

The crystal chemistry and space groups of natural and synthetic titanites

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Abstract

The chemical substitutions of primary importance in natural titanites are $(\text{Al,Fe})^{3+} + (\text{F,OH})^{-} \rightleftharpoons \text{Ti}^{4+} + \text{O}^{2-}$, where total Al + Fe is not greater than 30 mole percent, and Al is usually predominant. Electron microprobe analyses and bond strength considerations suggest that Al and Fe occupy octahedral sites in natural titanites, whereas ubiquitous rare earths substitute for Ca.

The formation of out-of-step linear domains parallel to [100] (the octahedral chain direction) is favored by substitutions of Al + Fe for Ti. Pure CaTiOSiO_4 is primitive ($P2_1/a$), with weak but sharp $k + l$ odd reflections. Increasing Al + Fe substitution increases the frequency of domains and the $k + l$ odd reflections become diffuse, eventually disappearing as the average structure attains space group $A2/a$.

The lattice parameters of titanites vary directly with the effective octahedral cation radius. As in zircon, partial metamictization of some titanites causes increases in unit-cell dimensions and decreases in density, possibly accompanied by the inclusion of water in the recoil-damaged structure.

Introduction

The purpose of this investigation of titanite (or "sphene," CaTiOSiO_4) is to evaluate previous chemical analyses with regard to stoichiometry and charge balance, to present new data obtained by electron and ion probe microanalysis, and to determine the relations between the cell parameters and the chemical substitutions of primary importance in natural titanites: $(\text{Fe,Al})^{3+} + (\text{F,OH})^{-} \rightleftharpoons \text{Ti}^{4+} + \text{O}^{2-}$. It is demonstrated herein that the primitive space group $P2_1/a$ is observed only in synthetic or chemically "clean" natural titanites (< 3-4 mole percent substituents for Ti), whereas those with > 4 mole percent (Al+Fe) have diffuse reflections $k + l$ odd which become unobservable above ~20 mole percent substituents (space group $A2/a$). In addition, information on some of the rare earth elements and the effects of metamictization on density, lattice parameters, and characteristic X-ray intensity yield under electron bombardment are reported for selected specimens.

The first significant crystal chemical observations of titanite were made by Zachariasen (1930), who found that it was an orthosilicate with Ti in octahe-

dral coordination and Ca in an irregular seven- to nine-coordinated polyhedron. He explained chemical substituents as isomorphous replacements in a structure with general formula $ABXS\text{SiO}_4$, where A is a large cation (Ca plus rare earths and Na) of radius 0.67 to 1.35 Å, B is an octahedrally-coordinated cation (Ti plus Al, Fe, etc.) of radius 0.57 to 0.67 Å, and X is O^{2-} , F^{-} , or OH^{-} . Zachariasen concluded that, by partially replacing the underbonded O(1) oxygen (designated X) with F^{-} or OH^{-} , the strength of the bonds which reach this site from the neighboring cations would be more nearly equal to the charge of the average anion occupying the site, in addition to charge-balancing other substitutions. Further structural studies of titanite were not undertaken until 1968, but in the meantime numerous chemical analyses (e.g., Young, 1938; Prince, 1938; Jaffe, 1947) appeared along with some attempts to relate chemistry to physical properties.

Sahama (1946) analyzed seven titanites and concluded that natural specimens are "defect" (non-stoichiometric) structures, since according to his analyses, the amount of F and OH substitution was independent of the substitution of Ca and Ti by cations of other valences (Fig. 1a). Zabavnikova

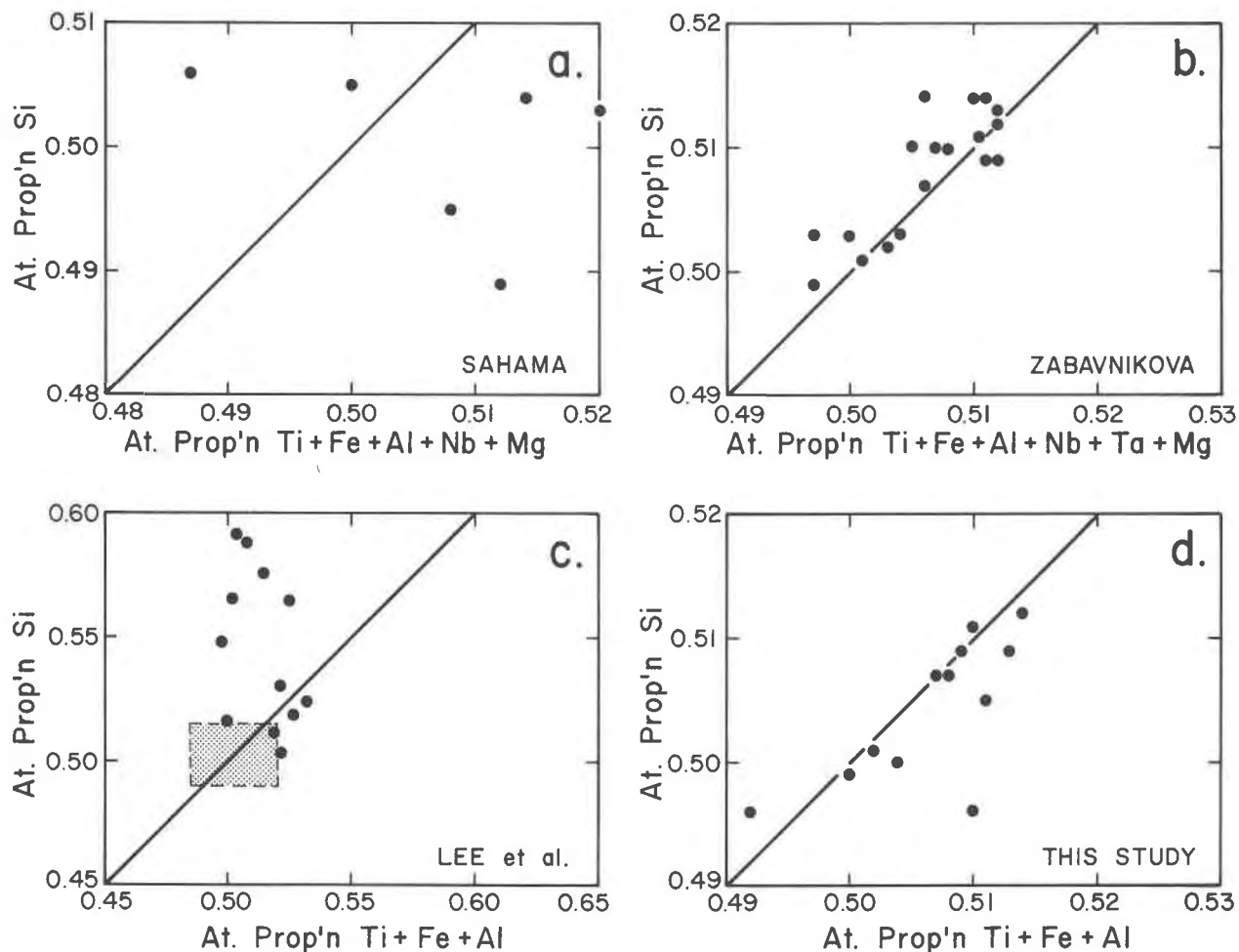


FIG. 1. Plot of atomic proportions Si versus atomic proportions of octahedral cations for titanites analyzed by (a) Sahama (1946), (b) Zabavnikova (1957), (c) Lee *et al.* (1969), (d) this study (Table 1). The data points in a, b, and d all fall within the stippled area of c.

(1957) analyzed 18 specimens, and her analyses show exceptionally good stoichiometric balance between octahedral and tetrahedral cations (Fig. 1b). Lee *et al.* (1969) reported X-ray fluorescence analyses for major elements which differ significantly and distressingly from other titanite analyses appearing in the literature and in this work (Fig. 1c). It is small wonder, then, that chemistry and the cell parameters and optical properties measured on these titanites do not correlate well with each other.

In 1972 Cerny and Sanseverino determined lattice parameters for the six titanites analyzed by Sahama (1946), in addition to the specimen used in the structure refinement by Mongiorgi and Sanseverino (1968), and an annealed metamict titanite previously examined by Cerny and Povondra (1970). They plotted cell dimensions of four specimens versus the sum (Fe+Mg+Al) which presumably substituted for

Ti in the octahedral site. Apparently they did not recognize that the substitution of Fe for Ti should have an effect on lattice parameters opposite to that of Al substituting for Ti, because the effective ionic radius of Fe^{3+} is greater than that of Ti, and the radius of Al is less. They also assigned significant amounts of Al to the tetrahedral (Si) site in certain samples. Their data will be discussed later.

Although there is abundant information on titanite, most work does not successfully correlate physical properties with chemical data. Attempts to correlate optical properties with chemistry have been frustrated because of the complex substituent profile of natural titanites, especially at the minor and trace element level. Similarly, density varies only slightly because only minor element substitution is involved, and in any case the most common substitution is Al (at. wt. 27) + Fe (at. wt. 56) for Ti (at. wt. 48). Part of

the observed density variation is undoubtedly related to metamictization, which may be accompanied by incorporation of water into the recoil-damaged structure as in zircon (Grünenfelder *et al.*, 1964).

The present work has concentrated on obtaining quantitative microprobe analyses of the major elements, Ca, Ti, Si, Fe, Al, and F, as well as Ce, the most abundant of the rare earths. Precise lattice parameters have been determined for most specimens, and using X-ray precession methods, the class of reflections $k + l$ odd were found to vary from sharp to diffuse to absent with increasing substitution of Al + Fe for Ti.

Experimental procedures

Electron microprobe analyses

The titanites were analyzed by conventional methods for Ca, Ce, Ti, Al, Fe, and F with an ARL microprobe, using the EMPADR VII computer program (Rucklidge and Gasparrini, 1969) for data reduction. Na and Mg were not detected at the 0.05 weight percent level in any of the specimens; Ta was not detected, but specimen 12 contained ~0.7 weight percent Nb.

Ion microprobe mass analysis

The same polished samples analyzed with the electron probe were examined using an Applied Research Laboratories ion microprobe mass analyzer (IMMA) (Andersen and Hinthorne, 1972, 1973) at Hasler Research Center, Goleta, California.¹ The sample surfaces were bombarded with a negatively-charged primary beam of monatomic oxygen ($^{16}\text{O}^-$) at 17 kV. In order to determine F concentrations quantitatively, the secondary ion intensities of the $^{19}\text{F}^+$ isotope and the $^{30}\text{Si}^+$ isotope were counted. Silicon was used for intersample normalization since secondary ion intensity for a given element is dependent on matrix factors and sample orientation. It was assumed for these analyses that silicon is stoichiometric in natural titanites (*i.e.*, one out of every eight atoms per formula unit is silicon). Fluorine contents were determined by both electron and ion microprobe techniques. The IMMA results were calculated from the working curve of Hinthorne and Andersen (1975) and correlate linearly with those determined by elec-

tron probe, although the slope is 1.07, rather than 1.00 as expected. This probably indicates a slight systematic bias in one or the other methods, but it is hardly significant at the levels detected (0.0 to 2.3 wt. % F). Qualitative mass spectrum scans were run for selected samples to determine ratios of rare earths, lead isotopes, and uranium and thorium. In particular, the La, Pr, Nd, Sm, and Eu to Ce ratios were measured and corrected for natural isotopic abundances in order to arrive at a quantitative estimate of total La-, Pr-, Nd-, Sm- and Eu-oxides relative to Ce, which was quantitatively determined by electron microprobe. Further rare earth, lead and U/Th isotope data are forthcoming in a detailed ion-probe study in cooperation with J. R. Hinthorne.

Lattice parameters

Unit cell parameters of nine specimens were obtained from X-ray powder patterns using BaF_2 , annealed at 800°C ($a = 6.1971 \pm 0.002 \text{ \AA}$; D. A. Hewitt, personal communication) as an internal standard. The patterns were recorded at $0.5^\circ 2\theta/\text{min./inch}$, using monochromatized $\text{CuK}\alpha$ radiation. Two oscillations were measured, and peaks were indexed with reference to the structure refinement of Speer and Gibbs (1976). Unit weights were assigned to all reflections and the lattice parameters were refined using the least-squares program of Appleman and Evans (1973).

Density measurements

Densities, corrected for temperature, were determined on several hand-picked samples, using a Ber-man balance with toluene as the buoyant medium.

Discussion of results

The results of electron microprobe analyses and lattice parameter measurements are listed in Table I for twelve natural titanites (selected from a larger suite of 40 specimens) that exhibit a wide range of substitution of Fe + Al for Ti.

Site assignments of substituents

Understanding the crystal chemistry of titanite requires that the elemental substituents be correctly assigned to their respective coordination polyhedra in the structure. The average unit cell of an *A*-centered titanite contains six nonequivalent crystallographic sites, three of which are occupied by anions and three by cations. The O(2) and O(3) sites [and O(4) and O(5) in primitive titanites] are occupied by oxygen atoms bonded to the tetrahedral cation. The O(1) site

¹ Dr. J. R. Hinthorne and Mr. Ray Conrad are acknowledged for their generous contributions of time and effort in this part of the investigation, which is continuing and will be reported elsewhere.

is located at the shared octahedral vertex and is occupied primarily by oxygen but may contain small amounts of F and/or OH (see below). Fluorine is common and although OH was not determined quantitatively, ion microprobe mass scans indicated the presence of H in all specimens (*cf.* Beran, 1970).

The tetrahedral site in natural titanites is occupied by Si, although several workers have assigned small amounts of Al to the tetrahedral site to make up apparent deficiencies of Si in their analyses. In this work, however, all Al has been assigned to the octahedral site, and it has been assumed that the tetrahedral site is occupied only by Si. These assumptions may be justified in two ways: (1) by examining the effect of substituting a trivalent cation in the titanite structure in terms of Pauling's (1960) electrostatic valence rule, and (2) by observing that there is essential stoichiometric balance between tetrahedral Si and the sum of the presumed octahedral cations—Ti, Al, Fe, Ta, and Nb.

Pauling's second rule states that in a stable ionic structure the valence of each anion, with changed sign, is exactly or nearly equal to the sum of the strengths of the electrostatic bonds to it from the adjacent cations. In the titanite structure with composition CaTiOSiO_4 , the average bond strengths at the O(2) and O(3) sites are slightly greater than 2.00 while the O(1) site is strongly underbonded. This local electrostatic imbalance can be improved by substituting trivalent cations in octahedral sites along with the substitution of a monovalent anion (F or OH) in the O(1) site to retain overall charge balance. Figure 2 illustrates the changes in Pauling bond strengths and formal charges resulting from the coupled substitution $M^{3+} + (\text{F,OH})^{1-} \rightleftharpoons \text{Ti}^{4+} + \text{O}^{2-}$. The average bond strength to the O(2) and O(3) sites reaches a value of 2.00 at almost the same composition at which the charge at the O(1) site is equal to the bond strength received at the O(1) site. Taylor and Brown (1976) have also rationalized the coupled substitution in terms of Brown and Shannon (1973) bond strengths at the O(1) site. Both models lead to the conclusion that monovalent anions are most likely to substitute for oxygen in O(1) and that concomitantly trivalent cations substitute for Ti in octahedral coordination.

Natural titanites have been reported to incorporate a number of other metals in their structures including Nb, Ta, Cr, V, Mn, Mg, and Sn (Sahama, 1946; Clark, 1974), and it is assumed that these cations substitute for Ti in the octahedral site. Although many previous wet-chemical analyses report divalent

iron in natural titanites, there is no independent analytical evidence for it. In this work all Fe has been assumed to be trivalent and located in the octahedral site; a Mössbauer study of an Fe-rich titanite is clearly desirable.

In order to compare the analyses of previous workers (Sahama, 1946; Zabavnikova, 1957; Lee *et al.*, 1969) with those of this work and to determine the effect of assigning all Fe and Al to the octahedral site, a plot of atomic proportions of Si versus atomic proportions of the sum of the octahedral cations is presented in Figure 1. Assuming that all tetrahedral sites are filled with Si and that all Fe + Al is octahedrally coordinated, the data points should fall on the 45° line on each graph. The proximity of the data points to the 45° line for the analyses of Zabavnikova (1957) and this study suggests that assigning Ti + Fe + Al to the octahedral site is reasonable with respect to octahedral-tetrahedral stoichiometry, and that within the experimental errors of chemical analysis (even at the level of $\pm 2\%$ of the amount present of any element) there is no need to assign Al to the tetrahedral site. In light of the plots for Zabavnikova (1957) and this work, the spread of data points of Sahama's (1946) analyses seems to indicate less accurate determination of some of the metals, but the analyses of Lee *et al.* show an extremely large deviation and must be regarded as unreliable.

Stoichiometric charge balances have been calculated successfully for other orthosilicates (*cf.* Jones *et al.*, 1969), but for titanite the amounts of $(\text{OH})^-$ substituting for O^{2-} , entered in Table 1 as OH_{calc} , are in all cases less than 0.7 weight percent. The significance of these numbers is highly questionable for the following reasons: (1) not all the possible cation substituents were analyzed for (*e.g.*, the heavy rare earths) and (2) the cumulative estimated standard errors in microprobe analyses for Ca, Ti, and Si may be as high as 1 to 2 percent of the amount present, with larger relative errors for the more minor elements.

The large seven-coordinated cation site in the titanite structure is occupied primarily by Ca; however, previous chemical analyses and the ion microprobe analysis carried out during this study indicated that a number of trace elements, particularly rare earths, probably occupy this site. As mentioned in our discussions of the IMMA method, we determined the ratios of certain rare earth isotopes to the ^{140}Ce isotope by measuring peak heights on mass spectral scans. At this stage we have reported only La, Pr, Nd, Sm, and Eu as REE in Table 1; others are present,

TABLE 1. Chemical analyses and lattice parameters of titanites

Specimen No.	1	2	3	4	5	6	7
Original No.*	USNM R26731	BMNH 1966,501	BMNH 1968,124	USNM B20360	VPI&SU-27	USGS 04-065	S-2
Locality	Goschener Alp. Switz.	San Quintin, Baja Calif., Mexico	Okehampton, Devon, Eng.	Piedmont, Italy	Capahalina, Brazil	Hemet Quad., California	Yl18j1rvi, Finland
WEIGHT PERCENT OXIDES							
SiO ₂	30.61	30.70	30.34	29.99	30.44	29.82	30.09
CaO	28.57	28.75	28.60	28.40	28.41	27.65	27.77
Ce ₂ O ₃	n.d.**	n.d.	n.d.	n.d.	n.d.	0.80	0.18
RE ₂ O ₃ ***	n.d.	n.d.	n.d.	n.d.	n.d.	1.54	0.31
TiO ₂	39.43	38.80	38.59	38.10	37.84	37.45	36.97
Fe ₂ O ₃	1.14	0.37	0.42	0.34	0.80	1.02	1.01
Al ₂ O ₃	0.09	1.01	1.16	1.19	1.17	1.46	1.34
F (OH _{calc})	0.00 (0.3)	0.07 (0.3)	0.28 (0.2)	0.13 (0.4)	0.10 (0.5)	0.31 (0.2)	0.23 (0.4)
-(F=0)	0.00	0.03	0.12	0.05	0.04	0.13	0.10
Total (excluding OH _{calc})	99.84	99.67	99.27	98.10	98.72	99.92	97.80
ATOMS PER UNIT CELL NORMALIZED TO ONE SILICON							
Si	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ca	1.000	1.003	1.010	1.004	1.000	0.994	0.989
REE	n.d.	n.d.	n.d.	n.d.	n.d.	0.027	0.006
Ti	0.969	0.950	0.956	0.955	0.935	0.944	0.924
Fe	0.028	0.009	0.010	0.009	0.020	0.026	0.025
Al	0.004	0.039	0.045	0.047	0.045	0.058	0.052
Ti+Fe+Al	1.001	0.998	1.011	1.011	1.000	1.028	1.001
F	0.000	0.007	0.029	0.014	0.010	0.033	0.024
Effective Octa- hedral Radius (Å)	0.606	0.602	0.602	0.602	0.602	0.602	0.602
LATTICE PARAMETERS							
a (Å)	7.062(3)	not determined		7.061(1)	7.061(2)	7.053(1)	7.057(2)
b (Å)	8.708(4)			8.708(1)	8.706(3)	8.702(1)	8.705(3)
c (Å)	6.557(2)			6.553(1)	6.555(2)	6.555(1)	6.555(1)
β (°)	113.78(2)			113.86(1)	113.93(3)	113.83(1)	113.89(2)
V (Å ³)	369.0(2)			368.5(1)	368.3(1)	367.8(1)	368.2(1)

* USNM = U.S. National Museum; BMNH = British Museum of Natural History; VPI&SU = VPI&SU Collections; USGS = United States Geological Survey; S-2 = Sahama (1946) Specimen No. 2.

** Detected on ion microprobe but only present at background level (<0.01%) on electron microprobe.

*** Calculated from IMMA spectral scans, using ¹³⁹La [natural abundance, 99.9%], ¹⁴¹Pr [100%], ¹⁴³Nd [12.2%], ¹⁴⁷Sm [15.0%], ¹⁵¹Eu [47.8%] ratioed to ¹⁴⁰Ce [88.5%]. The ratios were corrected for isotopic abundances, and weight percent RE₂O₃ was determined in proportion to weight percent Ce₂O₃ as measured by electron microprobe.

but their primary peaks are overlapped by LaO, CeO, PrO, NdO, SmO, EuO, and other monoxide peaks.

Stoichiometry of synthetic CaTiOSiO₄

Analysis of a CaTiOSiO₄ crystal synthesized by D. A. Hewitt in this laboratory and used by Speer and Gibbs (1976) in their crystal structure analysis, shows a slight deficiency (~3% of the amount present) with respect to Ca, when the formula is normalized to five oxygens. This probably resulted from the glass being slightly off stoichiometric composition due to the presence of discrete grains of CaSiO₃ found by microprobe analysis in this specimen.

Lattice parameters

The lattice parameter ranges observed for natural titanites are: $a = 7.039\text{--}7.088$ Å; $b = 8.643\text{--}8.740$ Å; $c = 6.527\text{--}6.584$ Å; $\beta = 113.74\text{--}114.15^\circ$ (Table 1 and Cerny and Sanseverino, 1972). These ranges are con-

sistent with the small amounts of chemical substitution observed. Since the major chemical substitutions in natural titanites occur in the octahedral site, changes in lattice parameters are directly related to changes in the average size of the cation occupying this site. The M-O bonds associated with this site are aligned more or less parallel to the three crystallographic axes, so that changes in the effective size of the octahedral cation should be discernible more or less equally along all three crystallographic axes. In order to observe the expected relationship between chemistry and lattice parameters, some function of the chemistry of the octahedral site is required to plot versus lattice parameters. Cerny and Sanseverino (1972) plotted the sum of the atomic proportions of Fe + Al + Mg versus lattice parameters, and even though substituting Fe and Al for Ti has opposite effects on the size of the octahedron, they obtained a graph which changed in the expected direction by

TABLE 1, continued

Specimen No.	8	9	10	11	11 (heated) [†]	12	12 (heated) [†]
Original No.	VPI&SU-44	VPI&SU-43	VPI&SU-38	VPI&SU-42	VPI&SU-42	VPI&SU-41	VPI&SU-41
Locality	Cape North, Cape Breton Is., N.S.	Grisons, Switz.	Cameron Brook Pluton Cape Breton Is., N.S.	Renfrew Co. Canada	Renfrew Co. Canada	Pierceville New York	Pierceville New York
WEIGHT PERCENT OXIDES							
SiO ₂	30.44	30.70	29.99	29.83	30.56	30.75	30.47
CaO	27.96	28.54	27.48	27.01	27.68	27.96	28.04
Ce ₂ O ₃	n.d.	n.d.	0.77	0.28	0.28	0.48	0.48
RE ₂ O ₃	n.d.	n.d.	0.91	0.36	0.36	0.74	0.74
TiO ₂	36.79	36.77	36.19	30.79	31.92	30.39	30.76
Fe ₂ O ₃	0.59	0.48	1.18	2.76	2.69	2.92	2.83
Al ₂ O ₃	2.07	2.41	1.22	3.67	3.85	4.93	5.46
F ^(OH_{calc})	0.46 (0.4)	0.18 (0.7)	0.37 (0.3)	1.50 (0.4)	1.50 (0.4)	2.27 (0.1)	2.27 (0.3)
-(F=0)	0.19	0.08	0.16	0.63	0.63	0.95	0.95
Total (excluding OH _{calc})	98.12	99.00	98.59	95.56	98.21	100.49	101.10
ATOMS PER UNIT CELL NORMALIZED TO ONE SILICON							
Si	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ca	0.984	0.996	0.982	0.970	0.970	0.974	0.986
REE	n.d.	n.d.	0.020	0.008	0.008	0.015	0.015
Ti	0.909	0.901	0.907	0.776	0.785	0.743	0.759
Fe	0.015	0.012	0.045	0.069	0.066	0.072	0.070
Al	0.080	0.092	0.048	0.145	0.149	0.189	0.211
Ti+Fe+Al	1.004	1.005	1.000	0.990	1.000	1.004	1.040
F	0.048	0.019	0.039	0.149	0.146	0.236	0.236
Nb						0.015	0.015
Effective Octahedral Radius (Å)	0.600	0.598	0.603	0.597	0.596	0.593	0.592
LATTICE PARAMETERS							
a(Å)	not determined		7.060(2)	7.088(2)	7.052(1)	7.085(4)	7.055(8)
b(Å)			8.724(2)	8.740(2)	8.690(2)	8.714(5)	8.680(10)
c(Å)			6.565(2)	6.584(2)	6.542(1)	6.572(3)	6.556(7)
β(°)			113.80(2)	113.95(3)	113.98(1)	114.15(5)	113.93(9)
V(Å ³)			369.94(1)	372.7(1)	366.3(1)	370.2(2)	367.0(5)

[†] Specimens heated under vacuum at 1100°C for three hours.

using data only from Fe-poor titanites. In this study an effective octahedral cation radius (abbreviated EO CR) has been calculated using the following equations:

$$\text{EOCR} = 0.605 - (0.075 \text{ Al/Si}) + (0.04 \text{ Fe/Si})$$

where 0.605 is the radius of quadrivalent Ti in six-fold coordination, Al/Si and Fe/Si are the atomic proportions of Al and Fe normalized to one silicon, and 0.075 and 0.04 are the respective differences between the radii of Al and Ti and Fe and Ti (effective ionic radii from Shannon and Prewitt, 1969, 1970). If more Fe than Al is present, EO CR is greater than 0.605 since Fe³⁺ is larger than Ti⁴⁺, whereas if more Al is present, EO CR is smaller than 0.605. Effective radii of octahedral cations have been calculated for the specimens listed in Table 1 and those of Cerny and Sanseverino (1972) for which lattice parameters have been reported. They range from 0.587 to 0.606 Å. Figure 3 illustrates the relation between the chemistry of the octahedral site and lattice parameters of our specimens, Hewitt's synthetic titanite, and the

eight specimens of Cerny and Sanseverino. Several factors probably affect the scatter in data points, including the assumption that only Fe, Al, and Ti are present in the octahedral site and that minor changes in chemistry of the calcium site have no effect on lattice parameters.

As a matter of passing interest, the *b* cell dimension reported by Takenouchi (1971) is in disagreement with all other values of *b* for synthetic titanites. This aberrant value can be traced to the misindexing of the 140 peak as 21 $\bar{3}$, 13 $\bar{3}$ as $\bar{4}02$, and 251 as $\bar{4}04$ (J. A. Speer, personal communication).

Metamict titanites

During the initial plot of lattice parameters versus EO CR it was noted that two specimens (nos. 11 and 12) had lattice parameters inconsistent with the other specimens. The glassy appearance of specimen 11 and the broad diffraction peaks in its powder pattern suggested that it might be partially metamict. Confirmation of its metamict character was obtained by ion microprobe analysis which showed significant

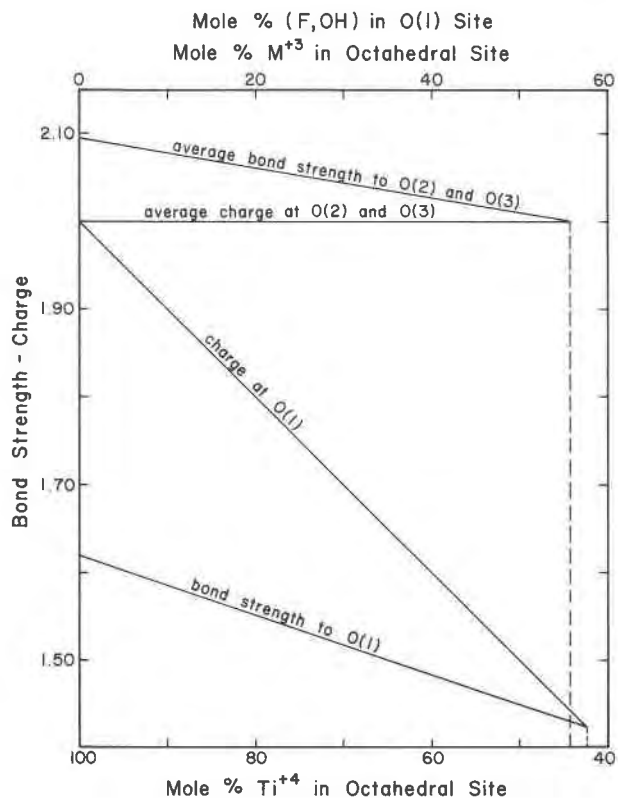


FIG. 2. Change in Pauling bond strength and formal charge at the O(1), O(2), and O(3) anion sites with substitution of $M^{3+} + (F,OH)^-$ for $Ti^{4+} + O^{2-}$.

Th^{232} and U^{238} , in addition to radiogenic lead. Because Holland and Gottfried (1955) had found that density decreased while the cell dimensions increased with increasing metamictization of zircon, and because Cerny and Sanseverino (1972) had reported a completely metamict titanite in which the structure was restored after heating for three hours at $800^\circ C$, we decided to anneal those of our specimens which had discrepant lattice parameters. Specimens 11 and 12 were heated at $1100^\circ C$ for three hours in evacuated silica-glass tubes, and upon cooling were reanalyzed with the electron microprobe. Lattice parameters of the heated specimens were redetermined (Table 1). Cell edges of both specimens decreased and are represented on Figure 3 by the data points connected by nearly vertical dashed lines. Several other specimens were also heated under identical conditions: specimen 10 registered only slight changes in lattice parameters, but specimens 1 and 5 showed none.

Another interesting change which was noted after

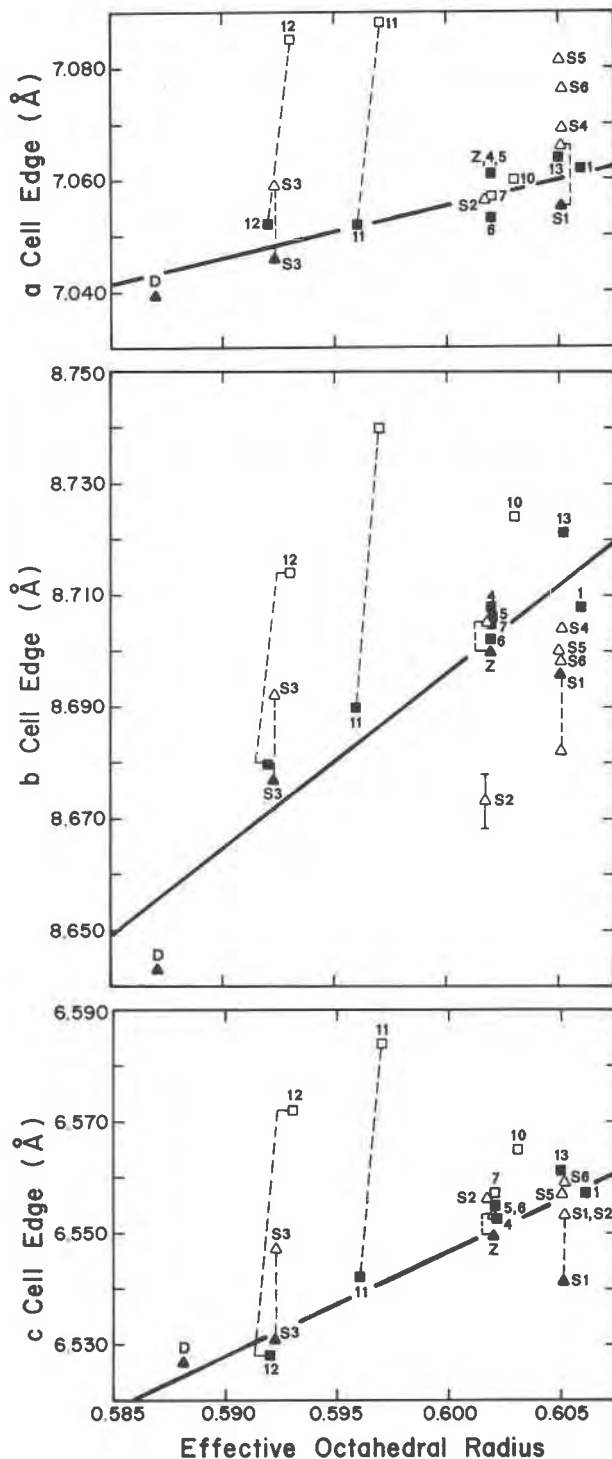


FIG. 3. Variation of effective octahedral cation radius with *a*, *b*, and *c* cell edge. Triangles represent data from Cerny and Sanseverino (1972), squares are data from this work. Open symbols indicate unheated specimens and filled symbols represent heated specimens. The regression line was calculated using only data from heated specimens.

heating specimen 11 is related to the microprobe analyses. Specimen 11 had consistently yielded low oxide weight percent totals (~95%) before heating; however, after heating the weight percent of each element analyzed increased by 2 to 5 percent of the amount present, yielding a total of ~98 percent. In order to be sure that this effect was not due to chemical zonation or other properties peculiar to one grain, several grains of unheated and heated sample were analyzed side by side and all heated grains showed the same increase in elemental percentages with respect to the unheated samples. This phenomenon at first suggested to us that density differences in the metamict and recrystallized titanite might have an effect on the characteristic X-ray intensity yield of the constituent elements; the recrystallized grains yielded higher X-ray intensities for all elements checked. But of course it is possible that the relatively higher X-ray yields simply resulted from a loss of water upon heating. The densities of the unheated and heated sample 12 were determined with the Berman balance and were found to be 3.510 g/cm³ and 3.585 g/cm³, respectively. This 2.1 percent increase in density upon heating agrees well with the observed 1.7 percent decrease in cell volume. Although specimen 12 did not show any change in composition upon heating, possibly because it did not contain water, the decrease in lattice parameters is consistent with the observed increase in density.

Effects of chemical substitution on space groups of natural and synthetic titanites

Modern refinements of the crystal structure of titanite are reported by Mongiorgi and Sanseverino

(1968) for a natural *A2/a* titanite and by Speer and Gibbs (1976) and Taylor and Brown (1976) for synthetic CaTiOSiO₄, which has space group *P2₁/a* at room temperature but inverts by a displacive transformation to *A2/a* at 220 ± 20°C. The structure has been described as infinite parallel chains of corner-sharing TiO₆ octahedra cross-linked by SiO₄ tetrahedra. Two oxygens of each SiO₄ group are shared by adjacent octahedra in a chain, and the other two tetrahedral oxygens are shared with octahedra in adjacent chains. Thus each tetrahedron cross-links with three different octahedral chains. Large cavities in this framework of corner-sharing octahedra and tetrahedra are filled with calcium which is coordinated by seven to nine oxygen atoms (*cf.* Taylor and Brown, 1976, Fig. 3).

Robbins (1968) synthesized CaTiOSiO₄ and its germanium analog, CaTiOGeO₄, by crystallizing melts of high-purity oxides on an iridium wire loop in a platinum crucible. Examination of these substances by the X-ray precession method showed that both crystallized in space group *P2₁/a* instead of *A2/a*, the presumed space group for natural titanite. Robbins postulated that his synthetic CaTiOSiO₄ might contain "two symmetrically inequivalent formula units" related by a face-centering translation, and that if a disorder amounting to a random succession of the two types of units were introduced, the resulting average structure would be face-centered. He also predicted that natural titanites with low water and halide content would be primitive.

Recently Speer and Gibbs (1976) refined the structure of CaTiOSiO₄ crystallized from high-purity oxides at 1150°C for 5 weeks in a platinum crucible.

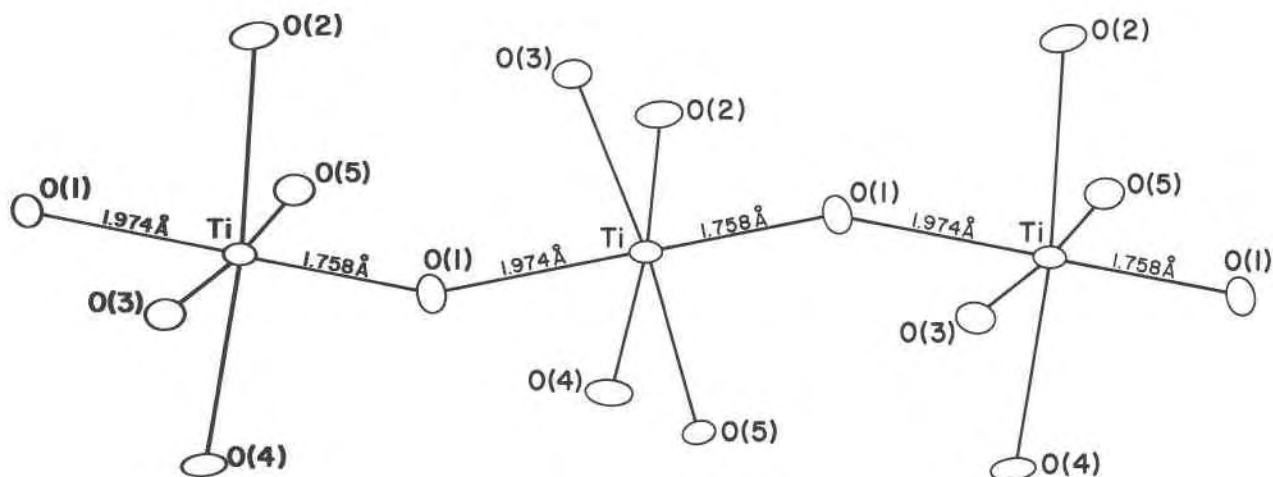


FIG. 4. A portion of the octahedral chain in *P2₁/a* titanite showing alternating long and short Ti-O(1) bonds. Courtesy of J. A. Speer.

TABLE 2. $k + l$ odd reflection data for titanites containing Al + Fe in octahedral coordination

Specimen No*	Mole percent		$k + l$ odd
	Fe	Al	
13	0.0	0.0	sharp
1	2.8	0.3	sharp
5	2.0	4.5	diffuse
6	2.5	5.6	diffuse
34	3.6	2.8	diffuse
35	3.6	2.5	diffuse
11	7.1	18.8	absent
12	7.0	14.6	absent

*Specimen numbers are taken from Table 1, except for 13 (Speer and Gibbs, 1976) and 34 and 35 which are from Carson Pass, California, and whose analyses are not reported in this study.

Crystals of this material exhibit weak "difference" reflections ($k + l$ odd) consistent with space group $P2_1/a$, a subgroup of $A2/a$. Their refinement indicated that the primary difference between the primitive synthetic material and A -centered titanites is the position of the titanium atom in the TiO_6 octahedron. In the natural titanite refined by Mongiorgi and Sanseverino (1968) the titanium is located midway between two O(1) atoms, whereas in the primitive synthetic material, the titanium atom is displaced along the octahedral chain direction (Fig. 4) giving alternate short (1.766 Å) and long (1.974 Å) Ti-O(1) bond lengths. In one chain, the long-short alternation is in the [100] direction, while in adjacent parallel chains related by centers of symmetry the displacement is in the $[\bar{1}00]$ direction (*cf.* Fig. 4 in Taylor and Brown, 1976).

Linear domains in titanite

J. A. Speer (personal communication, 1973) examined a natural titanite from Capahalina, Brazil and noted diffuse streaks in place of the $k + l$ odd reflections which distinguish the primitive from the centered lattice type, and as a result Speer and Gibbs (1976) modified Robbins (1968) domain theory for natural titanites, proposing that natural titanites which exhibit diffuse or no reflections of the type $k + l$ odd consist of domains of the $P2_1/a$ titanite related by a half-turn parallel to b . They also suggested that substitution of Al and Fe for Ti in natural titanites might favor domain formation. An octahedral site containing Al or Fe might serve as a boundary so that linear domains of octahedra on either side will contain Ti atoms displaced in opposite directions along the chain, and charge-balancing monovalent anions,

concomitantly substituting for oxygen at the O(1) site, may facilitate domain formation (Taylor and Brown, 1976). If a large number of these oppositely oriented domains were present in an octahedral chain, the positional parameters of the octahedral cations would be "averaged" by X-rays, and the octahedral chain would appear to contain (Ti + Al + Fe) atoms equidistant from O(1) atoms. If most of the octahedral chains in the structure were similarly affected, the lattice would appear centered ($A2/a$). Substitution of smaller amounts of (Al + Fe) for Ti might result in the formation of fewer domains, and this partial linear disorder would be evidenced by planes of diffusely scattered X-ray intensity perpendicular to the octahedral chains. These planes appear as diffuse streaks when viewed edge on in an

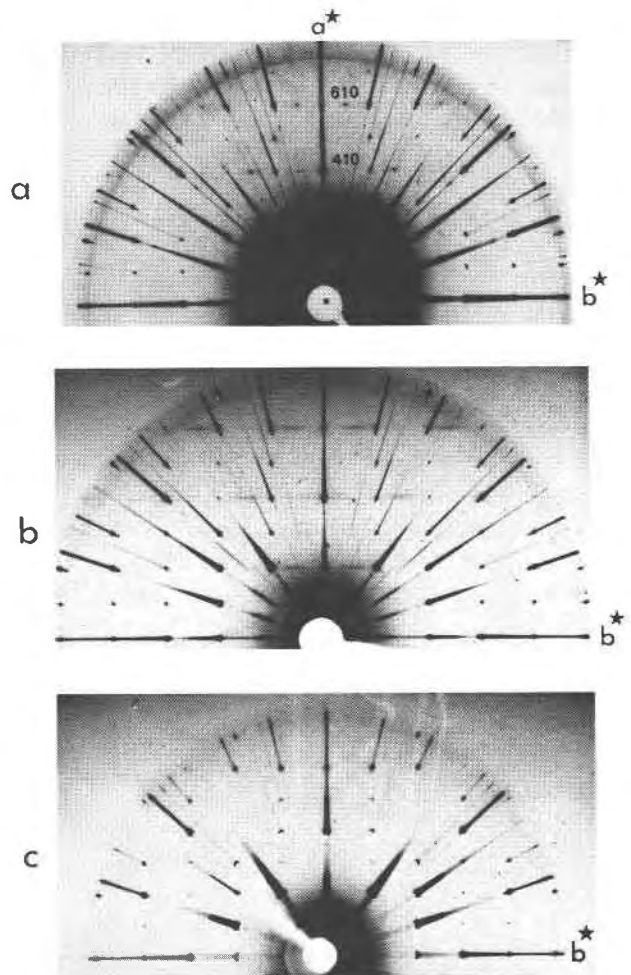


FIG. 5. Zero-level a^*b^* precession photographs of: a. Specimen 1 with sharp $k + l$ odd reflections (610, 410) indicating a primitive lattice (space group $P2_1/a$). b. Specimen 5 showing diffuse $k + l$ odd reflections. c. Specimen 11 showing no $k + l$ odd reflections or diffuse streaks indicating a centered lattice (space group $A2/a$).

a^*b^* precession photograph (Fig. 5b) but are more dramatically imaged by electron diffraction (Fig. 6).

Concentration of chemical substituents related to space group

In order to confirm the relationship between space group and chemistry, eight titanites were chosen from a group of thirty analyzed specimens for study by the X-ray precession method. They represent the observed range of chemical compositions with respect to Al and Fe substitution for Ti. (Table 2). Figure 5a is an a^*b^* zero-level precession photograph of a natural titanite from Göschener Alp, Switzerland, which contains 2.8 mole percent Fe and 0.3 mole percent Al. Reflections of the type $k + l$ odd are present and are represented on the photograph by the 410 and 610 reflections. Very faint diffuse streaks are associated with each $k + l$ odd reflection indicating the presence of at least some domain texture. Figure 5b is a similar photograph of a titanite from Capahalina, Brazil, which contains 2.0 mole percent Fe and 4.5 mole percent Al. The photograph exhibits only diffuse

streaks in place of $k + l$ odd reflections and indicates a higher frequency of domains than the previous specimen. Electron diffraction patterns of the Capahalina titanite (Fig. 6) emphasize the continuous nature of the streaks which, as has been previously mentioned, are actually planes of diffuse X-ray intensity viewed edge on. There are unexplained nodes of intensity observable in these planes. Due to the weak intensity of the streaks it was not possible to image the linear domains. The precession photograph in Figure 5c of a titanite from Pierceville, New York, containing 7.1 mole percent Fe and 18.8 mole percent Al, exhibits no $k + l$ odd reflections or diffuse streaks. The absence of $k + l$ odd reflection data indicates extensive domain formation and the "average" structure of this titanite appears to have a centered lattice.

Conclusions

The results of these X-ray investigations indicate that natural titanites exhibit reflections consistent with primitive and centered as well as intermediate structures. The space group of both synthetic and

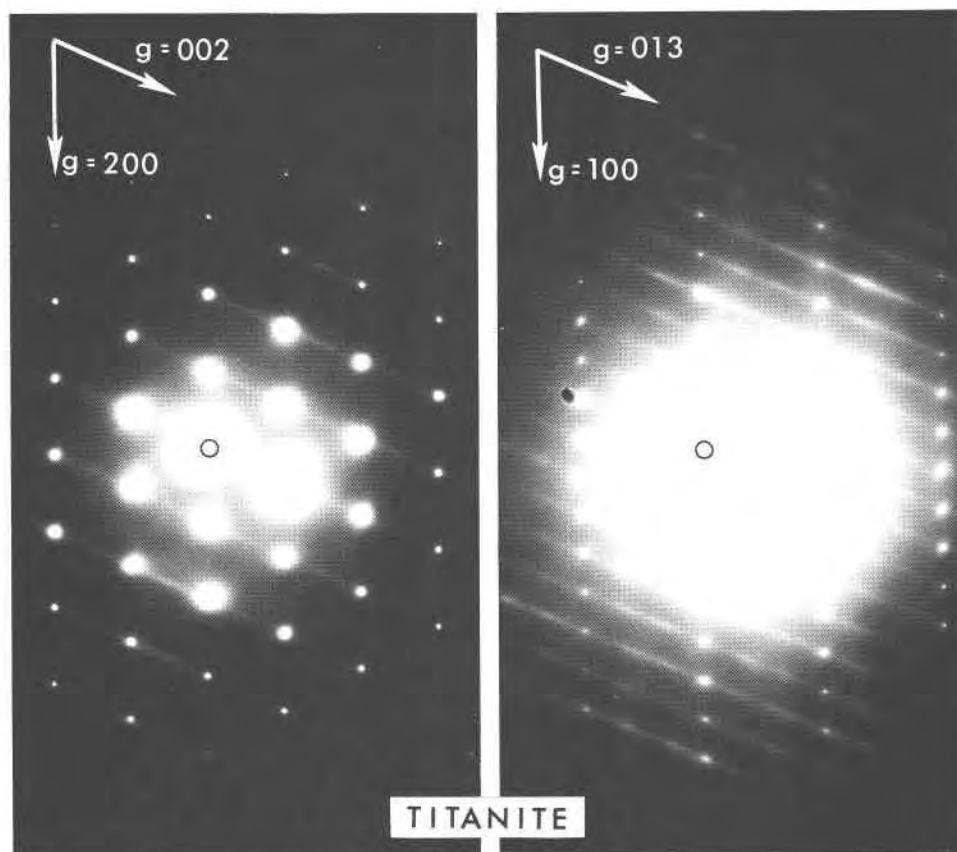


Fig. 6. Electron diffraction patterns of specimen 5 illustrating diffuse planes of intensity normal to [100]. Nodes are present in diffuse streaks between $k + l$ reflections. Courtesy of Miss Florence Lee.

natural titanites at the unit cell scale is $P2_1/a$, but the formation of domains due to chemical substitution in the octahedral chains causes the average structure of most natural titanites to be "disordered" relative to synthetic and nearly pure natural specimens, producing an increasing diffuseness in $k + l$ odd reflections and resulting in an apparent absence of these reflections in the most (Al + Fe)-rich titanites.

Summarizing the earlier portion of this study, it is obvious that the chemical substitutions of primary importance in natural titanites are $(\text{Al,Fe})^{3+} + (\text{F,OH})^- \rightleftharpoons \text{Ti}^{4+} + \text{O}^{2-}$, where Al + Fe is not greater than ~30 mole percent, and Al is usually predominant. Electron microprobe analysis and bond strength considerations suggest that Al occupies the octahedral site in natural titanites, whereas ubiquitous rare earth elements substitute for Ca. Preliminary ion microprobe studies indicate that Pb, U, and Th are present in all but two specimens examined, both of which are from pegmatites.

The lattice parameters of titanites vary directly with the effective octahedral cation radius, except for those specimens in which partial metamictization has caused increases in unit-cell dimensions and decreases in density. Annealing at 1100°C for three hours restores these structures so that their lattice parameters are consistent with nonmetamict titanites.

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