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Niobian rutile in Cr-V-bearing rocks of the Sludyanka metamorphic complex (*Southern Baikal area*)

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Abstract

Cr-V-bearing rocks of the Sludyanka metamorphic complex in the Southern Baikal area contain accessory niobian rutile with Nb contents unusually high for metamorphic rocks (10–12 to 20–25 wt.% Nb_2O_5, or, occasionally, up to 36–37 wt.%). Incorporation of Nb^{5+} into the rutile structure is balanced by Cr^{3+} and V^{3+}, which reach 16 wt.% Cr_2O_3 and 8 wt.% (or, rarely, up to 20 wt.%) V_2O_3. The distribution of Nb, Cr, and V in rutile is very uneven, down to the microscale. It does not depend on *PT* conditions, being rather controlled by crystallization kinetics of minerals competing with rutile in the paragenesis.

Keywords: rutile; niobium; chromium; vanadium, isomorphism; metamorphism

Introduction

Rutile is characterized by a high capacity for isomorphic substitutions with respect to many elements, including high-field strength elements (HFSE), for which rutile is often the principal host. Mineral chemistry of rutile is of special interest, given that HFSE can be used as tracers of geological processes (e.g., magmatism in subduction zones). Niobium is a common HFSE isomorphic impurity in rutile: accessory Nb-bearing rutiles with Nb_2O_5 from fractions of one to several percent are known from terrestrial (eclogites, mantle xenoliths, solid inclusions in kimberlitic diamond) and extraterrestrial (lunar rocks and meteorites) occurrences (Brenan et al., 1994; El Goressy, 1971; Hlava et al., 1972; Marvin, 1971; Ryerson and Watson, 1987; Rossman and Smyth, 1990; Rudnick et al., 2000; Schmidt et al., 2009; Shlyukova et al., 1986; Sobolev and Yefimova, 2000; Sobolev et al., 1997, 2011; Zack et al., 2002).

Nb-rich rutile with 10–12 to 20–25 wt.% Nb_2O_5 or higher is restricted to granitic rocks (mainly rare-metal granites and pegmatites), with few exceptions. It was discovered more than 150 years ago in the Ilmen mountains and was originally distinguished as a separate species with the formula $Fe_xTi_{3-x}(Nb, Ta)_{2x}O_6$ or $(Ti, Nb, Fe)_3O_6$, named 'ilmenorutile' after the place of the discovery. The mineral was referred to as 'ilmenorutile' in Russian publications of the 1960s (Chukhrov and Bonshtedt-Kupletskaya, 1965; Kornetova, 1963) but as niobian rutile (Deer et al., 1962) in the English literature of that time; the nomination of ilmenoutile as a separate species was officially invalidated as late as 2007. The Nb_2O_5 limit for niobian rutile, not specified in earlier publications, is tentatively assumed to be 10–12 wt.% in this paper: Nb_2O_5 is above this limit in niobian rutile and below it in Nb-bearing rutile.

Metamorphic rocks typically contain Nb-bearing rutile with Nb contents of tens to hundreds ppm or more rarely from 0.*n* to 1% (Luvizotto and Zack, 2009; Luvizotto et al., 2009; Zack et al., 2004). The same holds for Cr- and (or) V-bearing metamorphites, for which the presence of Nb has never been reported, except for two cases of Cr-bearing quartzite from

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the Archean Ghatti Hosa Halli greenstone belt with 3.61 wt.% Nb_2O_5 (Raase et al., 1983) and from Northwest Nelson in New Zealand with ~4% Nb_2O_5 and Ta_2O_5 in rutile (Challis et al., 1995). In this respect, niobian rutile found in the Sludyanka Cr-V-bearing metasedimentary rocks is exceptional by high Nb contents along with high Cr and V, which have almost no analogs in nature.

Natural occurrence

Composition, genesis, and geological setting of Cr-V-bearing metamorphic rocks from Southern Baikal area were discussed in several earlier publications (Konev et al., 2001; Reznitskiy et al., 2011; Vasiliev et al., 1981), and some issues are summarized below.

Metasedimentary rocks with Cr-V mineralization and accessory niobian rutile make up to 5–6% of the Slyudanka Group, a stratigraphic unit in the Khamar-Daban metamorphic terrane which belongs to the Central Asian Orogenic Belt (CAOB). The study area is located south of Lake Baikal, within the Sludyanka complex in the high-grade part of the terrane adjacent to the basement inlier of the Siberian craton. The regional metamorphism of the complex, reaching the medium-pressure granulite facies, occurred in the Ordovician and acted upon a volcanic-sedimentary protolith which was deposited, possibly, in the latest Neoproterozoic time (Kotov et al., 1997; Kovach et al., 2013).

Local geologists classify the Sludyanka rocks as 'quartz-diopside' metamorphic rocks derived from siliceous-dolomitic sediments. These rocks have a banded structure of alternating 0.5 to 5–10 cm thick layers of significantly quartz and substantially diopsidic composition with very low Ti, Fe, and Mn oxides (0.0*n* wt.%), Na and K (0.0*n*–0.*n* wt.%) and aluminum (from 0.*n* to 1–2 wt.% Al_2O_3), but locally high phosphorus (up to 10–60% fluorapatite).

The Sludyanka quartz-diopside rocks have sporadic Cr and V enrichment and respective diverse Cr-V mineralization. The identified Cr and V phases and Cr-V-bearing minerals are silicates (clinopyroxenes, garnets, micas, chlorite, epidote, tremolite), simple and complex Cr-V and Ti-Cr-V oxides, tourmaline, titanite, sulfides, and some new species (Konev et al., 2001).

Rutile is quite a common Cr-V-bearing accessory in the quartz-diopside rocks. It occurs as Nb-bearing or niobian varieties: Nb-bearing rutiles are more abundant than niobian rutiles which are restricted to microinclusions in other minerals, most often Ti-V oxides. Bulk-rock Nb contents are 0.2 to 1–2 ppm (rarely 5 ppm) Nb and Nb_2O_5 is few wt.% in rutiles from these rocks. Relatively high Nb contents of 15.1 and 43.3 ppm were measured in two out of more than 100 rock samples, and niobian rutiles in these two samples had grain sizes large enough for analysis. Both samples are typical quartz-diopside banded rocks containing Cr-V minerals (goldmanite-uvarovite garnet, Cr-V spinel, karelianite-escolaite, Cr-V-bearing dioctahedral micas and titanite), mainly in the quartz bands, also rock-forming quartz and Cr-V-bearing diopside, and retrometamorphic tremolite and minor calcite.

Methods

Rutile was studied in pre-extracted specimens as its percentage in the Sludyanka quartz-diopside rocks is too low for detection and analysis. Opaque minerals were extracted from crushed rock of <0.18 mm fraction by electromagnetic separation and precipitation in weakly diluted Clerici solution (density 3.8–4.0 g/cm^3). The extracted grains were mounted on a film covered with carbonic glue and scanned on *LEO1430VP* and *JSM-6510* scanning electron microscopes, both with an Oxford Instruments *INCA Energy 350* analytical system, in Ulan-Ude and Novosibirsk, respectively.

The identified and preliminarily analyzed grains of Nb-rutiles and their intergrowths with other minerals were placed in epoxy resin blocks for making polished sections. The polished sections were analyzed at the Institute of Geochemistry (Irkutsk) on a *Jeol JXA-8200* SuperProbe, a high resolution SEM and a WD/ED Combined Electron Probe Microanalyzer (EPMA), equipped with 5 wavelength dispersive X-ray spectrometers (WDS) and an energy dispersive X-ray spectrometer (EDS) with a 133 eV lithium drift type silicon semiconductor detector. The grain interior was examined by electron microscopy in back-scattered (BSE) images at different magnifications. Elements were determined by their characteristic X-ray wavelengths on wave-dispersion spectrometers, at the following operation conditions: accelerating voltage 20 kV, beam current 20 nA, beam diameter 1 μm, count time 10 s along peak line plus 5 s for background on both sides of the peak line. The proprietary software was used for data processing. The element abundances were quantified by relating the peak intensities to certified laboratory standards of natural minerals and synthetic compounds: TiO_2, Cr_2O_3, V_2O_5, and Fe_2O_3 oxides; Nb, $NaLa(MoO_4)_2$ (La), and ZnS (Zn) metals; Sr-glass (Sr), ferberite $FeWO_4$ (W), diopside (Si, Mg), rodonite (Mn), pyrope (Al), zirconium (Zr), and F-apatite (F).

Thus measured concentrations of major oxides are about background values varying from 0.01 to 0.04 wt.% for different elements (Table 1). The table lists the oxides that were found in many grains (SiO_2, Al_2O_3, and ZnO) and those missing from some grains though being high in others (WO_3, Ta_2O_5, and Fe_2O_3). They are quoted to demonstrate the presence of the respective elements in rutile, though in minor amounts. Table 1 misses the oxides found in background concentrations in few cases only (ZrO_2, SrO).

Results

Among several tens of rutile grains extracted from two samples, 30 grains are niobian rutiles with Nb_2O_5 exceeding 10–12 wt.%. The grain sizes are mostly within 100–150 μm and crystal morphology correlates with composition. The rutiles with Nb_2O_5 < 12–15 wt.% are most often euhedral and