Xenotime-(Y) and Sn-rich thortveitite in miarolitic pegmatites from Baveno, Southern Alps, Italy

A. GUASTONI1, F. NESTOLA1,*, C. FERRARIS2 AND G. PARODI2

1 Department of Geosciences, University of Padova, Via Gradenigo 6, I-35131 Padova, Italy
2 Laboratoire de Minéralogie et Cosmochimie Muséum National d’Histoire Naturelle, Rue Buffon 61, CP52, 75005 Paris, France

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ABSTRACT

Xenotime-(Y), (Y,REE)PO₄, and thortveitite, (Sc,Y)₂Si₂O₇, in a miarolitic cavity in a niobium, yttrium, fluorine (NYF) granitic pegmatite at Baveno, Verbania, Southern Alps, Italy, were investigated by electron microprobe analysis and single-crystal X-ray diffraction. Fluorine has an important role as a complexing agent for Y and REEs in supercritical pegmatitic fluids; annite-siderophyllite and chamosite are the most likely sources of the Y and REEs. The thortveitite from Baveno contains up to 3.20 wt.% SnO₂, an unusually high Sn content. Xenotime-(Y) is enriched in Gd in comparison to other Alpine xenotimes. Quantitative chemical data and measurements of the lattice parameters show that a higher scandium content results in a smaller unit-cell volume in thortveitite. The substitution of REEs for Y up to ~20 mol.% has little effect on the unit cell of xenotime-(Y). The textures of xenotime-(Y) and thortveitite provide information about the dissolution and crystallization processes in the miarolitic cavity.

KEYWORDS: Baveno, miarolitic cavities, NYF pegmatite, thortveitite, xenotime-(Y).

Introduction

CRYSTALLIZATION processes of accessory minerals which occur in miarolitic cavities support the role of water, fluorine and carbonate as complexing agents to transport incompatible elements at lower temperatures in silicate melts containing niobium, yttrium, fluorine (NYF) rare-element pegmatites (Wood, 1990; Gramaccioli et al., 2000b; Pezzotta et al., 2005; London, 2008; Guastoni and Nestola, 2010).

Crystal growth processes in pegmatites are controlled by factors including the kinetics of nucleation, diffusion and the selective adsorption of elements at fluid–crystal interfaces. These processes are primarily controlled by the satura-

* E-mail: fabrizio.nestola@unipd.it
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recent set of analyses of thortveitite, associated with xenotime-(Y), from this occurrence, have high SnO$_2$ contents (Guastoni and Nestola, 2010). Elevated SnO$_2$ contents in thortveitite have also been reported by Raade et al. (2004); they reach 5.6 wt.% in crystals from miarolitic cavities in the Heftetjern granitic pegmatite in Norway.

This work describes the partial dissolution of xenotime-(Y) and subsequent crystallization of Sn-rich thortveitite in the miarolitic cavity. The role of supercritical fluids during dissolution of xenotime-(Y) and crystallization of Sn-rich thortveitite is discussed. Detailed studies of such systems provide insights into natural processes in systems that are difficult to reproduce in laboratory experiments.

**Geological sketch of the Baveno granite**

The Baveno pink and white granites have been extensively quarried for ornamental purposes from the eighteenth century (Barzan, 1853). The late-Hercynian Baveno magmatic intrusion in the Western-Southern Alps is characterized by multiple intrusions, which are grouped in the Laghi Granite series (Boriani et al., 1988, 1995). These are small- to medium-sized granitic plutons, including the Montorfano, Baveno-Mottarone and Alzo-Roccapietra granites, with a metaluminous calc-alkaline character. They are enriched in large ion lithophile elements, suggesting a hybrid nature for their parental melts (Pinarelli et al., 2002). The magmas that formed the Laghi Granites are the products of combined assimilation fractional crystallization of mantle-derived hybrid magmas residing at the base of the crust (Stille and Buletti, 1987; Pinarelli et al., 2002). The best estimates of the age Laghi Granites from Rb–Sr whole-rock studies are 277±8 Ma (Pinarelli et al., 1988) and 276±7 Ma (Schaltegger and Brack, 2007). The Baveno granite contains pegmatite pockets and miarolitic aplite/pegmatite dykes, most commonly in the pink granite. The pockets and cavities contain accessory minerals including fluorite, fluorapatite, fluorine-rich annite and siderophyllite, gadolinite-group minerals and a number of Nb-, Ta- and Y-bearing oxides. These minerals allow the pegmatites to be classified in the NYF (niobium, yttrium, fluorine) family of the miarolitic rare earth element (MIREE) subclass (Pezzotta et al., 1999; Černý and Ercit, 2005).

**Experimental**

Backscattered-electron (BSE) images of Sn-rich thortveitite and xenotime-(Y) were collected on a Jeol 5600 LV instrument at the Museo di Storia Naturale di Milano at 20 keV under low vacuum conditions (15 Pa). The chemical compositions of xenotime-(Y) and Sn-rich thortveitite were determined using a Cameca-Camebax SX50 electron microprobe operating in WDS mode at an accelerating voltage of 20 kV, current of 20 nA, with a ~1 μm beam diameter, and with 10 and 5 s counting times on the peak and background, respectively. These data were converted to oxide wt.% using the PAP correction program supplied by Cameca (Pouchou and Pichoir, 1985).

The following standards, lines and analysing crystal were used: wollastonite (SiKα, CaKα: TAP); corundum (AlKα: TAP); apatite (PKα: TAP); Fe$_2$O$_3$ (FeKα: LiF), MnTiO$_3$ (MnKα: LiF); ScPO$_4$ (ScKα: PET); Zr-Y-REE-silicates (ZrLα, YLα, REELα and NdLβ: LiF), UO$_2$ and ThO$_2$ (UMα and ThMα: PET), Nb (NbLα: PET). The elements Ca, Ce, Hf, La, Mg, Pb and U were sought but found to be below the experimental detection limits.

Lattice parameter determinations were performed by single-crystal X-ray diffraction using a STOE STADI-IV four-circle diffractometer equipped with a CCD detector. The sample–detector distance was 60 mm and graphite-monochromated MoKα radiation used at 50 kV and 40 mA. The crystal sizes were $0.13 \times 0.10 \times 0.07$ mm and $0.11 \times 0.08 \times 0.06$ mm for thortveitite and xenotime-(Y), respectively.
Occurrence and mineral chemistry

The specimen used for this study is from the collection of the Galerie de Mineralogie et de Geologie of the Musee National d'Histoire Naturelle in Paris. The sample investigated is one of several studied by AG under a European ‘Synthesys’ project devoted to the study of Baveno minerals in European museum mineral collections.

Platy prismatic Sn-rich thortveitite crystals, up to 600 μm in size, are intergrown with xenotime-(Y) on the specimen (Fig. 1). The xenotime-(Y) occurs as bipyramidal crystals up to 500 μm long, which have corroded bipyramidal faces produced by dissolution (Fig. 2). Both minerals occur in a miarolitic cavity in laminated pale blue albite, which forms part of an aplite/pegmatite vein in the pink granite. Associated minerals include hingganite-(Y), fluorite, albite, quartz, K-feldspar, kristiansenite (Guastoni and Pezzotta, 2004) and Sn-rich ixiolite.

Backscattered-electron images of polished fragments of xenotime-(Y) and Sn-rich thortveitite show that the xenotime-(Y) is chemically homogeneous whereas the Sn-rich thortveitite is zoned from core to rim. The electron-microprobe analyses of xenotime-(Y) are reported in Table 1. Xenotime-(Y) from Baveno is particularly rich in gadolinium, with the largest amount of any xenotime from the pegmatites and hydrothermal fissures of the Alps and the Southern Alps (Demartin et al., 1991).

The electron-microprobe analyses of Sn-rich thortveitite (Table 1) show that the compositions of the core and rim of crystal are different. At the core, compositions are in the range 40.60–42.10 wt.% Sc₂O₃, 3.60–6.10 wt.% Y₂O₃, 2.78–3.20 wt.% SnO₂, 1.48–2.28 wt.% Fe₂O₃(calc), and 1.28–1.73 wt.% MnO. The Gd₂O₃, Dy₂O₃ and Er₂O₃ contents are 0.12–0.18 wt.% REE₂O₃, and Yb₂O₃ is in the range of 0.39–0.59 wt.%. The total REE₂O₃ content of the Baveno thortveitite is less than the REE₂O₃ contents of thortveitite from several localities reported by Bianchi et al. (1988)

Scandium is significantly enriched in the rim of the crystal (at up to 45.01 wt.% Sc₂O₃) whereas Y₂O₃ falls to as little as 1.59 wt.% and Sn reduces slightly to 2.01 wt.% SnO₂. The heavy REE in Sn-rich thortveitite display variation with the highest Gd, Dy, Er and Yb values being found at the core of the crystal. The Sn content of up to 3.20 wt.% SnO₂ has not been reported previously in thortveitite from this locality (Pezzotta et al., 2005).

X-ray diffraction data

Single-crystal X-ray diffractometry was used to identify the two phases in the miarolitic cavity as thortveitite and xenotime-(Y). In the following discussion we show that the unit-cell dimensions of thortveitite (e.g. Bianchi et al., 1988; this work) can be used as a preliminary indication of the Sc, Y and Yb content of the mineral, but a similar approach cannot be used for xenotime-(Y), which does not show significant changes in its unit-cell dimension if REEs substitute for Y. This observation is in agreement with the very small differences in the cation radii of the REEs.

Thortveitite

The unit-cell data for thortveitite are similar to those published by Bianchi et al. (1988) on their sample number 4. Bianchi et al. (1988) investigated thortveitite specimens from the Setesdal district in Norway and Befano in Madagascar. Each of these samples had a unit-cell volume that could be related to the Y-Se-Yb content; unit-cell volumes of 262.4, 257.9 and 257.9 Å³, were reported for samples 1, 2 and 3 respectively, with Y₂O₃ ranging from 8.4–17.7 wt.% , Sc₂O₃ from 25–27 wt.% and Yb₂O₃ from 2.6–7 wt%. The unit-cell volume of sample 4 was significantly smaller (254.0 Å³) and this sample had the highest Sc₂O₃ content (47.8 wt.%) and contained very little Y₂O₃ (2.31 wt.%) and Yb₂O₃ (0.18 wt.%). X-ray diffraction data for thortveitite and

Fig. 2. A BSE image showing a partially dissolved bipyramidal crystal face of xenotime-(Y).
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Table 1. Representative chemical analyses of thortveitite and xenotime-(Y) from Baveno.

<table>
<thead>
<tr>
<th></th>
<th>Thortveitite (wt.%)</th>
<th>Xenotime-(Y) (wt.%)</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Rim Range</td>
<td>Core Range</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.26 0.20–0.31</td>
<td>0.27 0.22–0.35</td>
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<tr>
<td>SiO₂</td>
<td>45.26 43.71–45.60</td>
<td>43.46 42.33–43.82</td>
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<tr>
<td>Sc₂O₃</td>
<td>44.61 43.19–45.01</td>
<td>41.85 40.60–42.10</td>
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<tr>
<td>MnO</td>
<td>1.49 1.28–1.73</td>
<td>1.50 1.30–1.56</td>
</tr>
<tr>
<td>FeO₅*</td>
<td>1.90 1.48–2.28</td>
<td>1.54 1.34–1.63</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>1.71 1.59–2.47</td>
<td>4.78 3.60–6.10</td>
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<tr>
<td>ZrO₂</td>
<td>0.14 0.10–0.19</td>
<td>0.12 0.05–0.18</td>
</tr>
<tr>
<td>Nb₂O₃</td>
<td>0.06 0.05–0.10</td>
<td>0.07 0.05–0.09</td>
</tr>
<tr>
<td>SnO₂</td>
<td>2.54 2.01–3.07</td>
<td>2.98 2.78–3.20</td>
</tr>
<tr>
<td>Gd₂O₃</td>
<td>0.18 0.11–0.23</td>
<td>0.36 0.25–0.45</td>
</tr>
<tr>
<td>Dy₂O₃</td>
<td>0.17 0.10–0.22</td>
<td>0.34 0.10–0.52</td>
</tr>
<tr>
<td>Er₂O₃</td>
<td>0.12 0.10–0.20</td>
<td>0.31 0.19–0.41</td>
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<tr>
<td>Yb₂O₃</td>
<td>0.48 0.37–0.59</td>
<td>0.74 0.59–0.87</td>
</tr>
<tr>
<td>Total</td>
<td>98.92</td>
<td>98.32</td>
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Formula based on 7 oxygen atoms

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<tr>
<th></th>
<th>Formula based on 4 oxygen atoms</th>
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<tbody>
<tr>
<td>Si</td>
<td>2.021</td>
</tr>
<tr>
<td>Al</td>
<td>0.014</td>
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<tr>
<td>ΣT</td>
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<tr>
<td>Sc</td>
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<tr>
<td>Mn</td>
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<tr>
<td>Fe³⁺</td>
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</tr>
<tr>
<td>Y</td>
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<tr>
<td>Zr</td>
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<tr>
<td>Nb</td>
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<tr>
<td>Sn</td>
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</tr>
<tr>
<td>Gd</td>
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</tr>
<tr>
<td>Dy</td>
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</tr>
<tr>
<td>Er</td>
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<tr>
<td>Yb</td>
<td>0.007</td>
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<tr>
<td>ΣO</td>
<td>1.960</td>
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</table>

* The Fe₂O₃ value is calculated from FeO total.

Xenotime-(Y) from Baveno gave the following unit-cell parameters: \(a = 6.528(2)\), \(b = 8.500(2)\), \(c = 4.684(1) \text{ Å} \), \(β = 102.87(3)°\) with \(V = 253.38(13) \text{ Å}^3\) for thortveitite; and \(a = 6.888(1)\), \(c = 6.030(1) \text{ Å}\) with \(V = 286.09(8) \text{ Å}^3\) for xenotime-(Y).

The sample of thortveitite described in this study has a different chemical composition to sample 4 of Bianchi et al. (1988) but the unit-cell volumes are very similar [253.4 Å³ of our sample compared to 254.0 Å³ for that of Bianchi et al. (1988)]. Our measurements on the Sn-rich thortveitite from Baveno support the observation that an increasing Sc₂O₃ content (if the Y₂O₃ and Yb₂O₃ contents remain low) causes a reduction in the unit-cell volume. This is due to the larger ionic radii of Y and Yb compared to Sc (Shannon, 1976). The presence of up to 3.20 wt.% SnO₂ in thortveitite (\(^{VI}\text{Sn}^{4+}\) is slightly larger than \(^{III}\text{Sc}^{3+}\)) appears to have little effect on the unit-cell volume; the relatively small Sn content is insufficient to produce an obvious \(^{VI}\text{Sn}^{4+}\)-related volume change.

The charge imbalance produced by the incorporation of Sn⁴⁺ into the thortveitite structure appears to be compensated by Mn²⁺; the mean MnO content is ~1.5 wt.% (Table 1). In our thortveitite it seems likely that a coupled substitution of the form SnO₂ \(\leftrightarrow\) MnO \(\leftrightarrow\) Sc₂O₃ + Y₂O₃ occurs. This substitution mechanism is
supported by previous work in which significant amounts of $Zr^{4+}$ in thortveitite were found to be charge balanced by $Mn^{2+}$, $Ca^{2+}$ and $Mg^{2+}$ (Bianchi et al., 1988).

**Xenotime-(Y)**

Mogilevsky et al. (2006) compared the unit-cell dimensions of several synthetic xenotime-type structures with natural xenotime-(Y) crystals from Novo Horizonte in Brazil and found that synthetic $YPO_4$ has a unit cell that is practically indistinguishable from the Brazilian samples. Although the natural xenotime-(Y) studied by Mogilevsky et al. (2006) has a composition in which 24 mol.% $Y$ is replaced by other $REE$ cations, the difference in the $a$ and $c$ unit-cell parameters compared to synthetic xenotime-(Y) is extremely small, with $a = 6.898$ and $c = 6.037$ Å for the natural Novo Horizonte xenotime-(Y), compared to $a = 6.883$ and $c = 6.021$ Å (Ushakoy et al., 2001) and $a = 6.884$ and $c = 6.020$ Å (Aldred, 1984) for synthetic $YPO_4$. Further comparisons can be made with xenotime-(Y) from granitic rocks at Nanling, southeast China (Ni et al., 1995). This has a composition which contains 77 mol.% $Y$, the remaining 23 mol.% being almost entirely other $REE$ cations; the unit-cell dimensions are $a = 6.895(1)$ and $c = 6.027(1)$ Å, which is also extremely close to synthetic xenotime.

The natural sample of xenotime-(Y) from Baveno described here has unit-cell dimensions $\ell = 6.888(1)$ and $c = 6.030(1)$ Å and ~20 mol.% $REE$s substituting for $Y$. Thus our data confirm the observation that this level of substitution of $REE$ cations for $Y$ does not alter the unit-cell dimensions of xenotime significantly.

**Crystallization processes in the miarolitic cavities at Baveno: the role of fluids**

The granitic pegmatites at Baveno contain millimetre- to centimetre-sized miarolitic cavities, which represent unique relatively well-sealed geochemical environments. Crystallization of the pegmatites begins from silicate liquids. As the melts cool, the high concentrations of B, F, P and $H_2O$, in the melt lead to a transition which produces silicate melt and a coexisting supercritical aqueous fluid (London, 1987, 1992, 1997, 2005). Incompatible elements including tin, scandium, yttrium and $REE$s partition into the silicate liquid melt and contribute to the formation of the rare accessory phases that are characteristic of pegmatites. At Baveno these include the miarolitic cavity minerals xenotime-(Y) and thortveitite.

The xenotime-(Y) crystals are corroded (Fig. 2) but the thortveitite crystals have plane crystal faces with a vitreous lustre. The thortveitite at Baveno commonly has incipient reaction border zones; the crystals are usually opaque and are covered by other phases including $REE$-bearing carbonates (Gramaccioli et al., 2000a; Pezzotta et al., 2005).

Crystallization processes are controlled by factors including the kinetics of nucleation, adsorption and diffusion of elements along the fluid-crystal interfaces, saturation, temperature and pressure in fluids. Taking these into consideration it can be assumed that the crystallization and growth of xenotime-(Y) started in a geochemical environment controlled by low $\Delta T$ undercooling and supersaturation of $SiO_2$ (London et al., 1999).

After the xenotime-(Y) crystallized, it was partially dissolved, with the major dissolution affecting the bipyramidal crystals faces (Fig. 2). The corrosion mechanism can be probably be best represented using a dissolution reaction at low pH such as $YPO_4 + 3H^+ \rightarrow Y^{3+} + H_3PO_4$ (Cetiner et al., 2005; Liu and Byrne, 1997). Assuming a pure endmember $Y$-phosphate, the reaction is controlled by the solubility product $K_{s0} = a_{Y^{3+}}a_{PO_4}$; unfortunately, experimental solubility data at high temperatures are still lacking for almost all $REE$-bearing minerals (Cetiner et al., 2005). At this stage aggressive supercritical fluids probably liberated the yttrium that was incorporated into the thortveitite crystals.

Experimental studies at different temperatures support the role of complexing agents such as fluoride, chloride, sulfate, carbonate and hydroxide ions in the transportation of $REE$s, yttrium and scandium in supercritical fluids (Kosterin, 1959; Bilal et al., 1987; Wood, 1990). In miarolitic pegmatites, fluorine and carbonate are the best candidates as complexing agents for $Y$ and $REE$ (Gramaccioli et al., 2000b; Wood, 1990). Fluorine plays an important role in the enrichment of tin, scandium, yttrium and $REE$s in supercritical and high-temperature hydrothermal aqueous fluids (London, 1987; Keppler, 1993).

The source of the $Y$ and $REE$ in the supercritical fluids at Baveno is likely to be mica-group minerals and related sheet silicates. These minerals behave like a sponge, and incompatible elements are commonly incorporated in their
structures. Indeed, annite-siderophyllite and chamosite are widespread at Baveno, the former in the granite and the latter lining miarolitic cavities, where they commonly show incipient alteration (Guastoni, 2012).

Conclusions
Thortveitite from miarolitic cavities at Baveno contains up to 3.20 wt.% SnO₂. Xenotime-(Y) from Baveno is enriched in the gadolinium in comparison to specimens from other pegmatites and hydrothermal fissures of the Alps and Southern Alps. The unit-cell parameters of thortveitite can be used as preliminary indicators of its Sc₂O₃, Y₂O₃, Yb₂O₃ content, but a similar approach cannot be used for xenotime-(Y), as it does not show significant differences in unit-cell size as a function of substitution. Thortveitite and xenotime-(Y) are found in miarolitic cavities where they illustrate late-stage dissolution and crystallization processes. The source of the Y and REEs is probably the alteration of sheet silicates (annite-siderophyllite and chamosite) by supercritical aqueous fluids.

Acknowledgements
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