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.

INTRODUCTION

Titanite is the most common Ti silicate. Its simplified composition is CaTiSiO5. 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)O4(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 Gobarkar, 1980; Brugger and Gieré, 1999; Paterson and Stephens, 1992). Such atomic substitutions as SiTi1 and AlFTi10 (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:

$$\text{CaTiO}_3 + \text{H}_4\text{SiO}_4 = \text{CaTiSiO}_5 + 2\text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{FeTiO}_3 + \text{Ca}^{2+} + \text{H}_4\text{SiO}_4 = \text{CaTiSiO}_5 + \text{Fe}^{2+} + 2\text{H}_2\text{O}$$  \hspace{1cm} (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 $T = 150$-$300^\circ\text{C}$). They are restricted to moderately acidic conditions and relatively low partial pressures of $\text{CO}_2$ (Fig. 2). Titanite is unstable at higher $a(\text{H}^+)$ or $P(\text{CO}_2)$ in the fluid, yielding anatase ± calcite (Hollabaugh et al., 1989; Mitchell and Chakhmouradian, 1998):

$$\text{CaTiSiO}_5 + \text{CO}_2 + 2\text{H}_2\text{O} = \text{TiO}_2 + \text{CaCO}_3 + \text{H}_4\text{SiO}_4$$  \hspace{1cm} (3)

$$\text{CaTiSiO}_5 + 2\text{H}^+ + \text{H}_2\text{O} = \text{TiO}_2 + \text{Ca}^{2+} + \text{H}_4\text{SiO}_4$$  \hspace{1cm} (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 $P(\text{CO}_2)$. Textural evidence indicates that precipitation of deuteritic 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 deuteritic 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 $\text{CaTiSiO}_5$. 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 $T > 700^\circ\text{C}$ (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)
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Table 1
Titanite samples: a summary

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

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 sōvite 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, K₂ZrSi₆O₁₅. This paragenesis is in accord with thermodynamic
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 SiO₄ 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 ZrSiO₄ is stable at silica activities higher than the perovskite-titanite equilibrium (Barker, 2001), euhedral crystals of zircon and its overgrowths on baddeleyite (ZrO₂) 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 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.% Nb₂O₅ (0.12 apfu Nb relative to a total of 3 cations), 15.3 wt.% ZrO₂ (0.26 apfu Zr) and 0.4 wt.% HfO₂ (Afrikanda). Primary titanite contains up to 4.1 wt.% Nb₂O₅ and 6.8 wt.% ZrO₂ (Prairie Lake). Whereas comparable levels of Nb have been documented previously in samples from nepheline syenites and granitic pegmatites (but not carbonatites), the maximum ZrO₂ 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: NbAlTi₂, NbFe³⁺Ti₂ and NaNbCaTi. Some late-stage crystals exhibit extreme enrichment in Al and Fe³⁺ (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.% H₂O), i.e. (Al,Fe³⁺)(OH)Ti₉O₁₆. 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 Na₂O content (1.6 wt.% or 0.10 apfu Na) was observed in late-stage titanite from Seblijav. The total amount of La, Ce, Sr and other large cations substituting for Ca is limited to a few atomic percent, primarily because these elements favor phosphate and carbonate phases (like apatite or ancylike) 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: Ca₂Ti₂Si₃O₁₀, CaZrSiO₄, Ca(Fe³⁺,Al)SiO₄(OH), and Ca(Fe³⁺,Al)₀.₅Nb₀.₅SiO₅.

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. 1d,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(CO2);
(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 carbonatic melts/fluids, and crystallization order of the associated mineral phases.

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