Submicrometer yttrian zircon coating and arborescent aeschynite microcrystals on truncated bipyramidal anatase: An electron microscopy study of miarolitic cavities in the Cuasso al Monte granophyre (Varese, Italy)

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Abstract

In this paper, we describe a unique occurrence of submicrometer polycrystalline zircon and arborescent aeschynite microcrystals on anatase with truncated bipyramidal habit, which were formed during low-temperature hydrothermal alteration of miarolitic cavities in a granophyre from Cuasso al Monte (Italy). The results suggest that temperatures in the range 100–250 °C and acidic conditions characterized the formation of anatase and that the preservation of this metastable phase was due to the presence of Nb (Nb/Ti atomic ratio ~0.032). We also detected an increase in the Nb content along the anatase rim. This is related to the incipient segregation of Nb driven by the transition toward the thermodynamically more stable rutile phase, which is possibly arrested by cooling below the diffusion blocking temperature. In these samples, zircon clearly postdates anatase and predates aeschynite. The resulting possible scenario is that F-rich hydrothermal fluids altered primary minerals at relatively high temperature and then, on cooling below 250 °C, deposited in the following sequence: anatase, zircon, and aeschynite, which reflects both elemental saturation and fluid fractionation with decreasing temperature. Finally, the aeschynite identified in this study through TEM-EDS shows an unusual chemical composition \([\text{Fe}_{0.15}\text{Ca}_{0.22}\text{Th}_{0.15}\text{U}_{0.13}\text{Y}_{0.10}\text{Pb}_{0.11}\text{Nb}_{0.05}\text{Ti}_{0.09}\text{Al}_{0.04}\text{As}_{0.02}\text{Sb}_{0.02}\text{O}_{1.94}]\), which cannot be reconciled with any known aeschynite sub-species. Conventional classification suggests that it should be called niobioaeschynite-(Y), although Y is present at only 0.10 apfu, and Fe (0.35 apfu) predominates in the A-site. This suggests that the aeschynite-group mineral classification system should be re-considered.

Keywords: Anatase, zircon, aeschynite, transmission electron microscopy (TEM), electron diffraction tomography (EDT)

Introduction

Anatase is one of the three natural polymorphs of TiO2, the other two being rutile and brookite. Minimum-energy structural configuration energies calculated using the electron-gas model (Post and Burnham 1986) show that rutile is more stable with respect to anatase and brookite by 4.0 and 20 kJ/mol, respectively. Rutile is the stable polymorph as bulk crystal at all temperatures and pressures (Smith et al. 2009) and, not surprisingly, the recurrent TiO2 phase in nature. Notwithstanding, anatase tends to form metastably under low-temperature hydrothermal conditions. Moreover, anatase is stable with respect to rutile when the TiO2 particle size is in the nanometer range (Zhang and Banfield 1998; Barnard and Curtiss 2005) because of its lower surface energy (0.74 vs. 2.22 J/m2, respectively; Levchenko et al. 2006). Anatase is tetragonal (space group \(I4_1/amd\), \(a = 3.784\), \(c = 9.515\) Å; Horn et al. 1972) with a structure based on CCP anions and consists of TiO octahedra that share four edges with other such octahedra (Fig. 1a).

Zircon (ZrSiO4) is a common accessory mineral occurring in a wide variety of igneous, metamorphic, and sedimentary rocks, in the latter case as detrital rather than as authigenic mineral.

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Reports on hydrothermal zircon are rare and mostly refer to low-temperature and low-pressure events associated with ore mineral deposition (Hoskin and Schaltegger 2003). The ability to incorporate minor and trace elements makes zircon a source of isotopic information and a desirable candidate for geochemical studies, including the ones concerning the evolution of the Earth’s crust and mantle, as well as geochronological applications. Able to resist to several geological cycles, zircon is a major constituent in the heavy-mineral fraction of sediments and is widely used in rock source provenance studies (Harley and Kelly 2007). Because of its chemical and physical durability, zircon has been proposed as candidate waste form for the long-term geological disposal of actinides from dismantled nuclear weapons and spent nuclear fuel (Ewing 1999). The large number of applications makes zircon one of the most studied minerals.

Zircon crystallizes in the same space group \(I4_1/amd\) as anatase, with cell parameters \(a = 6.604\), \(c = 5.979\) Å (Robinson et al. 1971). The structure consists of ZrO2 dodecahedra that share edges with each other and form chains parallel the two equivalent [100] and [010] directions. The chains are cross-linked by isolated, corner sharing SiO4 tetrahedra. The Si and Zr polyhedra also form edge-sharing chains of alternating SiO4 and ZrO2 polyhedra along [001] (Fig. 1b).