i - a - b \cdot x_i$, where a is the intercept and b the slope of the linear regression line.

[5] Two-sided discordancy block procedure using Tietjen and Moore's E_k-statistic (see BARNETT and LEWIS, 1987, p. 176).

($r_{cor} = 0.777$) must be the result of variable F/(F + OH) ratios in titanite. This is actually confirmed by analytical data, showing that Al-poor cores are enclosed by Al-rich overgrowths, which have identical F contents and where the higher Al contents are not compensated by REE (see Tab. 5 in GIERÉ and WILLIAMS, 1992). Variation of the F/(F + OH) ratio in the Adamello titanites is confined to values between 0.35 and 0.8 (Fig. 5). This variable F/(F + OH) ratio, thus, probably reflects fluctuations in the fluid composition during formation of the different growth zones within individual titanite grains. Similarly, variations in the fluid composition were inferred from the analysis of the U and REE zoning patterns observed in the studied titanites (GIERÉ and WILLIAMS, 1992).

Since iron most likely occurs as ferrous iron in the Adamello titanites, the charge-balance requirements do not readily allow for it to be included in substitution (6). Thus, another equation has to be formulated to account for the heterovalent replacement of Ti^{4+} by Fe^{2+} in the octahedral positions. This substitution could be written, for example, as

$$Fe^{2+} + \square <==> Ti^{4+} + O^{2-} \qquad (7)$$

where $\square$ stands for a vacancy. An alternative substitution was suggested by EXLEY (1980) who found that the amount of ferrous iron was related to the total REE content in titanites from granites on the Isle of Skye (see also NAKADA, 1991); he described the observed relationship by the equation

$$Fe^{2+} + 2\,REE^{3+} <==> Ti^{4+} + 2\,Ca^{2+}. \qquad (8)$$

Substitution (8) was derived from extremely REE-rich titanites with very high FeO contents ($\Sigma[REE_2O_3] \approx 46$ wt%, FeO ≈ 11 wt%). In the Adamello example, however, the contents of both total REE and total iron are too low, and the respective analytical errors too large to confirm this substitution. Furthermore, only a limited number of REE data is available (see above), and thus, does not allow for correlation diagrams to be plotted.

Another possibility was proposed by ZABAVNIKOVA (1957) who suggested that ferrous iron could be incorporated into titanite by the coupled substitution

$$Fe^{2+} + 2\,(OH,F)^{-} <==> Ti^{4+} + 2\,O^{2-}. \qquad (9)$$

No correlation, however, was observed between ferrous iron and fluorine for the Adamello titanites. In order to find a possible relationship between OH and Fe^{2+}, it is necessary to determine the amount of OH which is not required for achieving charge-balance in substitution (6). With the assumption that substitution (6) completely describes the incorporation of trivalent cations into the octahedral site the amount of OH required for this substitution is given by

$$[OH_{M^{3+}}] = [M^{3+}] - [F]$$

where $[M^{3+}] = [Al^{3+}] + [Cr^{3+}]$ in the Adamello example (all Fe as Fe^{2+}). From $[OH_{M^{3+}}]$ and the total hydroxide content (Tab. 1) the amount of OH available for substitution (9) can be calculated from the relation

$$[OH_{Fe^{2+}}] = [OH_{tot}] - [OH_{M^{3+}}].$$

The calculations reveal that $[OH_{M^{3+}}] < [OH_{tot}]$ in all but two cases[6], pointing to the presence of excess hydroxide which could compensate for the accommodation of ferrous iron according to substitution (9). As demonstrated by figure 7, there is a relatively good correlation ($r_{cor} = 0.814$) between $[OH_{Fe^{2+}}]$ and the analyzed iron content. With the large cumulative 2σ-errors for $[OH_{Fe^{2+}}]$ in mind, it is concluded from the linear regression data (see

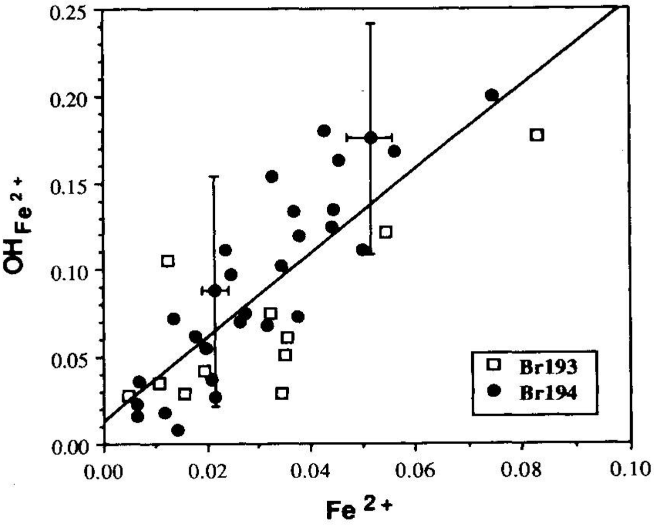

Fig. 7 Variation of $[OH_{Fe^{2+}}]$ and Fe^{2+} in titanites from the pargasite (Br193) and the phlogopite (Br194) zones. The data are based on Σ(cations) = 12.0. The two negative $[OH_{Fe^{2+}}]$ values (see text) were omitted from the diagram and the regression analysis. Error bars for Fe^{2+} represent 2σ-errors resulting from counting statistics; error bars for $[OH_{Fe^{2+}}]$ were calculated by Gaussian error propagation from 2σ-analytical errors for F and for the cations (see Tab. 1). The plotted regression line has a slope of 2.422 ± 0.571, an intercept of 0.013 ± 0.020, and a correlation coefficient of 0.814.

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[6] The two exceptions have $[OH_{Fe^{2+}}]$ values of −0.002 and −0.003 (based on 3 cations) showing that Al^{3+} and Cr^{3+} are not completely compensated by F^{-} and OH^{-}.

Fig. 7) that incorporation of ferrous iron in titanite is most probably bound to simultaneous accommodation of 2 OH^-; this can be described by

$$Fe^{2+} + 2\,OH^- \Longleftrightarrow Ti^{4+} + 2\,O^{2-} \qquad (10)$$

which is a simplified version of substitution (9). This conclusion may be justified even in the presence of small amounts of ferric iron, as suggested by calculations with fixed Fe^{2+}/Fe^{3+} ratios[7]. Thus, the data indicate that $[OH_{tot}]$ in titanite consists of two components which compensate for the heterovalent replacement of Ti^{4+} by Fe^{2+} and Al^{3+} (along with F^-), respectively.

The electron microprobe data further demonstrate that the tetrahedrally coordinated Si-site is, with two exceptions, always filled with Si by more than 98.1% of the theoretical value of 1.000 when normalized to three cations (average value: > 98.4%). The two exceptions have Si contents of 0.975 and 0.976 (Br193-1, Tab. 1) which, however, may be within less than 1.5% of the theoretical value when the analytical uncertainties are considered. Thus, if any substitution would occur in the tetrahedral position (HOLLABAUGH and ROSENBERG, 1983), it would be of minor importance in these samples (cf. OBERTI et al., 1991).

Conclusions

The occurrence of titanite in graphite- and pyrrhotite-bearing assemblages from the Adamello contact aureole suggests that iron is present mainly in the bivalent oxidation state. Compositional variation within individual crystals is due to pronounced discontinuous zoning. The data indicate that the main substitutions observed for the Adamello titanites may be described by the exchange vectors $Al(OH,F)Ti_{-1}O_{-1}$ and $Fe^{2+}(OH)_2Ti_{-1}O_{-2}$.

Zoning is not only distinct for the major elements but also for trace elements such as REE, U and Th, and most probably reflects compositional fluctuations of the metasomatic fluid during progressive vein formation.

The crystal chemical data presented here show that it is imperative to analyze for fluorine in naturally occurring titanites, even when they are not particularly rich in aluminum or ferric iron.

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References

AHRENS, L.H. (1952): The use of ionization potentials. Part 1. Ionic radii of the elements. Geochim. Cosmochim. Acta 2, 155–169.

BARNETT, V. and LEWIS, T. (1987): Outliers in statistical data. Wiley & Sons, 2nd ed. Chichester.

BIANCHI, A. and DAL PIAZ, G.B. (1948): Differenziazioni petrografici fondamentali del plutone dell'Adamello. Rend. Soc. Mineral. It. 5, 79–102.

BIANCHI, A., CALLEGARI, E. and JOBSTRAIBIZER, P.G. (1970): I tipi petrografici fondamentali del plutone dell'Adamello. Mem. Ist. Geol. Mineral. Univ. Padova XXVII.

BRACK, P. (1984): Geologie der Intrusiva und Rahmengesteine des Südwest-Adamello. Ph. D. thesis No. 7612, ETH Zürich.

BRACK, P. (1985): Multiple intrusions – examples from the Adamello batholith (Italy) and their significance on the mechanisms of intrusion. Mem. Soc. Geol. It. 26, 145–157.

ČERNÝ, P. and POVONDRA, P. (1972): An Al, F-rich metamict titanite from Czechoslovakia. N. Jb. Mineral. Mh. 9, 400–406.

ČERNÝ, P. and RIVA DI SANSEVERINO, L. (1972): Comments on crystal chemistry of titanite. N. Jb. Mineral. Mh., 97–103.

COOMBS, D.S., NAKAMURA, Y. and VUAGNAT, M. (1976): Pumpellyite-actinolite facies schists of the Taveyanne formation near Loèche, Valais, Switzerland. J. Petrol. 17, 440–471.

DEER, W.A., HOWIE, R.A. and ZUSSMANN, J. (1982): Rock-forming minerals 1A (Orthosilicates). Longman, London 1982.

DEL MORO, A., PARDINI, G., QUERCIOLI, C., VILLA, I.M. and CALLEGARI, E. (1985): Rb/Sr and K/Ar chronol-

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[7] With 8.7% of the total iron present as Fe^{3+} (i.e. the same Fe^{2+}/Fe^{3+} ratio as in coexisting pargasite), a regression line with a slope of 2.463 ± 0.626 and an intercept of 0.013 ± 0.020 is obtained for the correlation between $[OH_{Fe^{2+}}]$ and Fe^{2+} ($r_{cor} = 0.793$).

ogy of Adamello granitoids, Southern Alps. Mem. Soc. Geol. It. 26, 285–299.

Exley, R.A. (1980): Microprobe studies of REE-rich accessory minerals: implications for Skye granite petrogenesis and REE mobility in hydrothermal systems. Earth Planet. Sci. Letters 48, 97–110.

Franz, G. and Spear, F.S. (1985): Aluminous titanite (sphene) from the eclogite zone, south-central Tauern window, Austria. Chem. Geol. 50, 33–46.

Gieré, R. (1986): Zirconolite, allanite and hoegbomite in a marble skarn from the Bergell contact aureole: implications for mobility of Ti, Zr and REE. Contrib. Mineral. Petrol. 93, 459–470.

Gieré, R. (1990a): Hydrothermal mobility of Ti, Zr and REE: examples from the Bergell and Adamello contact aureoles (Italy). Terra Nova 2, 60–67.

Gieré, R. (1990b): Quantification of element mobility at a tonalite/dolomite contact (Adamello Massif, Provincia di Trento, Italy). Ph. D. thesis No. 9141, ETH Zürich.

Gieré, R. and Williams, C.T. (1992): REE-bearing minerals in a Ti-rich vein from the Adamello contact aureole (Italy). Contrib. Mineral. Petrol. (in press).

Hansmann, W., Oberli, F. and Steiger, R.H. (1985): U–Pb ages on zircon from the southern Adamello. Mem. Soc. Geol. It. 26, 319–321.

Higgins, J.B. and Ribbe, P.H. (1976): The crystal chemistry and space groups of natural and synthetic titanites. Am. Mineral. 61, 878–888.

Holényi, K. and Annersten, H. (1987): Iron in titanite: a Mössbauer-spectroscopy study. Can. Mineral. 25, 429–433.

Hollabaugh, C.L. and Rosenberg, P.E. (1983): Substitution of Ti for Si in titanite and new end-member cell dimensions for titanite. Am. Mineral. 68, 177–180.

Miller, J.C. and Miller, J.N. (1988): Statistics for analytical chemistry. 2nd edition. Ellis Horwood, Chichester.

Mrázek, Z. and Vrána, S. (1984): Highly aluminian titanite from plagioclase-fluorite pegmatite in skarn at Vlastéjovice, Czechoslovakia. N. Jb. Mineral. Mh. 6, 251–256.

Muir, I.J., Metson, J.B. and Bancroft, G.M. (1984): ^{57}Fe Mössbauer spectra of perovskite and titanite. Can. Mineral. 22, 689–694.

Nakada, S. (1991): Magmatic processes in titanite-bearing dacites, central Andes of Chile and Bolivia. Am. Mineral. 76, 548–560.

Oberti, R., Smith, D.C., Rossi, G. and Caucia, F. (1991): The crystal-chemistry of high-aluminium titanites. Eur. J. Mineral. 3, 777–792.

Pan, Y. and Fleet, M.E. (1992): Mineral chemistry and geochemistry of vanadian silicates in the Hemlo gold deposit, Ontario, Canada. Contrib. Mineral. Petrol. 109, 511–525.

Paterson, B.A., Stephens, W.E. and Herd, D.A. (1989): Zoning in granitoid accessory minerals as revealed by backscattered electron imagery. Mineral. Mag. 53, 55–61.

Pouchou, J.L. and Pichoir, F. (1984): Un nouveau modèle de calcul pour la microanalyse quantitative par spectrométrie de rayons X. Partie I: Application à l'analyse d'échantillons homogènes. Rech. Aérosp 1984-3, 167–192.

Ribbe, P.H. (1980): Titanite. In: Ribbe, P.H. (ed.): Reviews in Mineralogy, Orthosilicates, vol. 5, 137–154. Mineral. Soc. Am., Washington.

Sahama, T.G. (1946): On the chemistry of the mineral titanite. Bull. Comm. Geol. Finlande. 138, 88–120.

Smith, D.C. (1977): Aluminium bearing sphene in eclogites from Sunnmøre (Norway). Geolognytt 10, 32–33.

Smith, D.C. (1981): The pressure and temperature dependence of Al-solubility in sphene in the system Ti–Al–Ca–Si–O–F. Progr. Exp. Petrol. N.E.R.C. Publ. Ser. D-18, 193–197.

Tulloch, A.J. (1979): Secondary Ca–Al silicates as low-grade alteration products of granitoid biotite. Contrib. Mineral. Petrol. 69, 105–117.

Ulmer, P., Callegari, E. and Sonderegger, U.C. (1985): Genesis of the mafic and ultramafic rocks and their genetical relations to the tonalitic trondhjemitic granitoids of the southern part of the Adamello batholith (Northern Italy). Mem. Soc. Geol. It. 26, 171–222.

Whittaker, E.J.W. and Muntus, R. (1970): Ionic radii for use in geochemistry. Geochim. Cosmochim. Acta 34, 945–956.

Zabavnikova, I.I. (1957): Diadochic substitutions in sphene. Geochemistry 3, 271–278.

Zachariasen, W.H. (1930): The crystal structure of titanite. Z. Krist. Abt. A. 73, 7–16.

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