

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 $[(\text{Fe}_{0.35}\text{Ca}_{0.22}\text{Th}_{0.15}\text{U}_{0.13}\text{Y}_{0.10}\text{Pb}_{0.11})_{\Sigma 1.06}(\text{Nb}_{1.05}\text{Ti}_{0.69}\text{Al}_{0.14}\text{As}_{0.06})_{\Sigma 1.94}\text{O}_6]$, 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 TiO_2 , 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 TiO_2 phase in nature. Notwithstanding, anatase tends to form metastably under low-temperature hydrothermal conditions. Moreover, anatase is stable with respect to rutile when the TiO_2 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_6 octahedra that share four edges with other such octahedra (Fig. 1a).

Zircon (ZrSiO_4) 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.

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 ZrO_8 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 SiO_4 tetrahedra. The Si and Zr polyhedra also form edge-sharing chains of alternating SiO_4 and ZrO_8 polyhedra along [001] (Fig. 1b).

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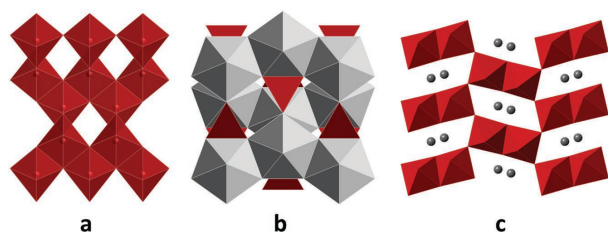


FIGURE 1. (a) TiO_6 polyhedra arrangement in the anatase structure (Horn et al. 1972) as seen down [100] (*c* vertical). (b) SiO_4 and ZrO_8 polyhedra arrangement in the structure of zircon (Robinson et al. 1971) as seen down [100] (*c* vertical). (c) A-site cations (gray circles) and B-site octahedra (red) arrangement in the structure of aeschynite (this study) as seen down [010] (*c* vertical). These three structures are unrelated to each other, i.e., they do not share any common feature(s) such as oxygen packing or polyhedral arrangement, consistently with the lack of crystallographic orientational relationship. (Color online.)

Aeschynite is a typical accessory mineral in granitic pegmatites (Černý and Ercit 1989), where it usually precipitates during the late-stage magmatic phase from Nb-, Ti-, Y-, HREE-enriched, and F-depleted fluids (Hanson et al. 1992). It has also been reported as a secondary mineral in hydrothermal alteration of Ti-silicates such as titanite (Papoutsas and Pe-Piper 2013; Prol-Ledesma et al. 2012), and chevkinite (MacDonald et al. 2015). Aeschynite has the general formula AB_2O_6 , where A is eightfold coordinated in a typical square antiprism and mostly occupied by Y, REE, Ca, and U, and B is sixfold coordinated and mostly occupied by Ti, Nb, and Ta. The structure is orthorhombic with space group $Pnma$ and cell parameters $a = 10.803\text{--}11.031$, $b = 7.448\text{--}7.532$, and $c = 5.150\text{--}5.189$ (Bonazzi and Menchetti 1999). It consists of pairs of edge-sharing BO_6 octahedra connected by corners to form double chains running in a zigzag pattern along the [010] (Aleksandrov 1962).

In this study, we employ scanning (SEM) and transmission electron microscopy (TEM), precession-assisted electron diffraction tomography (P-EDT), and energy-dispersive spectroscopy (EDS) to describe a unique occurrence of submicrometer polycrystalline zircon and arborescent aeschynite microcrystals on anatase with a truncated bipyramidal habit, which were formed during low-temperature hydrothermal alteration of miarolitic cavities in a granophyre from Cuasso al Monte (Italy). With this study, we aim to contribute to the understanding of remobilization and fractionation of incompatible rare-earth elements (REE, including Y), actinides (U, Th), and high field strength elements (HFSE) such as Zr, Nb, and Ti, during post-magmatic hydrothermal stages. This is fundamental to determine the complete history of the host rocks and, as a consequence, the mineralizing potential of the fluids and the value of the U/Pb and Th/Pb absolute dating.

SAMPLE AND GEOLOGICAL OUTLINES

Anatase crystals with a zircon coating were found in millimeter-sized miarolitic cavities in a granophyre from Cuasso al Monte. The Cuasso al Monte granophyre is a sialic hypoabyssal rock composed essentially of K-feldspar, albite, quartz, and minor biotite. Known by the commercial name of Red Porphyry, it is greatly appreciated for its warm and

vivid color, hardness, and resistance to erosion, and for these reasons largely employed to create floorings, coverings, and building elements.

The red porphyry crops out uninterruptedly along the western shore of Lake Lugano until Monte Martica (Fig. 2), and it is genetically associated with a late Hercynian post-orogenic magmatism of K-rich alkaline affinity from intermediate to acidic composition, known as the “Serie dei Laghi” (Boriani et al. 1992). The magma was emplaced either as andesitic to rhyolitic ignimbrites or as pink subsolvus granites at subvolcanic levels (Bakos et al. 1990). Isotopic investigations showed that it was generated from a mantle-derived primary magma that experienced crustal contamination (Pinarelli et al. 1993, 2002). The most felsic products (including the red porphyry) appear to have been generated mainly by crystal fractionation processes from an intermediate magma, already contaminated.

The representative bulk composition of the red porphyry is 75.26% SiO_2 , 13.39% Al_2O_3 , 5.11% K_2O , 3.37% Na_2O , 1.14% FeO , 0.85% H_2O , 0.75% CaO , 0.25% Fe_2O_3 , 0.10% MgO , 0.09% P_2O_5 , 0.08 TiO_2 , and 0.03% MnO . Rb/Sr dating indicates an age of 275 ± 8 Ma (Bakos et al. 1990). Millimeter-sized miarolitic cavities are widespread within the granophyre. Circulation of abundant late hydrothermal fluids was responsible for the local alteration of feldspars, chloritization of biotite, and the deposition of abundant carbonates, fluorite, and sulfides in the miarolitic cavities (Pezzotta et al. 1999, 2005). In the present study, in addition to K-feldspar, albite, and quartz, we found chamosite, fluorite, REE-carbonates, sphalerite, anatase (with zircon coating), and aeschynite (Fig. 3), the latter determined by TEM.

EXPERIMENTAL METHODS

SEM-EDS investigations on carbon-coated sample fragments were performed at the Department of Earth and Environmental Sciences at the University of Milano-Bicocca with a Tescan VEGA TS 5136XM instrument operating at 20 keV and equipped with an EDAX GENESIS 4000XMS EDS system.

TEM observations were performed at the Department of Physical Sciences, Earth, and Environment of the University of Siena with a JEOL JEM 2010 operating at 200 keV. Images were collected on Fuji imaging plates (3000×3760 pixels $\times$ 14 bits) and with an Olympus Tengra CCD camera (2000×2000 pixels $\times$ 14 bits). TEM foils were prepared using the FIB technique (Wirth 2009) at the German Research Center for Geosciences (GeoForschungsZentrum GFZ), Potsdam, Germany). In addition, micrometer-size aeschynite crystals were picked up using a micromanipulator and deposited on carbon-coated Cu-grids.

TEM energy-dispersive X-rays analyses were collected using two different systems: An Oxford Link EDS spectrometer attached to the JEOL JEM 2010 of Siena University; and an EDAX EDS spectrometer attached to a FEI Tecnai 20F (Department of Earth Sciences, Milano University). In both cases, the standardless method within the Cliff-Lorimer approximation (Cliff and Lorimer 1975) were used for semi-quantitative analyses.

Precession-assisted electron diffraction tomography (P-EDT) was performed operating the JEOL JEM 2010 (Siena University) in selected-area electron diffraction (SAED) mode and in combination with a SpinningStar precession device (NanoMEGAS). SAED patterns were acquired with the Olympus Tengra CCD camera. Two acquisition series were performed, one rotating the sample around the α -axis and the other rotating the sample around the β -axis of the specimen holder. For cell parameter determination, only the α -tilt acquisition was used. For ab initio structure determination and refinement, intensities from both acquisitions were merged with scale factor 1. Structure solution was obtained ab initio by direct methods as implemented in the SIR2014 program (Burla et al. 2015) employing reflections up to 0.8 Å resolution and adopting a fully kinematical approximation ($I_{hkl} \sim F_{hkl}^2$). Structure refinement was performed with the least-square method as implemented in the SHELX-97 program (Sheldrick 1997). Since electron scattering factors for Th, Y, and Nb are currently not available (Doyle and Turner 1968), U, Zr, and Mo scattering factors were used, respectively.

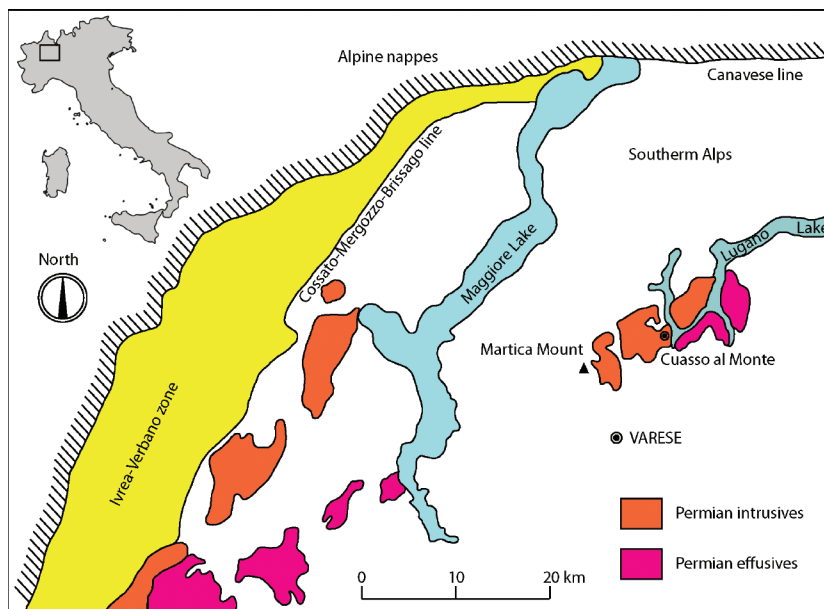


FIGURE 2. Map of the Hercynian plutonic and volcanic rocks in the Southern Alps and at the locality of Cuasso al Monte (modified from Pezzotta et al. 2005). (Color online.)

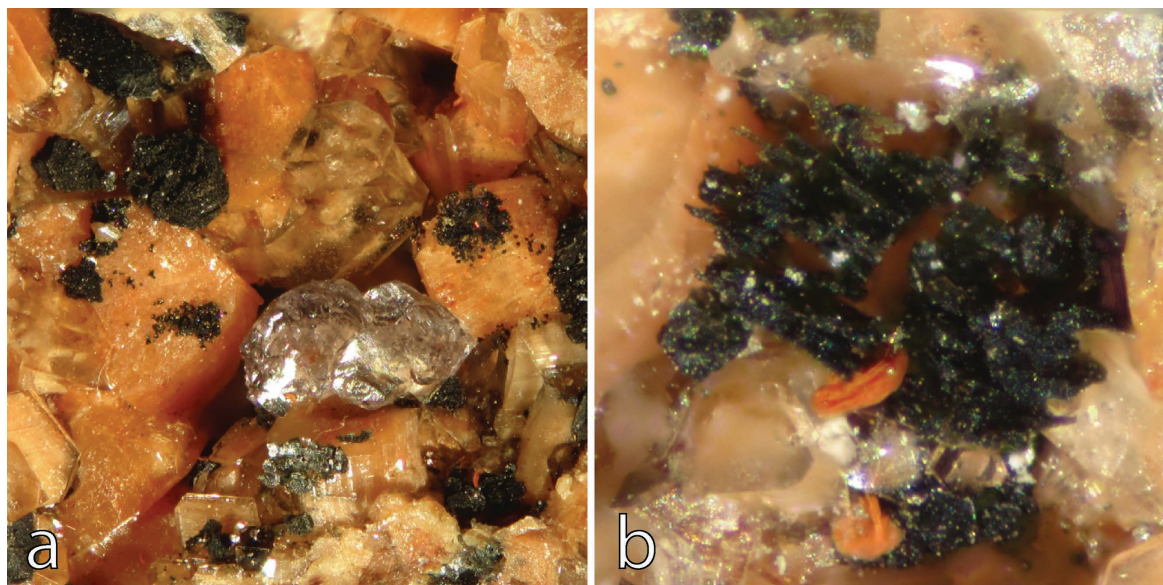


FIGURE 3. Optical stereomicrograph of a millimeter sized geode within the granophyre from Cuasso al Monte. (a) The large orange crystals forming most of the mineral association are K-feldspar; lamellar translucent crystals as in the lower left are albite (which also forms overgrowths on K-feldspar); the translucent mineral with botryoidal appearance at the center is fluorite and the translucent, faceted grain above fluorite is quartz; dark crystals are chamosite and anatase in granular aggregates. Chamosite forms lamellar, black-greenish grains (b) with iridescence due to zircon-coated anatase (not resolved). The small, orange, discoidal crystals with earthy luster at the center of the image are REE-carbonates [photograph width ~5 mm (a) and 1 mm (b)]. (Color online.)

RESULTS

The anatase crystals are ~50 μm in size and show a truncated bipyramidal habit, with ragged surfaces (Fig. 4a). Some growth features, possibly etch marks, are also observed on pinacoidal and pyramidal faces. In certain areas, arborescent crystals are also present (Fig. 4b). These crystals were identified as

aeschnite-group minerals by subsequent TEM investigations (see below). High magnification observations using SEM reveal that the ragged appearance of the anatase is due to submicrometer lenticular crystals in random orientations (Fig. 4c), whose major elements are Ti, Zr, Si, and O from SEM-EDS spectra, suggesting a mixture of anatase and zircon. Bright-field TEM

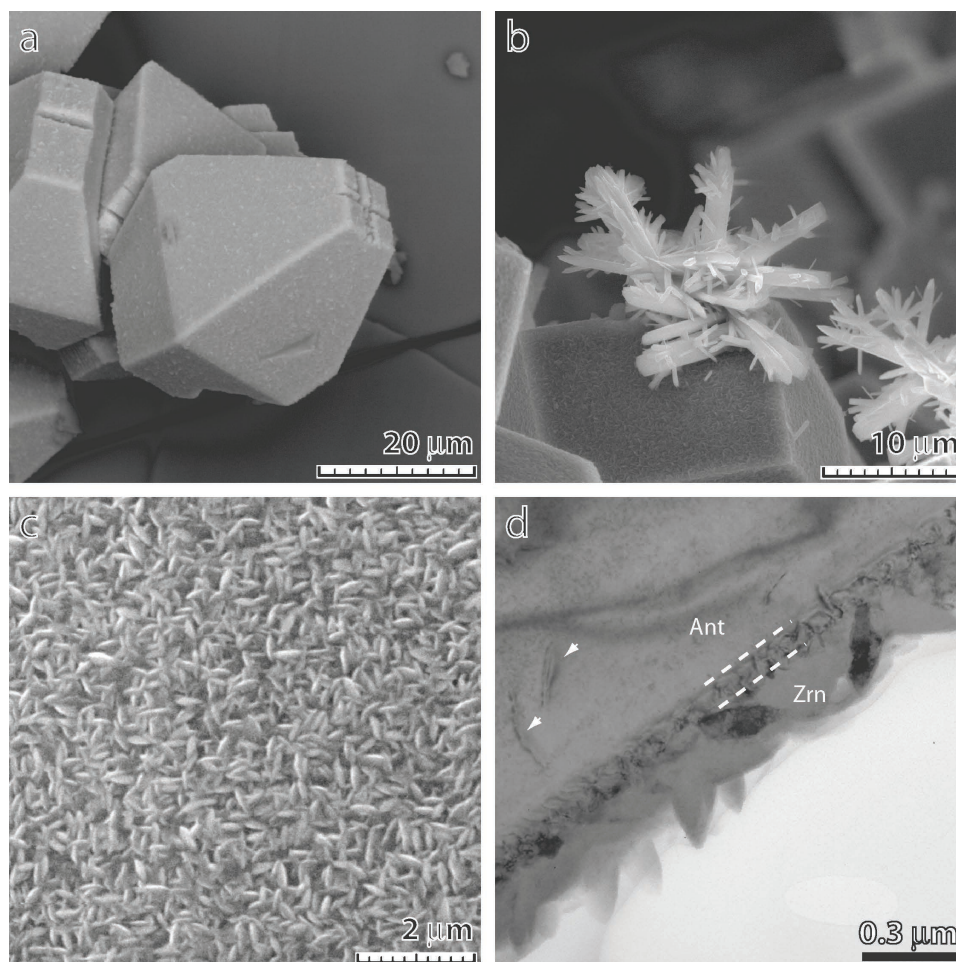


FIGURE 4. SEM-BSE images (a to c) and TEM-BF image (d) of anatase, zircon, and aeschynite: (a) anatase truncated tetragonal bipyramids. Note the roughness of the surface and the etch marks on pinacoidal and pyramidal facets. (b) Arborescent crystals of aeschynite on anatase. (c) High-magnification image of the anatase surface: the roughness is due to submicrometer lenticular crystals in random orientation. (d) A cross section of the zircon-anatase interface. Note the strained interface separating the randomly oriented zircon (Zrn) crystals from anatase (Ant). Some dislocations in anatase are also indicated (arrows).

TABLE 1. Semi-quantitative TEM-EDS compositions of anatase and zircon (average of 6 and 8 spot analyses, respectively) calculated on the basis of 4 O atoms (1 σ relative error in brackets; values in *italics* when below the 2 σ level)

	Anatase		Zircon	
	Mean	Range	Mean	Range
Si	0.03(1)	0.01–0.04	0.97(8)	0.91–0.99
Ti	1.89(4)	1.83–1.94	0.05(1)	0.03–0.07
Y	<i>0.00(1)</i>	<i>0.00–0.01</i>	0.25(6)	0.21–0.32
Zr	<i>0.00(2)</i>	<i>0.00–0.02</i>	0.78(6)	0.73–0.83
Nb	0.06(2)	0.03–0.09	<i>0.02(5)</i>	<i>0.00–0.05</i>
Cat	1.99	1.98–2.00	2.06	2.05–2.11

images and SAED patterns on FIB foils incorporating these crystals, confirm that a thin 0.3 μm thick layer of zircon crystals surrounds the anatase. The zircon crystals have lenticular shape, are a few hundred of nanometers long, and are inclined relative to the anatase surface (Fig. 4d). The zircon crystals appear to have nucleated on the periphery of anatase, from which they are separated by a band about 100 nm thick, characterized by a strong strain contrast. The dimension of the zircon crystals and their average separation are of the order of the wavelength of visible light, i.e., few hundreds of nanometers. This observation may explain why the anatase crystals appear iridescent at the optical stereomicroscope (Fig. 3b).

TEM-EDS spot analyses were taken on anatase, zircon, and on the interface between the two with a nominal spot size of 25 nm. Average compositions of anatase and zircon are reported in Table 1. Up to 0.32 atoms per formula unit (apfu) of Y were detected in zircon and up to 0.09 apfu of Nb in anatase. A compositional profile from anatase to zircon along a distance of about 600 nm across the interface is reported in the graph in Figure 5. It should be noted how the Nb concentration forms a maximum along the anatase rim, close to zircon. A possible explanation could be that the highly defective local structure at the zircon-anatase interface, as implied by the strong strain contrast, could provide a better coordination environment for Nb than in the adjoining ordered phases. Alternatively, this feature may indicate a diffusion of Nb from anatase toward the rim, revealing an incipient anatase-to-rutile phase transition (see discussion section).

Some arborescent crystals were picked up with a micromanipulator, deposited on carbon-coated Cu-grids and examined by TEM. A representative crystal is shown in Figure 6, along with the related SAED pattern and EDS spectrum. P-EDT allowed an *ab initio* structure determination, which was fully consistent with the aeschynite-group mineral structure (Fig. 1c; cf. CIF for the relevant experimental and crystallographic data¹).

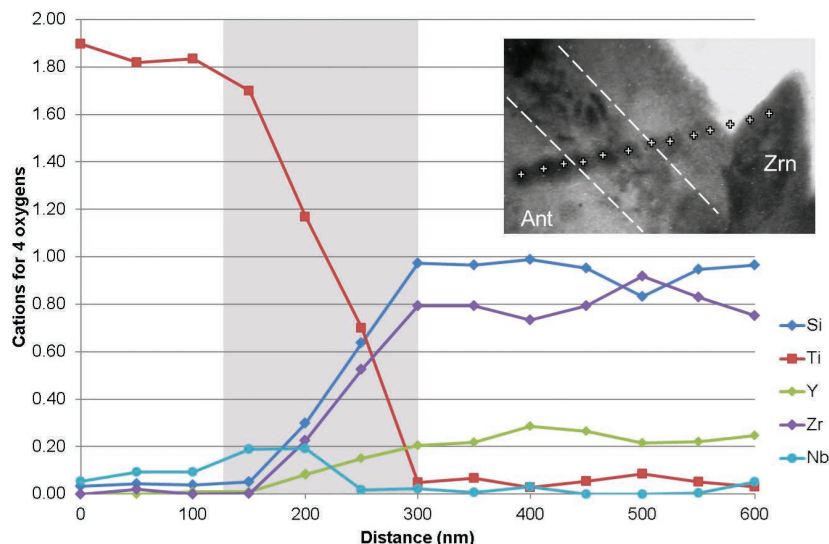


FIGURE 5. Compositional profile across the anatase/zircon interface for a distance of about 600 nm. The shadowed region in the plot corresponds to the band showing strain contrast and outlined by dashed lines in the inset. The inset also shows the trace of the compositional profile as resulting from the contamination stains formed at beam positions during spot analysis collection, which were taken at intervals of ~50 nm (crosses). Note the Nb maximum at the anatase/zircon interface. (Color online.)

Crystals are blade shaped, elongated along [010], and flattened on (001). Surprisingly, EDS spectra taken with three different spectrometers, either on TEM or SEM, revealed a peak at 1.74 keV that was systematically labeled as $\text{SiK}\alpha$ by the automatic peak assignment routine of the EDS system. However, it is well known that Si, which is always in tetrahedral coordination at ambient conditions, cannot be hosted in the aeschynite structure, which contains only octahedral or larger cation sites. Since the $\text{TaM}\alpha_1$ line at 1.71 keV falls close to the $\text{SiK}\alpha_1$ line and cannot be easily discriminated with EDS systems, Ta, which is a common constituent of aeschynite-group minerals, was assumed to be part of the composition. However, no reasonable peak fitting, nor a consistent chemical formula were obtained with Ta, which was often rejected by the quantification routine, pointing to the absence of $\text{TaL}\alpha_1$ at 8.15 keV and $\text{TaL}\beta_1$ at 9.34 keV in the spectra. Silicon was thus suspected to be present as silica inclusions or within metamict areas of the sample. This is supported by the bright-field (BF) images of the aeschynite, which show a mottled contrast typical of metamict minerals (Fig. 6a) and high-resolution (HR) images, which show brighter domains lacking lattice fringes indicative of long-range order (Fig. 6c). Although no compositional differences between the dark and bright domains could be spotted because the size of the domains is smaller than the actual TEM-EDS probe, the domains were assumed to contain Si, as often observed in other metamict minerals (e.g., Bonazzi et al. 2006, 2009). Silicon was therefore not considered in the derivation of the chemical formulas of aeschynite, which are reported in Table 2 for the three crystals investigated in this study. It should be noted that their composition varies considerably from crystal to crystal and within the same crystal, especially with regard to the Ti/Nb ratio. Moreover, all crystals contain large amount of Fe that was assumed to be Fe^{2+} and assigned to the A-site to fit the aeschynite-group mineral stoichiometry. In

one case (crystal 3), a significant excess of A-site cations and a deficiency of B-site cations arises, which may indicate that part of the Fe is oxidized and occupies the B-site. The average chemical composition of the investigated crystals calculated on the basis of 3 cations comes out as $(\text{Fe}_{0.35}\text{Ca}_{0.22}\text{Th}_{0.15}\text{U}_{0.13}\text{Y}_{0.10}\text{Pb}_{0.11})_{\Sigma 1.06}(\text{Nb}_{1.05}\text{Ti}_{0.69}\text{Al}_{0.14}\text{As}_{0.06})_{\Sigma 1.94}\text{O}_6$, which identifies the mineral as niobioaeschnite, but deviates considerably from any known aeschynite species considering the exceptionally high Fe content that predominates in the A-site.

DISCUSSION AND CONCLUSIONS

Several authors have suggested a strong hydrothermal alteration for many rocks of the “Serie dei laghi” suite, including the granophyre from Cuasso al Monte (e.g., Bakos et al. 1990; Pinarelli et al. 1993, 2002; Pezzotta et al. 1999, 2005). As reported by Pezzotta et al. (2005), a massive liberation of fluids occurred because of the saturation levels attained during the crystallization of the silicic melt. These fluids produced an alteration that changed the color of K-feldspar to pink, transformed biotite to chlorite, and altered the Ca-rich plagioclase to late-stage albite, epidote, and calcite.

A series of hydrothermal minerals were deposited in the miarolitic cavities with decreasing temperature during this stage. Pezzotta et al. (2005), in a study of Sc-silicates found in these miarolytic cavities, suggest two possible models to explain their mineral assemblage, one of which is consistent with a late hydrothermal alteration. According to this hypothesis, HFSE, Sc, and Y+REE were first incorporated into gadolinite-(Y) and siderophyllite crystallizing from the residual magma. The subsequent, aggressive effect of subcritical hydrous F-rich fluids on early formed gadolinite-(Y), siderophyllite, and feldspars provided the necessary elemental source (REE, Y, Fe, Ca, Ti, and possibly Nb, Ta, Sc, etc.) for the crystallization of secondary minerals. The

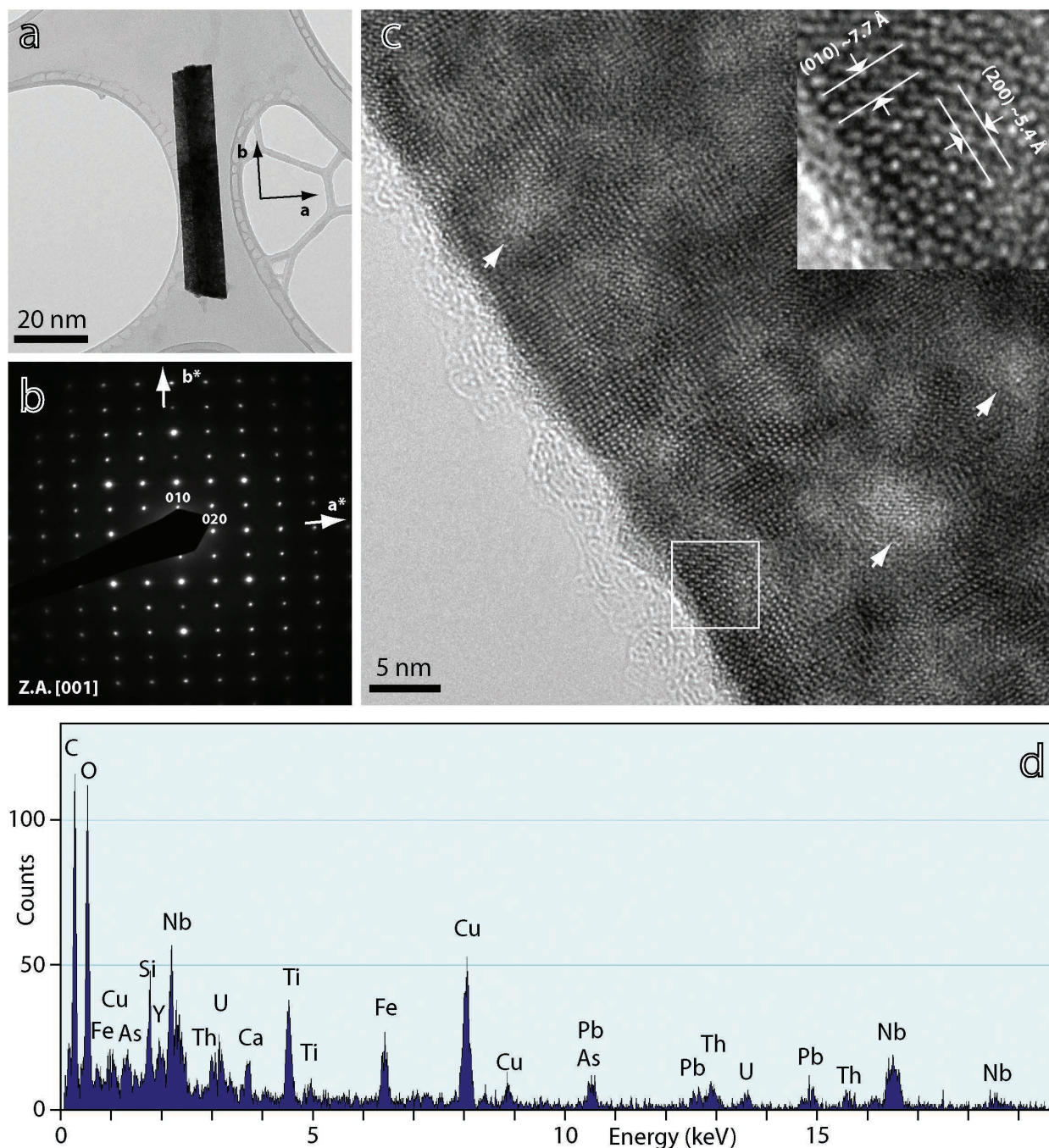


FIGURE 6. (a) BF-TEM image of an arborescent crystal picked up from the miarolitic cavity and put on a carbon coated Cu-grid and (b) related SAED taken with the incident beam parallel to [001]. This pattern is consistent, within the experimental error and net of dynamical effects— $0kl$ for $k = 2n$ only—with aeschynite ($Pnma$, $a \sim 10.80$, $b \sim 7.68$, $c \sim 5.10$ Å, Capitani et al. 2016). (c) HR-TEM image showing mottled contrast typical of metamict minerals, with brighter areas lacking of long-range order (arrows). The main lattice planes within a crystalline area (square) are showed (inset). (d) Representative EDS spectrum (Cu peaks are from the grid). (Color online.)

anatase, zircon, aeschynite, and minor REE-carbonates from the miarolitic cavities, and described in this study, may have formed from F-rich fluids.

In nature, anatase is known to form under low-temperature hydrothermal conditions. For example, in epithermal Au

systems the anatase-to-rutile transformation occurs at 150–200 °C (Hedenquist et al. 2000). Papoulis et al. (2009), in a study of volcanic rocks from the Limnos Island (Greece), report the formation of halloysite and anatase from hydrothermal alteration of ilmenite and biotite at temperatures as low as 100 °C. In a recent

TABLE 2. TEM-EDS compositions of niobioaeschynite crystals calculated on the basis of tree cations per formula unit (1 σ relative error in parentheses) and their average (standard deviation in parentheses); Ca, Fe, Y, Pb, Th, and U are assigned to the A-site; Al, Ti, As, and Nb to the B-site

	xx 1		xx 2		xx 3		Mean
	1	2	3	4	5	6	
Al	0.08(3)	0.15(1)	0.16 (2)	0.18 (2)	0.17 (4)	0.08 (4)	0.14 (5)
Ca	0.16(4)	0.25(1)	0.20 (2)	0.23 (2)	0.28 (3)	0.20 (3)	0.22 (4)
Ti	0.58(5)	0.72(2)	0.82 (3)	0.63 (3)	0.59 (4)	0.77 (5)	0.69(10)
Fe ²⁺	0.30(4)	0.35(2)	0.32 (2)	0.30 (2)	0.46 (4)	0.39 (4)	0.35 (6)
As ³⁺	0.05(6)	0.00 –	0.07 (3)	0.00 –	0.11 (3)	0.12 (3)	0.06 (5)
Y	0.07(4)	0.17(2)	0.10 (2)	0.09 (2)	0.05 (5)	0.10 (5)	0.10 (4)
Nb	1.31(10)	1.04(4)	0.98 (5)	1.22 (6)	0.93 (6)	0.83 (6)	1.05(18)
Pb ²⁺	0.12(6)	0.11(2)	0.07 (2)	0.07 (1)	0.15 (2)	0.15 (3)	0.11 (3)
Th	0.25(4)	0.15(1)	0.14 (2)	0.14 (2)	0.12 (2)	0.12 (2)	0.15 (5)
U ⁴⁺	0.08(4)	0.05(1)	0.14 (2)	0.13 (2)	0.13 (2)	0.25 (3)	0.13 (7)
Σ_A	0.98	1.08	0.97	0.97	1.19	1.20	1.06
Σ_B	2.02	1.92	2.03	2.03	1.81	1.80	1.94

Notes: Analyses on xx1 and xx1 were acquired with the Edax EDS system; analyses on xx3 with the Oxford EDS system. The latter refers to the crystal studied by P-EDT.

study, Andersen et al. (2016) describe an anatase-xenotime-brookite-fluorite mineral assemblage in carbonatite dikes and veins peripheral to the Bear Lodge alkaline complex (Wyoming), formed from low-temperature (<200 °C), F-rich fluids. Sabyrov et al. (2013) hydrothermally processed anatase nanoparticles at 250 °C and a pH 1 and 3, obtaining the rutile phase. They also found that the anatase-to-rutile transition and rutile particle growth rates increase as the initial anatase particle size and pH decrease. These observations suggest that anatase at Cuasso al Monte may have formed in a temperature range of 100–250 °C.

Barnard and Curtiss (2005) investigated the effects of surface chemistry on the morphology and phase stability of TiO₂ nanoparticles using a thermodynamic model based on surface free energy obtained from first-principle calculations. They found that anatase nanoparticles are stabilized with respect to rutile by surface adsorbates containing a large amount of hydrogen, i.e., in acidic conditions. Moreover, the crystal morphology is truncated bipyramidal under hydrogenated conditions, but starts to develop tetragonal prism facets under progressively lower hydrogenated conditions. This is in agreement with the fact that experimental synthesis of TiO₂ nanoparticles in acidic conditions almost exclusively result in truncated tetragonal anatase bipyramids with {101}, {001}, and {010} facets (Penn and Banfield 1999; Zaban et al. 2000; Gao and Elder 2000). These observations suggest that truncated bi-pyramidal anatase from Cuasso al Monte probably formed under acidic conditions. Bulk anatase, however, is metastable with respect to rutile at all temperatures and pressures (Smith et al. 2009), therefore, how could it remain stable during growth?

In annealing experiments between 600 and 900 °C, Arbiol et al. (2002) reported that the anatase-to-rutile phase transition is strongly hindered for Nb-doped TiO₂ samples. Before and during the phase transition, for amounts of Nb higher than 2–3% Nb/Ti atoms, they observed NbO segregation at the rims of the TiO₂ nanoparticles. Similarly, Hirano and Sato (2011), in annealing experiments between 800 and 1200 °C, found that the anatase-to-rutile transition in Y and Nb co-doped samples (Y_xNb_xTi_{1-2x}O₂, x = 0–0.20) is shifted toward higher temperatures. They also noticed a YTiNbO₄ aeschynite-type structure as a coexisting reaction product.

These high-temperature experiments suggest that Nb could be an inhibiting agent in the anatase-to-rutile transformation even at low temperature, since Nb can enter the TiO₂ structure through two principal heterovalent substitutions:



Both substitutions cause local charge unbalance and lattice strain because of the different charge and ionic radius of the involved octahedrally coordinated cations, namely Ti⁴⁺ (ionic radius = 0.61 Å), Nb⁵⁺ (0.64), and Ti³⁺ (0.67) (Shannon 1976). In addition, substitution (1) cause cation vacancies. Simple crystal-chemistry considerations suggest that the anatase structure can tolerate higher cation vacancies, and therefore higher Nb content, than the rutile structure. In fact, Ti-octahedra share four edges in anatase and only two in rutile. It follows that local charge unbalance can be better compensated by neighboring Ti cations in anatase than in rutile. Experimental results confirm this hypothesis, since anatase and rutile prepared from the same solution and heat treated at 600 °C show 20 and 10% of cation vacancies, respectively (Morales et al. 1995). On the other hand, the high value of the rutile bulk module (210 GPa) compared with that of anatase (178 GPa), suggests that the introduction of sterically costing defects in rutile would require a higher energy per defect than in the case of anatase (Arbiol et al. 2002 and references therein).

In summary, temperatures in the range 100–250 °C and low pH conditions led to the formation of anatase at Cuasso al Monte. The preservation of the metastable phase may be due to the presence of Nb (Nb/Ti atomic ratio ~0.032). On the other hand, the increase of the Nb content along the anatase rims may indicate an incipient segregation of Nb driven by the transition toward the thermodynamically more stable rutile phase, possibly arrested by cooling below the diffusion blocking temperature.

Hydrothermal zircon typically forms at temperatures between 600 °C (magmatic-to-hydrothermal transition) and 300 °C (mesothermal ore-forming systems) (Schaltegger 2007). However, Bojanowski et al. (2012) reported the formation of authigenic zircon in Mississippian shales (Scotland) at around 270 °C. Rasmussen (2005) reported about minute (typically <3 μm) zircon outgrowths on detrital grains in low-grade sedimentary rocks from different regions of the world at ~250 °C, and related their growth to the transport of Zr in aqueous fluids, possibly as F-complexes. Hay and Dempster (2009), in a study of detrital zircon in Carboniferous sandstones from Scotland, showed that metamict zircon alters and recrystallizes to nanocrystalline zircon at temperatures below 100 °C through a dissolution-reprecipitation process. This would imply that Zr can be remobilized at low temperatures and stabilized in the fluid in the presence of F until the combined effects of decreasing temperature and decreasing F-activity, possibly related to the crystallization of fluorite, cause the breakdown of Zr-complexes and the precipitation of low-temperature nanocrystalline zircon.

Recent experimental studies (i.e., Rapp et al. 2010; Tanis et al. 2015; Timofeev et al. 2015), although performed at *T* and *P* conditions beyond the range expected for Cuasso al Monte, demonstrate that the solubility and aqueous complexation of

Ti⁴⁺ and Nb⁵⁺ is extremely high in F-rich solutions, and that the removal of F during precipitation of F-bearing minerals decreases Ti+Nb solubility and promotes the crystallization of (Ti+Nb)-bearing minerals.

In the granophyre at Cuasso al Monte, the zircon coating on the anatase crystals clearly postdates the anatase and predates the aeschynite. A possible scenario is that F-rich hydrothermal fluids altered the primary minerals at relatively high temperature and then, on cooling, deposited anatase, zircon, and aeschynite in a sequence, which reflects elemental saturation and fluid fractionation with decreasing temperature over a range between 250 and 100 °C. At the same time, few REE-carbonates formed in pockets during this latest stage, testifying to the minor presence of CO₂ in the fluid.

IMPLICATIONS

In this study we describe a unique occurrence of microscopic anatase with a truncated bipyramidal habit coated with sub-micrometer polycrystalline zircon and arborescent aeschynite microcrystals, deposited under low-pressure (<500 bar; Bakos et al. 1990), low-temperature (250–100 °C), low-pH, hydrothermal conditions. While anatase is known to form under these conditions, the genesis of zircon, associated with hydrothermal activity, is usually placed between 600 and 300 °C (Schaltegger 2007), though there are exceptions to this rule (e.g., Bojanowski et al. 2012; Rasmussen 2005; Hay and Dempster 2009). In this work, we propose that Zr could be remobilized from primary minerals and recrystallized as new zircon at temperatures lower than 250 °C. This finding implies that secondary zircon might be used for the dating late-stage hydrothermal activities in magmatic rocks. On the other hand, it also suggests that the value of U/Pb and Th/Pb in geochronological studies involving zircon could be affected by late-stage remobilization of Th and U from the primary accessory minerals, as testified by the significant amount of these actinides in the aeschynite-group minerals.

EDS analyses are generally considered semi-quantitative, but sufficiently accurate for mineral identification (e.g., Rasmussen 2005; Papoutsas and Pe-Piper 2013; Capitani 2017), especially if a complementary technique is used for the characterization of the mineral, as in this case, i.e., electron diffraction tomography. The aeschynite identified in this study possess an unusual chemical composition that cannot be reconciled with any known member of the aeschynite supergroup. It should be named, according to the current nomenclature on rare earth minerals (Bayliss and Levinson 1988) niobioaeschnite-(Y), because Y, although present with only 0.10 apfu, is the only REE at the A-site, being Fe (0.35 apfu) the predominant cation at this site, followed by Ca (0.22). The finding of this unusual aeschynite composition asks for a reconsideration of the classification of this mineral group.

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