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Zr- and *LREE*-rich titanite from Tre Croci, Vico Volcanic complex (Latium, Italy)

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ABSTRACT

Titanite occurs in the groundmass of a holocrystalline volcanic ejectum collected in the pyroclastic rocks of the Vico Volcanic complex at Tre Croci, near Viterbo, Italy. The host rock is composed of abundant K-feldspar and minor plagioclase, biotite, clinopyroxene and a feldspathoid (sodalite). Titanite is typically associated with zirconolite, biotite and Fe-oxides. It has a medium Al content (Al_2O_3 + Fe_2O_3 = 4–6 wt.%) and contains significant amounts of Zr and *LREE*, with a chondrite-normalised *REE* pattern similar to those of titanites from other alkaline rocks. Titanite has been corroded by fluids probably rich in dissolved F and P during a late alteration stage, with evidence for some remobilization and redistribution of the *REE* and actinide elements.

KEYWORDS: Vico volcanic complex, titanite, chemistry, *REE* patterns, alteration.

Introduction

TITANITE is an accessory mineral which occurs in a wide variety of geological environments. In Latium (Italy), it occurs in syenitic holocrystalline ejecta (Della Ventura *et al.*, 1992) associated with the volcanic and pyroclastic deposits of the Roman comagmatic province (Washington, 1906). Giannetti and Luhr (1983) noted the presence of titanite from a trachytic tuff of the Roccamonfina Volcano (located south of Rome), and Belkin *et al.* (1996) reported some data on titanite from a feldspathoid-bearing xenolith entrained in a trachyte from Ponza Isle (Pontine Islands, south of Rome). Both occurrences are from volcanic complexes belonging to the same volcanic region. However, although a relatively common accessory mineral in these rocks (see also Stoppani and Curti, 1982), the mineral chemistry of titanite from Latium has not been fully studied.

Here we report the occurrence of titanite from the Vico volcanic area (Viterbo province, north of Rome), we characterize its mineral chemistry, and compare this occurrence with other examples in the literature. Titanite is one of a number of minerals from this area which hosts a range of incompatible elements, and this note is a further contribution to the role the accessory minerals can play in describing the behaviour of incompatible elements.

Occurrence

The titanite described here is from a holocrystalline volcanic ejectum (sample FVB1) collected in a pyroclastic level ('ignimbrite A' of Locardi, 1965) of the Vico Volcanic complex near Tre Croci (Viterbo, north of Rome). The rock is a massive, fine-grained alkali syenite composed mainly (>80%) of K-feldspar ($Or_{70}Ab_{30}$) with minor plagioclase (ranging in composition from An_{20} to An_{80}), biotite, augite and sodalite. The accessory phases include magnetite, ilmenite, fluorapatite, titanite, vonsenite and fluorite. Titanite occurs as euhedral, sphenoidal-rhombic, orange-yellowish coloured crystals up to 1 mm in size, and is invariably associated with sodalite and Fe,Ti oxides. It typically has inclusions of alkali-feldspars or plagioclase, zirconolite (essentially Ca,Ti,Zr oxide), baddeleyite (Zr oxide), and an unidentified Th, U, *REE*-silicate mineral (Fig. 1).

Chemical composition

Backscattered electron images (BSE), coupled with energy-dispersive analyses taken with a high-resolution SEM (Philips XL30 SEM-EDAX operated at 25 kV, 30 nA beam current), showed the titanite grains to be relatively homogeneous in composition, although some patchy zoning was observed (Fig. 1) which corresponds to minor variation in the Zr and *REE* concentrations. Wavelength-dispersive microprobe data, using a Cameca SX50 instrument operated at 20 kV accelerating voltage and 20 nA beam current were obtained, of which representative analyses are presented in Table 1, together with data of Belkin *et al.* (1996) for the Ponza titanite, and Giannetti and Luhr (1983) for the Roccamonfina sample.

Despite the fact that all Fe has been calculated as Fe_2O_3, the analytical totals are systematically low, in the range 96.5–98.5% (Table 1), suggesting the presence of water. Therefore, the crystal chemical formulae were normalized to 3 cations, and the OH content (Table 1) calculated following the procedure of Higgins and Ribbe (1976), Oberti *et al.* (1991) and Perseil and Smith (1995), where:

$$OH_{calc} = 10 - (\Sigma_{cat} + F);\ (\Sigma_{cat} = \text{total cation charge})$$

The data of Table 1 show that titanite from Tre Croci contains significant amounts of rare earth elements ($\Sigma[Y_2O_3 + REE_2O_3]$ vary between 1.54 and 3.57 wt.%). Also present in appreciable amounts are Nb (0.31–0.60 wt.% Nb_2O_5), Th (0.21–0.26 wt.% ThO_2) and Mn

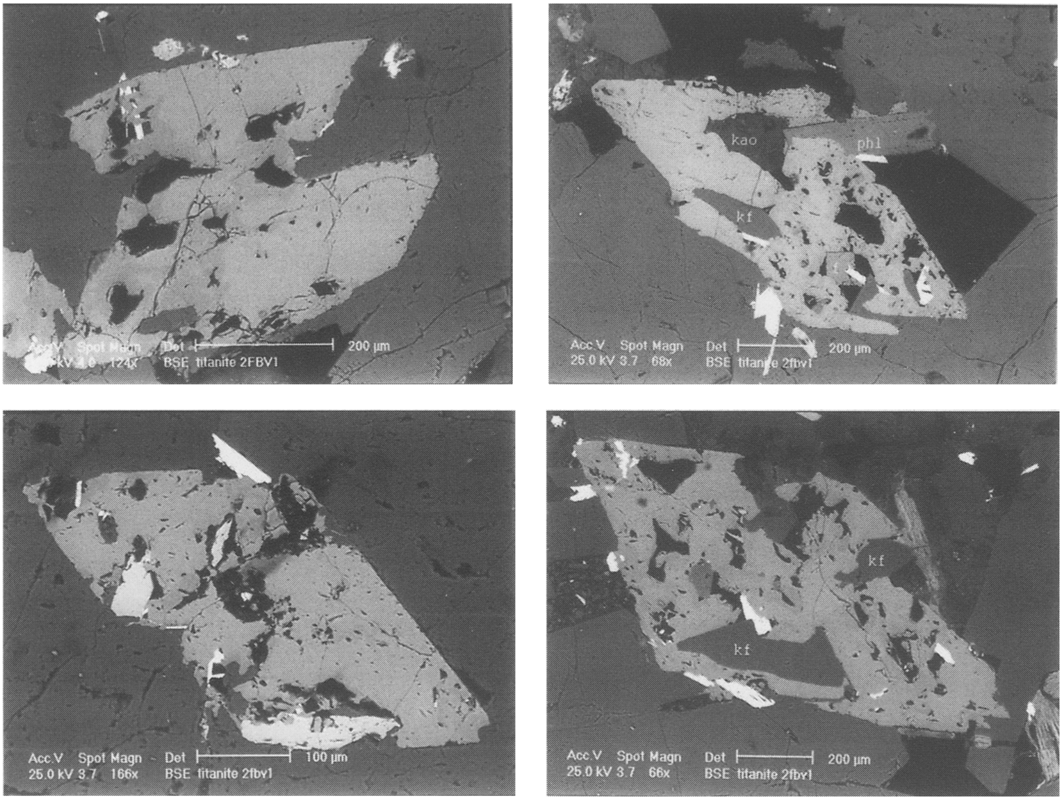

FIG. 1. BSE images of titanite from Tre Croci, Vico volcano. The high-Z contrast, white grains are zirconolite and unidentified Th,U,*REE*-silicate; kf = K-feldspar; kao = kaolinite; phl = fluor-phlogopite; f = fluorite.

TABLE 1. Microchemical analyses of titanites

Sample	TW1	TW2	TW3	TW4	TW5	PZ1	RM1
Nb_2O_5	0.60	0.39	0.60	0.47	0.31	0.51	0.62
SiO_2	28.48	29.00	28.59	28.69	29.35	30.01	29.49
TiO_2	30.35	32.10	31.20	30.66	34.21	34.42	30.59
ZrO_2	1.92	0.33	1.39	1.48	0.11	0.00	2.39
ThO_2	0.26	0.00	0.00	0.21	0.00	0.00	0.00
UO_2	0.00	0.00	0.00	0.19	0.00	0.00	0.00
Al_2O_3	2.63	2.86	2.47	2.62	2.31	1.26	2.37
$Fe_2O_3{}^a$	3.06	2.45	2.76	2.93	1.62	2.65	3.51
Y_2O_3	0.15	0.24	0.29	0.29	0.23	0.31	0.25
La_2O_3	0.37	0.27	0.42	0.36	0.00	1.03	0.43
Ce_2O_3	1.70	1.44	1.75	1.65	0.90	0.88	1.23
Nd_2O_3	0.69	0.49	0.95	0.69	0.41	0.45	0.47
Sm_2O_3	0.21	0.00	0.16	0.00	0.00	0.00	0.00
CaO	26.03	26.23	26.12	26.20	26.57	26.47	26.46
Mn_2O_3	0.10	0.30	0.11	0.10	0.36	0.16	0.09
Na_2O	n.a.	n.a.	n.a.	n.a.	n.a.	0.10	0.07
F	1.76	0.95	0.73	0.74	0.46	0.38	0.67
Total	98.31	97.05	97.54	97.28	96.84	98.72	99.08
-O≡F	0.74	0.40	0.31	0.31	0.19	0.16	0.28
Ctotal	97.57	96.65	97.23	96.97	96.64	98.56*	98.80**
$Y\mathit{REE}_2O_3$	3.12	2.44	3.57	2.99	1.54	2.67	2.38

Crystal chemical formulae based on 3 cations

Sample	TW1	TW2	TW3	TW4	TW5	PZ1	RM1
Ca	0.961	0.958	0.960	0.964	0.964	0.953	0.957
Th	0.002	0.000	0.000	0.002	0.000	0.000	0.000
U	0.000	0.000	0.000	0.001	0.000	0.000	0.000
Y	0.003	0.004	0.005	0.005	0.004	0.006	0.004
La	0.005	0.003	0.005	0.005	0.000	0.013	0.005
Ce	0.021	0.018	0.022	0.021	0.011	0.011	0.015
Nd	0.008	0.006	0.012	0.008	0.005	0.005	0.006
Sm	0.002	0.000	0.002	0.000	0.000	0.000	0.000
Mn^{3+}	0.003	0.009	0.003	0.003	0.010	0.004	0.003
Na	–	–	–	–	–	0.007	0.005
Σ [VII]	1.005	0.999	1.010	1.009	0.995	0.998	0.995
Ti	0.786	0.823	0.805	0.792	0.871	0.869	0.777
Al	0.107	0.115	0.100	0.106	0.092	0.050	0.094
Fe^{3+}	0.079	0.063	0.071	0.076	0.041	0.067	0.089
Nb	0.009	0.006	0.009	0.007	0.005	0.008	0.009
Zr	0.032	0.005	0.023	0.025	0.002	0.000	0.039
Σ [VI]	1.014	1.012	1.009	1.006	1.011	0.994	1.009
Si	0.981	0.989	0.981	0.985	0.994	1.008	0.996
F	0.192	0.102	0.079	0.080	0.049	0.040	0.072
$OH_{calc.}$	0.048	0.035	0.060	0.067	0.048	0.036	0.067
OH+F	0.144	0.137	0.139	0.147	0.098	0.077	0.138

[a] total Fe as Fe_2O_3; n. a. not analysed

* Includes: MgO 0.02 and BaO 0.07; Mg 0.001 and Ba 0.001

** Includes: V_2O_5 0.12, MgO 0.10, SrO 0.07, BaO 0.12 and K_2O 0.03

PZ1 – sample PZ53.11.13 from Belkin *et al.* (1996)

RM1 – sample 43SP from Giannetti and Luhr (1983)

(0.09–0.32 wt.% MnO). However, the most notable chemical feature of the Tre Croci titanite, compared with other titanites described in the mineralogical literature, is the high Zr concentration (up to 1.92 wt.% ZrO_2). Comparable Zr contents in titanites have been reported only in a few occurrences: two nepheline-syenites (Flohr and Ross, 1990; Woolley *et al.*, 1992), a nephelinite lava (Smith, 1970) and a trachytic tuff (Giannetti and Luhr, 1983).

Although the composition of titanite from Tre Croci is similar in many respects to that of the Ponza titanite (Table 1), as expected because of their similar environments of formation, some significant differences are apparent. Although both have similar total *REE* contents, and are both enriched in light rare-earths, the Vico sample has Ce > La, whereas the Ponza sample has La > Ce (Table 1).

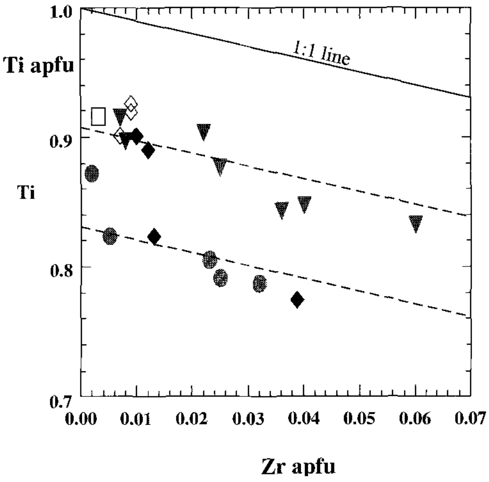

FIG. 2. Relationship between the Ti *vs.* Zr contents in titanites from various geological environments. Open square: nepheline syenite, Greenland (Jones and Larsen, 1985); open diamond: marble skarns, Bregaglia (Gieré, 1986); triangle down: nephelinite lavas (Smith, 1970); filled diamond: trachytic tuff, Roccamonfina (Giannetti and Luhr, 1983); filled circle: syenitic ejectum, this work.

Chemical substitutions

Titanite, ideally $CaTi(SiO_4)(O,OH,F)$, commonly shows considerable isomorphous substitutions (e.g. Sahama, 1946; Higgins and Ribbe, 1976; Oberti *et al.*, 1991). More recently Perseil and Smith (1995) have compiled a list of those elements which can enter the titanite structure, and have discussed the various possible substitution schemes, the most important being:

(i) $^{[6]}(Al,Fe^{3+}) + (OH,F)^{-} \rightleftharpoons {}^{[6]}Ti^{4+} + O^{2-}$; this is the main mechanism whereby (OH,F) replaces the O1 oxygen in the structure (Mongiorgi and Riva di Sanseverino, 1968; Isetti and Penco, 1968; Černý and Riva di Sanseverino, 1972; Enami *et al.*, 1993);

(ii) $^{[7]}M^{3+} + {}^{[6]}(Al,Fe^{3+}) \rightleftharpoons {}^{[7]}Ca^{2+} + {}^{[6]}Ti^{4+}$; where trivalent cations (M^{3+}), commonly *REE*, but also Sb (Perseil and Smith, 1995), substitute for $^{[7]}Ca$;

(iii) $^{[6]}M^{5+} + {}^{[6]}(Al,Fe^{3+}) \rightleftharpoons 2^{[6]}Ti^{4+}$; where pentavalent cations (M^{5+}), notably Nb and Ta (Clark, 1974; Paul *et al.*, 1981; Groat *et al.*, 1985; Russell *et al.*, 1994), are allocated at the octahedral site.

In Fig. 2 we plot the available chemical data for Zr-rich titanites from the mineralogical literature. Despite some scatter of the data, a reasonable correlation between Ti and Zr is apparent, suggesting that in Zr-bearing titanites there is an obvious substitution to consider, i.e. a direct isovalent octahedral substitution $^{[6]}Ti \rightleftharpoons {}^{[6]}Zr$. Note that the data points are shifted below the 1:1 line because some Ti is involved in several other cationic exchanges, as outlined above. An important point to consider with this regard is that all Zr-bearing titanites so far reported in the mineralogical literature are from high-temperature and alkali-rich volcanic environments. However, at present it is not clear whether this is a genuine paragenetic feature, or it is due to the scarcity of analyses for Zr in titanites.

Substitution (i) for titanite from Tre Croci and Ponza is shown in Fig. 3, where a well-defined positive correlation between (OH,F) and (Al,Fe^{3+}) is evident. Note that titanite from Tre Croci is fluorine-rich with only minor amounts of calculated OH present (Table 1). This indicates that the linear relationship observed in Fig. 3 is not an artifact of the procedure used to calculate (OH) on a charge-balance basis (see above). The shift of the data points below the 1:1 line in Fig. 3 is the result of some of the Al and Fe^{3+} involved also in substitution (ii), but could also be due in part to some F-loss during EMP analysis.

Substitution (ii) is shown in Fig. 4 where all data points plot along the 1:1 line confirming that the substitution of Ca+Ti is balanced by the trivalent cations, including REE^{3+}.

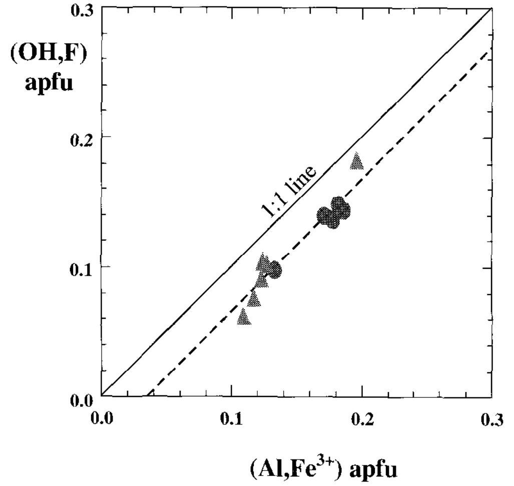

FIG. 3. Relationship between (OH,F) *vs.* (Al,Fe^{3+}) for the Tre Croci titanites in comparison with the Ponza titanites (Belkin *et al.*, 1996). The dotted line is the 1:1 line for substitution (i) (see text). Filled circle: Tre Croci; filled triangle: Ponza.

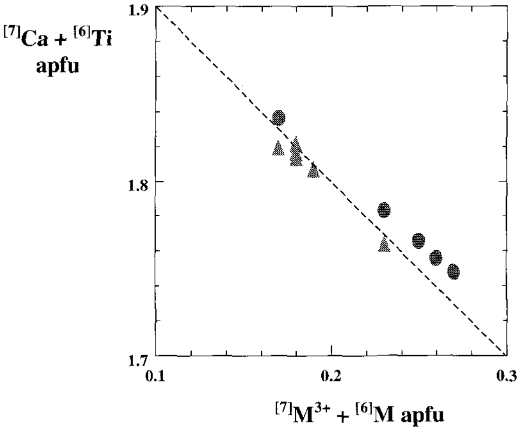

FIG. 4. $^{[7]}$Ca+ $^{[6]}$Ti *vs.* $^{[7]}$M^{3+} + $^{[6]}$(Al,Fe^{3+}) substitutions (equation (ii), see text) for the Tre Croci and Ponza titanites (Belkin *et al.*, 1996). The dotted line represents the 1:1 line for equation (ii). Same symbols as in Fig. 2.

REE patterns

Titanite is one of the most common accessory phases occurring in a wide variety of geological environments and is able to incorporate significant amounts of incompatible elements, in particular *REE*, but also Th, U, Zr, Nb, Ta, Sr and Ba. Because mineral/melt partition coefficients for the *REE* in titanite do not vary significantly from light- to heavy-*REE* (Henderson, 1980), the distribution of these elements in the mineral reflects their availability in the environment of formation. In a study of titanite from different occurrences in Alaska, Staatz *et al.* (1977) showed that the *REE* patterns in titanite could be correlated with the *REE* patterns of the host rocks. From an assessment of a large number of analyses from a range of geological environments, Fleischer and Altschuler (1969) and Fleischer (1978) were able to show a relative enrichment of light- to intermediate- and heavy-*REE* in titanite from alkalic to basic rocks.

Titanites from Tre Croci and Ponza, when plotted on a ternary diagram (Fig. 5) with apices of light-*REE* (La to Nd), intermediate-*REE* (Sm to Ho) and heavy-*REE* (Er to Lu), lie close to the La-Nd apex of the diagram, and are consistent with the trend observed by Fleischer (1978). In Fig. 6, the data are displayed in a different manner, better suited to microprobe analyses, because Y has a much better detection limit than the heavy-*REE*, and can proxy for Ho in most geological environments. Finally in Fig. 7, based on the same data as in Figs 5 and 6, it can be seen that whereas the Tre Croci titanite follows the general trend seen for a large number of literature

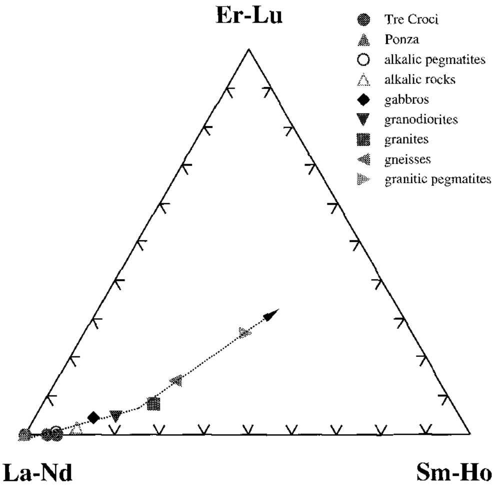

FIG. 5. (La-Nd)–(Sm-Ho)–(Er-Lu) compositional triangle (Fleischer, 1978).

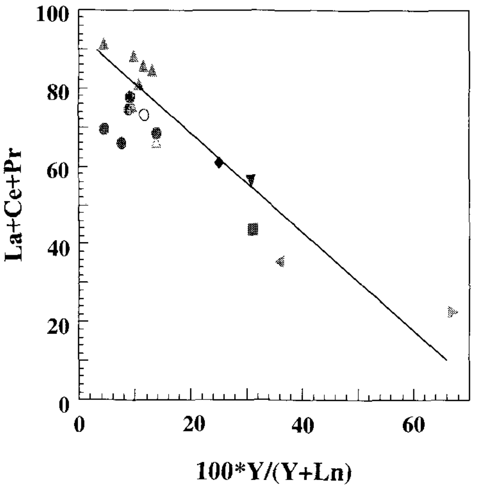

FIG. 6. La+Ce+Pr *vs.* 100 × Y/(Y+Ln) plot (Fleischer, 1978). Same symbols as in Fig. 5.

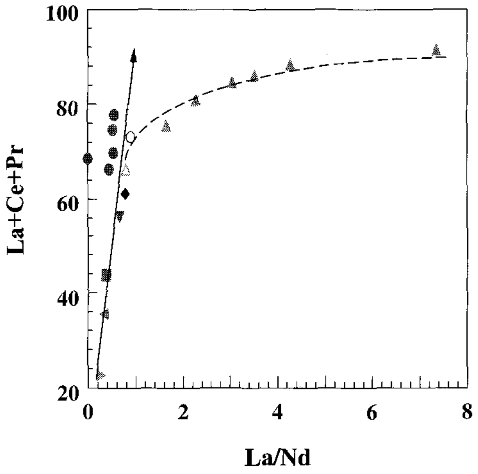

FIG. 7. La+Ce+Pr *vs.* La/Nd (Fleischer, 1978). Same symbols as in Fig. 5. The dotted curve represent the trend of the Ponza data (Belkin *et al.*, 1996).

data (Fleischer, 1978), the Ponza titanite departs significantly from this trend, showing an anomalous enrichment in La relative to Ce. Chondrite-normalised (cn) *REE* patterns for titanites from alkali-rich environments generally have $Ce_{(cn)} > La_{(cn)}$ (e.g. Staatz *et al.*, 1977; Henderson, 1980; Green and Pearson, 1986; Paterson *et al.*, 1989; Russell *et al.*, 1994), even when the host rock is enriched in $La_{(cn)}$ relative to $Ce_{(cn)}$, as shown for instance (Fig. 8) by the Mt. Bisson case (Russell *et al.*, 1994). The Tre Croci titanite has this typical $REE_{(cn)}$ pattern, as does the Roccamonfina titanite (Fig. 9). However, the Ponza titanite is markedly different in having $La_{(cn)} >> Ce_{(cn)}$, and the only reported occurrence of a similar $REE_{(cn)}$ pattern is from an alkali-rich intrusive rock

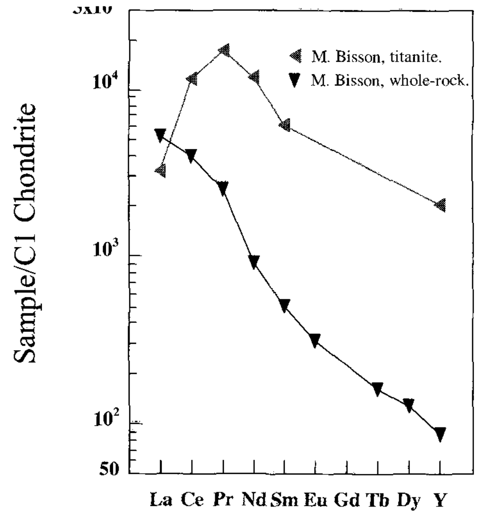

FIG. 8. Whole-rock REE_{cn} plot for the Mt. Bisson alkaline intrusion and for titanite from the same sample (Russell *et al.*, 1994).

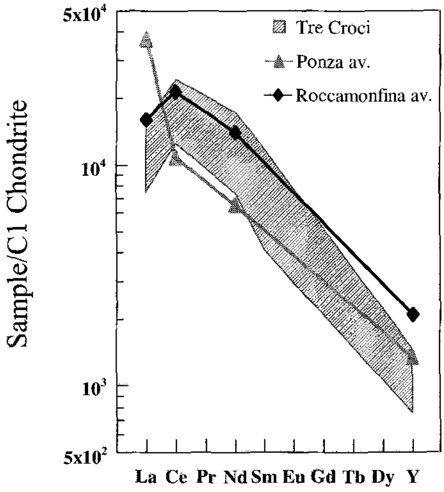

FIG. 9. Chondrite normalized concentration of the *REE* in titanites from Tre Croci (stippled area), Ponza (Belkin *et al.*, 1996) and Roccamonfina (Giannetti and Luhr, 1983).

(ijolite) from Seabrook Lake, Ontario (Cullers and Medaris, 1977). The main factors that affect *LREE* incorporation into *LREE*-bearing accessory phases are (Lloyd *et al.*, 1996):

1) *LREE* preference for one mineral structure over another;

2) competition for *LREE* between two or more co-crystallizing *LREE*-bearing phases;

3) the effect of varying f_{O_2} on the Ce contents.

Factor (1) cannot be the cause of the different *LREE* compositions of the Tre Croci and Ponza samples since we have shown that, in general, titanite has a strong preference of Ce over La. It follows that factors (2) and (3) could be both responsible for the extreme La enrichment of the Ponza sample, but at present the data do not provide a definitive explanation for the observed trends.

Late alteration in titanite

Titanite occurs as euhedral to subhedral crystals and is clearly an early crystallizing phase in the host syenite. Scanning electron images show that the titanite grains underwent variable degrees of corrosion, both along the margins and along internal fractures (Fig. 1), indicating alteration by a late-stage fluid associated with the volcanic process. Pan *et al.* (1993) described a case of late hydrothermal alteration in titanite with subsequent formation of *REE*-minerals within the crystal grains or along the crystal boundaries. In that example, the titanite was commonly bordered by an irregular zone of altered titanite which was depleted in *REE* and actinides. Pan *et al.* (1993) concluded that the associated *REE*-rich minerals were formed from *REE* leached from the titanite host. Allen *et al.* (1986) also report inclusions of secondary *REE*-rich minerals along fractures and grain boundaries in titanite.

The chemical and textural relationships of titanite described in this study provide another example of late-stage alteration, although we propose a slightly different interpretation from that of Pan *et al.* (1993). The Tre Croci titanite contains several fine-grained mineral inclusions of Nb,Th,U-bearing zirconolite, (a crystal-chemical study of this mineral is currently being undertaken, and will be the focus of a forthcoming paper), fluorite, apatite, ilmenite and an unidentified *REE*,Th,U,Ca-silicate, probably britholite: $(Ce,Ca)_5(SiO_4,PO_4)_3(OH,F)$. Although the patchy alteration of titanite from Vico shows many features very similar to those described by Pan *et al.* (1993), mass-balance calculations suggest that its altered zones cannot account for all *REE*-bearing minerals present in the rock, and at least part, if not most, of the *REE* and actinides must have been supplied to the system from an additional (probably external) source.

Although we have not been able to identify the origin and the nature of the hydrothermal fluids responsible for the alteration of titanite from Tre Croci, some of the mineralogical, textural and chemical data presented here provide a likely scenario. Gieré (1996) and Rubin *et al.* (1993), among others, suggested that the presence of dissolved halides, phosphate, sulphate and carbon dioxide plays an important role in the mobility of *REE*, actinides, Zr and Ti in hydrothermal systems. At Tre Croci, the abundance of fluorite and the common association of phosphates in the rock suggests that the fluids were rich in dissolved F^- and $(PO_4)^{3-}$, and the close association of titanite with Zr- (zirconolite and baddeleyite) and *REE*-bearing minerals (britholite?) indicates a fluid composition rich in Zr, *REE*, Th and U. These observations lead us to infer that the fluids responsible for the alteration of titanite controlled also the formation of the relatively rare mineral assemblage described here.

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