Titanite in carbonatitic rocks:
Genetic dualism and geochemical significance

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ABSTRACT. — Titanite is a relatively rare Ti silicate in carbonatitic rocks. It is a primary phase in alkali-rich carbonatites, and may also occur in silicocarbonatites whose composition was modified by assimilation of wallrock silicate material. More typical is late-stage titanite that forms by reaction of a precursor Ti mineral with deuteric fluids. Both genetic types show significant variations in chemical composition arising mostly from the substitution of Ti with Al, Fe, Nb and Zr. Cationic substitutions at the Ca site are limited to several atomic per cent. Zoning in primary titanite typically involves a decrease in the proportion of Nb and Zr toward the rim, whereas deuteric crystals show the reverse zoning pattern.

RIASSUNTO. — La titanite è un Ti silicato relativamente raro nelle rocce carbonatitiche. Questo minerale è una fase primaria nelle carbonatiti ricche in alcali e può trovarsi anche nelle silicocarbonatiti la cui composizione è stata modificata dall'assimilazione di meteriale silicatico costituente il condotto. Più tipicamente la titanite è un minerale di stadio tardivo e si forma per la reazione di un minerale di Ti precursore con fluidi deuterici. Entrambi i tipi gentici mostrano variazioni nella loro composizione chimica essenzialmente data dalla sostituzione di Ti con Al, Fe, Nb e Zr. La sostituzione cationica nel sito del Ca è limitata ad alcuni punti in percento atomico. La titanite primaria ha zonazione tipica consistente in un decremento della concentrazione di Nb e Zr verso i bordi, mentre i cristalli deuterici mostrano una zonazione inversa.

KEY WORDS: *titanite, carbonatite*.

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INTRODUCTION

Titanite is the most common Ti silicate. Its simplified composition is $CaTiSiO_5$. However, the crystal structure of this mineral is so tolerant to atomic substitutions that more than 20 different elements have been observed to replace Ca, Ti, Si or O in significant proportions. With this in mind, the general formula of titanite can be rewritten as follows:

Ca,Na,REE,Y,Sr,Mn,Sc)(Ti,Fe,Al,Nb,Sn,Ta, Zr,Mn,Cr,V,Sb,As)(Si,Al)O_4(O,OH,F).
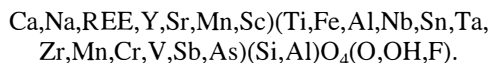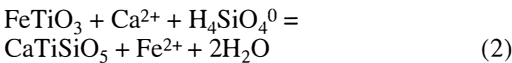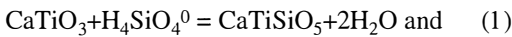
The morphology, composition and zoning of naturally occurring titanite reflect (changes in) the chemistry of its crystallization environment, and the conditions (including kinetics) of its growth (*e.g.*, Franke and Ghobarkar, 1980; Brugger and Gieré, 1999; Paterson and Stephens, 1992). Such atomic substitutions as $SiTi_{-1}$ and $AlFTi_{-1}O_{-1}$ (Knoche *et al.*, 1998; Troitzsch and Ellis, 2002), are important for constraining the *P-T* parameters and fluid regime of crystallization. Complex replacement assemblages involving titanite and other Ti phases have been documented virtually from all petrographic settings and, in several cases, characterized thermodynamically (*e.g.*, Hollabaugh *et al.*, 1989; Chakhmouradian and Zaitsev, 2002). Thus, the compositional variation of titanite, its crystal morphology and
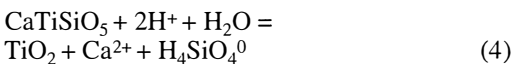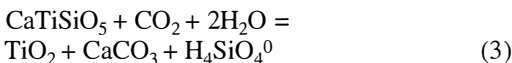
relations with associated minerals provide valuable insights into the evolutionary history of their host rocks. Whereas titanite from some rock types (for example, regional metamorphic: Franz and Spear, 1985; Enami *et al.*, 1993) has been studied in sufficient detail, the available data on the occurrence and chemistry of titanite from carbonatites are very limited.

Titanite occurrence in carbonatites

Samples from several carbonatite occurrences worldwide were examined for this study (Table 1). Accessory titanite occurs predominantly in early plutonic carbonatites, phoscorites and associated metasomatic rocks (like phlogopitized clinopyroxenites). It is typically found in late-stage deuteric parageneses, where it forms by reaction of a primary Ti host (perovskite, ilmenite, titaniferous magnetite or, less commonly, schorlomite) with a fluid fractionated from the carbonatitic magma (Fig. 1 a,b). The two principal replacement reactions, involving perovskite and ilmenite, are:

$$CaTiO_3 + H_4SiO_4^0 = CaTiSiO_5 + 2H_2O \text{ and} \quad (1)$$

$$FeTiO_3 + Ca^{2+} + H_4SiO_4^0 = \\ CaTiSiO_5 + Fe^{2+} + 2H_2O \quad (2)$$

These reactions occur even at very low activities of silica in the fluid (*ca.* 10^{-4} for ilmenite and 10^{-5}-10^{-6} for perovskite at T = 150-300°C). They are restricted to moderately acidic conditions and relatively low partial pressures of CO_2 (Fig. 2). Titanite is unstable at higher $a(H^+)$ or $P(CO_2)$ in the fluid, yielding anatase ± calcite (Hollabaugh *et al.*, 1989; Mitchell and Chakhmouradian, 1998):

$$CaTiSiO_5 + CO_2 + 2H_2O = \\ TiO_2 + CaCO_3 + H_4SiO_4^0 \quad (3)$$

$$CaTiSiO_5 + 2H^+ + H_2O = \\ TiO_2 + Ca^{2+} + H_4SiO_4^0 \quad (4)$$

If the primary Ti phase in carbonatite is titanite (as in phlogopite-calcite carbonatite of Murun), it also may undergo late-stage

replacement by anatase under increasing $P(CO_2)$. Textural evidence indicates that precipitation of deuteric titanite is typically preceded by an episode of hydraulic fracturing. Consequently, this mineral is typically found as fracture fillings or euhedral crystals lining the newly formed openings. In the latter case, radial and sheaf-like aggregates, lineage structures and complex zoning patterns are common, indicating rapid disequilibrium growth. The late-stage titanite is paragenetically associated with diverse REE minerals (especially, ancylite), hydrous Ca-Al silicates, fibrous subsolidus amphibole developed after primary mafic silicates, and chlorite replacing primary amphiboles and micas (*e.g.*, Chakhmouradian and Zaitsev, 2002).

Formation of deuteric titanite may occur under closed-system conditions, either owing to the loss of vapor or general decrease in silica solubility with temperature. A possible example is silicocarbonatite (diopside+magnesiohastingsite+calcite) from the Afrikanda complex (Fig. 1b). Alternatively, wallrock metasomatism may be responsible for an increase in silica activity required to shift the equilibrium in reaction (1) or (2) toward $CaTiSiO_5$. This is observed in calcite carbonatites of Rocky Boy, where titanite pseudomorphs after ilmenite are restricted to contacts of the carbonatite with potassic alkaline syenite. Extensive sericitization of the wallrock syenite and abundance of phlogopite and potassium feldspar at the selvages indicate enrichment of the carbonatite in silica and K through metasomatic processes.

Igneous titanite is extremely rare in carbonatites, principally because its crystallization requires high silica activities unusual for carbonatitic magmas, possibly in excess of 10^{-1} at $T > 700$°C (Barker, 2001). At lower silica activities, perovskite (*sensu stricto*) is the stable liquidus phase. Primary titanite may coexist in equilibrium with diopside and phlogopite, but does not form in silica-poor forsterite or monticellite carbonatites. Euhedral wedge-shaped crystals of titanite are common in silicocarbonatite (diopside+phlogopite+calcite)

TABLE 1

Titanite samples: a summary

Locality	Rock type	Occurrence mode of titanite	Associated minerals
Sebljavr Kola Peninsula Russia	Calcite carbonatite	Fracture fillings in perovskite	Calcite, perovskite calcic amphibole
Afrikanda Kola Peninsula Russia	Silicocarbonatite	Fracture fillings in and mantles on perovskite, ilmenite and other Ti-bearing minerals	Calcite, loparite-(Ce), ancylite-(Ce), cerite-(Ce), richterite, chlorite
Kovdor Kola Peninsula Russia	Phoscorite	Fracture fillings in perovskite	Calcite, perovskite
Turiy Mys Kola Peninsula Russia	Carbonatite	Fracture fillings in perovskite	Calcite, perovskite, andradite, pyrrhotite
Murun Eastern Siberia Russia	Calcite carbonatite, phlogopite-calcite carbonatite	Euhedral crystals	Calcite, potassium feldspar, aegirine-augite, dalyite, tinaksite, turkestanite
Prairie Lake Ontario Canada	Silicocarbonatite	Sub- to euhedral crystals	Diopside, phlogopite, calcite, schorlomite, apatite, wöhlerite
Rocky Boy Montana USA	Contact of calcite carbonatite with syenite	Replacement product of ilmenite	Ilmenite, pyrochlore, zircon, apatite, calcite, phlogopite

from the Prairie Lake complex. These crystals fringe xenocrysts of clinopyroxene derived from wallrock ijolite (Fig. 1c). We interpret these textures to result from resorption of the xenocrysts in a carbonate-rich magma, leading to a local increase in the activity of silica and precipitation of titanite. At Prairie Lake, uncontaminated carbonatites contain liquidus perovskite and are devoid of titanite, providing further evidence of the effect that wallrock contamination may have on the evolution of carbonatites.

Primary titanite has been reported in silicate-rich natrocarbonatite from Oldoinyo Lengai in Tanzania and nepheline sövite from Dicker Willem in Namibia (Dawson *et al*., 1996; Cooper and Reid, 1998). At present, it is uncertain why their parental magmas precipitated titanite and not perovskite. The arguments of Barker (2001), suggesting a possibly cumulate origin for the Dicker Willem carbonatite, are clearly inapplicable to the case of phenocrystic titanite from Oldoinyo Lengai; further studies of these unusual rocks are required. Carbonatites of the Murun complex also contain abundant euhedral to subhedral crystals of titanite associated with potassium feldspar, aegirine-augite and exotic alkali silicates such as dalyite, $K_2ZrSi_6O_{15}$. This paragenesis is in accord with thermodynamic
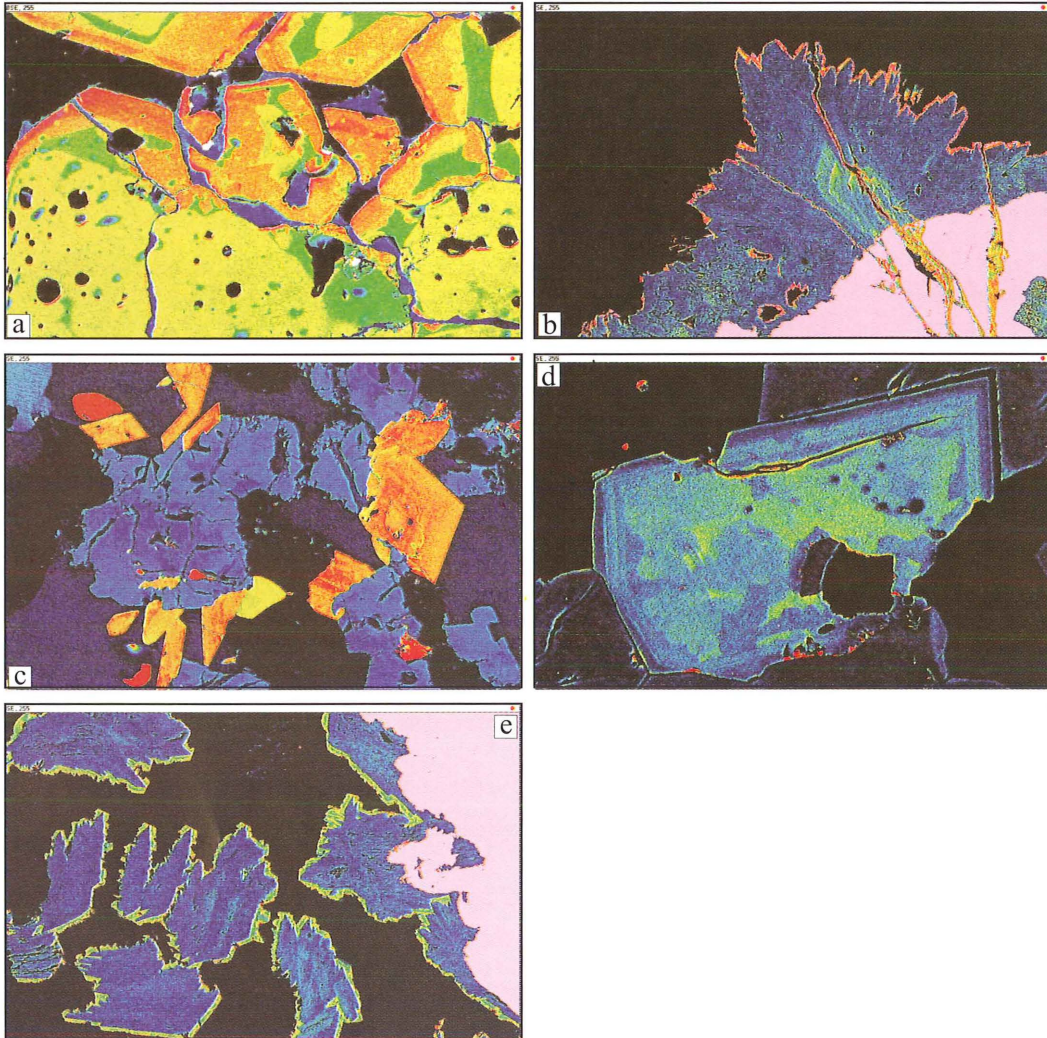
Fig. 1 – Modes of occurrence of titanite in carbonatites. (a) Titanite (dark gray) developed marginally and along fractures in zoned cumulus perovskite, Sebljavr (Russia), field of view (FOV) 400 mm; (b) ilmenite (light gray) overgrown by a «corona» of titanite (darker gray), Afrikanda (Russia), FOV 180 mm. (c) euhedral crystals of titanite (light gray) fringing clinopyroxene xenocrysts (darker gray), Prairie Lake complex (Ontario), FOV 200 mm; (d) zoned primary titanite with a resorbed Nb-Zr-enriched core (light gray) and Fe-enriched oscillatory rim (darker gray), Prairie Lake, FOV 220 mm; (e) deuteric titanite with an Al-rich core (dark gray) and a thin Nb-rich rim (lighter gray), Afrikanda, FOV 200 mm. Back-scattered electron (BSE) images.

calculations of Nesbitt *et al.* (1981), showing that perovskite is unstable in the presence of alkali feldspar, and will react to produce titanite plus leucite. Thus, it is clear that some carbonatitic magmas are capable of precipitating liquidus titanite. Possible reasons for the enhanced activity of silica in these magmas may include: (i) enrichment of the magma in alkalis, (ii) assimilation of wallrock silicate material, or (iii) increasing

polymerization of SiO_4 tetrahedra with decreasing temperature (Barker, 2001; Chakhmouradian and Zaitsev, 2002). This problem is also relevant to the occurrence in carbonatites of primary zircon, one of the major sources of radiogenic-isotope data for these rocks (*e.g.*, Amelin and Zaitsev, 2002). Although $ZrSiO_4$ is stable at silica activities higher than the perovskite-titanite equilibrium (Barker, 2001), euhedral crystals of zircon and its overgrowths on baddeleyite (ZrO_2) are significantly more common in carbonatites than the primary titanite.

COMPOSITIONAL VARIATION OF TITANITE FROM CARBONATITES

The chemical composition of titanite was determined by electron-microprobe analysis; in total, about 350 analyses were obtained (for operating conditions and standards, see Chakhmouradian and Zaitsev, 2002). These new data show that both primary and deuteric titanite exhibit a significant variation in

Fig. 2 – Stability field of titanite (double-contoured) with respect to ilmenite and anatase in late-stage carbonatitic fluids at $T = 200°C$. The equilibria were calculated from Gibbs free-energy changes and equilibrium constants for reactions (2)-(4). The titanite-free equilibria involving ilmenite, anatase and calcite are not shown for clarity.

chemistry, a feature that had not been recognized prior to our study. Depending on the availability and mobility of high-field-strength elements (HFSE) in the fluid, the deuteric variety may contain as much as 11.4 wt.% Nb_2O_5 (0.12 apfu Nb relative to a total of 3 cations), 15.3 wt.% ZrO_2 (0.26 apfu Zr) and 0.4 wt.% HfO_2 (Afrikanda). Primary titanite contains up to 4.1 wt.% Nb_2O_5 and 6.8 wt.% ZrO_2 (Prairie Lake). Whereas comparable levels of Nb have been documented previously in samples from nepheline syenites and granitic pegmatites (but not carbonatites), the maximum ZrO_2 content reported for any titanite in the literature is only 4.2 wt.% (*e.g.*, Cerný *et al.*, 1995; Dawson *et al.*, 1995). The incorporation of Nb involves three substitution mechanisms: $NbAlTi_{-2}$, $NbFe^{3+}Ti_{-2}$ and $NaNbCa_{-1}Ti_{-1}$. Some late-stage crystals exhibit extreme enrichment in Al and Fe^{3+} (up to 10.0 and 8.3 wt.% respective oxides, or 0.37 apfu Al and 0.21 apfu Fe) not accompanied by an increase in Nb content. These substitutions require extensive replacement of O with hydroxyl groups (up to 1.8 wt.% H_2O), *i.e.* $(Al,Fe^{3+})(OH)Ti_{-1}O_{-1}$. The levels of F in this deuteric titanite are negligible, in agreement with low pressure and temperature of its crystallization (*cf.* Enami *et al.*, 1993).

Titanite from carbonatites shows very little substitution in the Ca site. The highest Na_2O content (1.6 wt.% or 0.10 apfu Na) was observed in late-stage titanite from Sebljavr. The total amount of La, Ce, Sr and other large cations substituting for Ca is limited to a few atomic per cent, primarily because these elements favor phosphate and carbonate phases (like apatite or ancylite) associated with the titanite. Hence, the compositional variation of titanite from carbonatites and related rocks may be adequately characterized in terms of four end-members with different cation populations in the Ti site: $CaTiSiO_5$, $CaZrSiO_5$, $Ca(Fe^{3+},Al)SiO_4(OH)$, and $Ca(Fe^{3+},Al)_{0.5}Nb_{0.5}SiO_5$.

In BSE, many examples of primary and deuteric titanite exhibit growth zoning of oscillatory or sectorial type, as well as resorption features (Figs. 1 d,e). In terms of
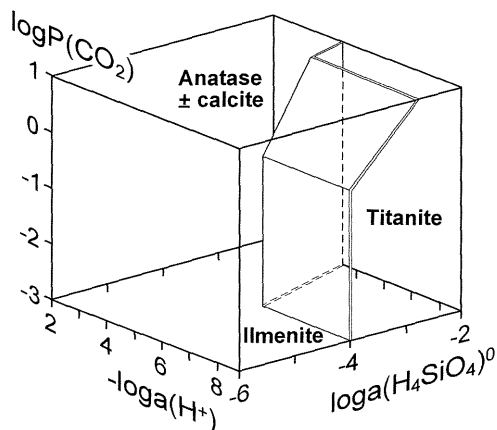
composition, zoning in primary titanite typically involves a decrease in Zr and/or Nb contents toward the rim, whereas late-stage crystals typically show a reverse pattern (Fig. 1 d,e). This difference may be explained by co-crystallization or dissolution of phases competing with titanite for HFSE (*e.g.*, pyrochlore, zircon and zirconosilicates).

Conclusions

(1) Titanite occurs in a wide variety of carbonatitic rocks; the mode of its occurrence depends principally on the activities of silica and alkalis in the parental magma, fluid regime and degree of wallrock-magma interaction;

(2) Igneous (primary) titanite is rare, and virtually restricted to (silico-)carbonatites enriched in alkalis, or contaminated with wallrock material;

(3) Titanite is comparatively more common in late-stage parageneses, and typically results from reaction of a precursor Ti mineral with deuteric fluids at relatively low temperature and $P(CO_2)$;

(4) Titanite is an important sink for high-field-strength elements (especially, Nb and Zr) in carbonatites; compositional zoning of such HFSE-enriched titanite provides clues to the relative mobility of HFSE in carbonatitic melts/fluids, and crystallization order of the associated mineral phases.

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