

XENOTIME-(Yb), YbPO₄, A NEW MINERAL SPECIES FROM THE SHATFORD LAKE PEGMATITE GROUP, SOUTHEASTERN MANITOBA, CANADA

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ABSTRACT

Xenotime-(Yb), ideally YbPO₄, occurs as a primary phase in the saccharoidal albite unit of a granitic pegmatite located near the margin of the Lac du Bonnet batholith in the Shatford Lake pegmatite group, southeastern Manitoba, Canada. Xenotime-(Yb) occurs as granular aggregates ≤50 μm across and as isolated small (~20 μm) grains encased in clots of ferrian muscovite, which are scattered throughout the saccharoidal albite unit. It is also associated with ferrocolumbite, albite, microcline and quartz. Xenotime-(Yb) is transparent, colorless to slightly yellowish or brownish with a white streak, vitreous luster and no observed fluorescence. Cleavage and parting were not observed, tenacity is brittle, and the fracture is uneven. Xenotime-(Yb) has no observable pleochroism and is uniaxial positive with $\omega = 1.715(3)$, $\varepsilon = 1.802(5)$. It is tetragonal, space group $I4_1/amd$, with $a = 6.866(2)$ Å, $c = 6.004(3)$ Å, $V = 283.0(2)$ Å³ and $Z = 4$. The strongest lines of the (Gandolfi) X-ray-diffraction pattern [d in Å(l)(hkl)] are: 4.52(7)(011), 3.44(10)(020), 2.73(3)(121), 2.56(8)(112), 2.14(3)(031) and 1.76(5)(132). Electron-microprobe analysis of one of the grains characterized by X-ray diffraction gave an average composition of (Yb_{0.48}Y_{0.20}Er_{0.11}Lu_{0.09}Dy_{0.05}Tm_{0.04}Ho_{0.01}Gd_{0.004}Tb_{0.003})Σ_{0.99}P_{1.00}O₄. The ratio Y/Yb (at.) varies between 0.39 and 0.68; this range is roughly comparable to the variation defined by xenotime-(Y) and xenotime-(Yb) in granitic pegmatites from the Kola Peninsula, Russia.

Keywords: xenotime-(Yb), new mineral species, phosphate, granitic pegmatite, Shatford Lake, Manitoba, Canada.

SOMMAIRE

Le xénotime-(Yb), dont la composition idéale est YbPO₄, constitue une phase primaire de l'unité intrusive à albite saccharoïde d'une pegmatite granitique située près du contact du batholithe du lac du Bonnet, et faisant partie du groupe de pegmatites du lac Shatford, dans le sud-est du Manitoba, Canada. Le xénotime-(Yb) se présente sous forme d'aggrégats de granules ≤50 μm de diamètre et en cristaux isolés d'environ 20 μm de taille encastrés dans des accumulations de muscovite ferrifère éparpillées dans cette unité intrusive. Il y est associé à ferrocolumbite, albite, microcline et quartz. Le xénotime-(Yb) est transparent, incolore ou jaunâtre ou brunâtre, à rayure blanche, éclat vitreux et sans fluorescence. Il ne semble pas y avoir de clivage ou de plan de séparation. Sa tenacité est cassante, et sa fracture, inégale. Il ne montre aucun pléochroïsme; il est uniaxe positif, $\omega = 1.715(3)$, $\varepsilon = 1.802(5)$. Il s'agit d'un minéral tétragonal, groupe spatial $I4_1/amd$, avec $a = 6.866(2)$ Å, $c = 6.004(3)$ Å, $V = 283.0(2)$ Å³ et $Z = 4$. Les raies les plus intenses du spectre de diffraction X (chambre de Gandolfi) [d en Å(l)(hkl)] sont: 4.52(7)(011), 3.44(10)(020), 2.73(3)(121), 2.56(8)(112), 2.14(3)(031) et 1.76(5)(132). Une analyse à la microsonde électronique d'un des grains que nous avons caractérisé par diffraction X a donné, comme composition moyenne, (Yb_{0.48}Y_{0.20}Er_{0.11}Lu_{0.09}Dy_{0.05}Tm_{0.04}Ho_{0.01}Gd_{0.004}Tb_{0.003})Σ_{0.99}P_{1.00}O₄. Le rapport Y/Yb (at.) varie de 0.39 à 0.68; cet intervalle se compare *grosso modo* à la variation qui a été décelée dans l'association xénotime-(Y) et xénotime-(Yb) des pegmatites granitiques de la péninsule de Kola, en Russie.

(Traduit par la Rédaction)

Mots-clés: xénotime-(Yb), nouvelle espèce minérale, phosphate, pegmatite granitique, lac Shatford, Manitoba, Canada.

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INTRODUCTION

During the course of work on the Shatford Lake (SHL) group of granitic pegmatites in southeastern Manitoba, a new mineral species was discovered: xenotime-(Yb), ideally YbPO_4 , is a member of the xenotime group (Buck *et al.* 1999). A similar composition was reported by Belolipetskii & Voloshin (1996) from "rand" pegmatites, Kola Peninsula, but no other data were provided. Following the recommendations of the International Mineralogical Association (Nickel & Grice 1998), the new mineral was named xenotime-(Yb) according to the Levinson (1966) system. The new mineral and its name have been approved by the Commission on New Minerals and Mineral Names, IMA (No. 98-049). The cotype material, which originated chiefly from two separate field samples, consists of several hand specimens, a vial of separates of mica clots containing the new mineral, several polished sections and two minute individual crystals, and is deposited in the R.B. Ferguson Museum of Mineralogy, Department of Geological Sciences, University of Manitoba (#M6998 – M7001). Additional cotype samples are deposited in the Department of Earth Sciences, Royal Ontario Museum.

In this paper, we document the physical and chemical properties of xenotime-(Yb) and speculate on the factors that led to its formation.

OCCURRENCE

Samples of the new mineral were collected in 1996 and 1997 from the Archean SHE-5 pegmatite, a member of the Shatford Lake pegmatite group (2657 ± 1 Ma; Baadsgaard & Černý 1993). The group is derived from the biotite granite phase of the Lac du Bonnet batholith, and corresponds to the gadolinite subtype of the NYF family of rare-element granitic pegmatites (Černý 1991). The SHE-5 pegmatite is located in Twp. 16, Rge. 15 EPM, Manitoba; its NTS map coordinates are 323750 mE, 5584800 mN, Zone 15U on the Rynerson Lake map sheet (52/L16).

The SHE-5 pegmatite consists of several interconnected dikes. The majority of the SHE-5 pegmatite is apparently enclosed in the leucogranite phase of the Lac du Bonnet batholith (Černý *et al.* 1981, 1987). Samples with xenotime-(Yb) were found in a small trench in the center of the main subvertical dike (striking 040°) near its southeastern end. This main pegmatite dike is at least 35 m long and ~1 m wide. A subordinate dike (45 m long) trends 163° and was traced within 4 m of the contact with metavolcanic rocks in the vicinity of the nearby SHE-1 pegmatite.

Xenotime-(Yb) occurs as granular aggregates ≤ 50 μm across and as separate small (up to 20 μm) grains encased in clots of ferrian muscovite (to ~1.5 mm in diameter) that also contain albite, microcline and quartz. The clots of mica are scattered throughout the saccha-

roidal albite unit, and are associated with ferrocolumbite, albite, microcline and quartz. Beryl, microlite, fluorite and molybdenite were identified in other units of the parent pegmatite. In general, the minerals of the pegmatite group also include biotite, chlorite, almandine, spessartine, topaz, zircon, titanite, epidote, thorite, gadolinite-(Y), allanite, apatite, monazite, xenotime-(Y), uraninite, cassiterite, magnetite, pyrite, niobian rutile and several metamict (*REE*, Ti, Nb)-bearing phases.

EXPERIMENTAL

Sample preparation

Xenotime-(Yb) was originally found during examination of polished mounts in the electron microprobe. Separation of individual grains for detailed study proved to be difficult. The clots of mica were liberated from the saccharoidal albite and chopped up in alcohol with a razor blade; the resultant slurry was then evenly dispersed onto a glass slide. After carbon coating, the slide was examined with a scanning electron microscope (SEM) in back-scattered electron (BSE) mode. The *REE*-phosphate grains were mapped on a BSE image to locate the grains for later retrieval. Three isolated grains with no adhering phases were recovered, either composite aggregates or single crystals up to ~50 μm in size. All three were initially used to obtain an X-ray-diffraction spectrum. Subsequently, the largest grain was mounted in epoxy and polished for electron-microprobe analysis (EMPA). The clearer of the two remaining grains was used for determination of optical and physical properties.

Chemical composition

Xenotime-(Yb) was analyzed using a Cameca SX-50 electron microprobe in wavelength-dispersion mode using the following conditions: operating voltage 20 kV, beam current 40 nA, beam size 3 μm . Counting times for peak and background determinations were 20 s and 10 s, respectively, for P, Y, Yb, Er and Lu; for the remaining elements, the values were 40 s and 20 s, respectively. Crystals were analyzed using the following standards: synthetic YbPO_4 ($\text{PK}\alpha$, $\text{YbL}\alpha$), synthetic ErPO_4 ($\text{ErL}\alpha$), and synthetic LuF_3 ($\text{LuL}\alpha$). Drake & Weill (1972) synthetic *REE* glasses were used for $\text{GdL}\alpha$, $\text{TbL}\alpha$, $\text{DyL}\beta$, $\text{HoL}\beta$ and $\text{TmL}\alpha$. F, Si, Fe, Zr, La, Ce, Pr, Nd, Sm, Eu, Th and U were found to be below detection limits. A single crystal recovered after X-ray diffraction was analyzed at three spots to test for homogeneity. The analytical data were reduced and corrected by the *PAP* method of Pouchou & Pichoir (1985).

Table 1 shows the chemical composition and unit formula of xenotime-(Yb). Phosphorus is the sole occupant of the tetrahedra; the other cations occupy the

(REE_8) polyhedron (Ni *et al.* 1995). Yb is the dominant *REE*, and hence the name is xenotime-(Yb). The average formula is $(Yb_{0.48}Y_{0.20}Er_{0.11}Lu_{0.05}Dy_{0.05}Tm_{0.04}Ho_{0.01}Gd_{0.004}Tb_{0.003})_{\Sigma 0.99}P_{1.00}O_4$.

The analytical total is low by ~4 wt.%. The most probable reason for this is charging of the microscopic grain in a carbon-coated mount of non-conductive epoxy, rather than metamictization and accompanying hydration. This interpretation is supported by the virtually ideal stoichiometry of the mineral, and by the acceptable totals obtained on other samples of xenotime-(Yb) that were analyzed while embedded in their silicate matrix (*cf.* sample YB2, Table 1).

Xenotime-(Yb) is the tenth mineral with a heavy rare-earth (*HREE*) component in its chemical formula and is the only phosphate of a heavy rare earth known to date.

Physical and optical properties

Xenotime-(Yb) is transparent, and colorless to pale yellowish or brownish. It has a white streak, vitreous luster and no observed fluorescence. Owing to the small grain-size, hardness was not determined. Cleavage and parting were not observed, tenacity is brittle, and fracture, uneven. Xenotime-(Yb) is nonpleochroic, uniaxial positive, with indices of refraction ω 1.717(3) and ϵ 1.802(5) for a wavelength of 589.9 nm. Density could not be measured because of the very small grain-size of the mineral; the calculated value is 5.85 g/cm³.

X-ray diffraction

Material suitable for single-crystal X-ray examination was not found. The three grains recovered as a result of the SEM study were mounted on a single glass fiber with nail polish. The diffraction pattern was recorded for 7 h in a Debye-Scherrer camera with a Gandolfi

attachment using a Philips 1729 generator operating at 40 kV, with a beam current of 40 mA and Ni-filtered $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The results are summarized in Table 2. The pattern of observed diffraction maxima is consistent with the space group $I4_1/amd$. The unit-cell parameters, a 6.866(2) and c 6.004(3) \AA , were refined from the diffraction angles of 14 measured X-ray diffraction lines between 4.515 and 1.228 \AA (Table 2).

There is a close correlation between unit-cell dimensions and average radius of the *REE* in synthetic *REE* phosphates of the monazite and xenotime structure-types (Ni *et al.* 1995). On the basis of our unit-cell parameters and the data of Ni *et al.* (1995), the predicted radius of the *REE* in xenotime-(Yb) is 1.01 \AA , in good agreement with the average radius of 1.00 \AA derived from Table 1.

GEOCHEMICAL CONSIDERATIONS

The occurrence of Yb-dominant xenotime in the Shatford Lake pegmatite group is rather puzzling. The ratio Y/Yb (atomic) varies between 0.39 and 0.68 for xenotime-(Yb) and attains at least 1.96 for xenotime-(Y) from the SHE-5 pegmatite. Compositions of xenotime analyzed from other pegmatite dikes of this group are intermediate between those recorded for xenotime-(Yb) and xenotime-(Y), with no apparent cor-

TABLE 1. CHEMICAL COMPOSITION (wt. %) AND UNIT FORMULAE (apfu) OF XENOTIME-(Yb)

		YB1		YB2	
wt. %	Range	σ	apfu*	wt. %	apfu*
Lu ₂ O ₃	7.12	7.04-7.17	0.06	Lu	0.093
Yb ₂ O ₃	36.37	35.91-36.78	0.36	Yb	0.481
Tm ₂ O ₃	2.86	2.81-2.90	0.04	Tm	0.039
Er ₂ O ₃	8.29	8.21-8.39	0.07	Er	0.113
Ho ₂ O ₃	0.94	0.89-0.98	0.04	Ho	0.013
Dy ₂ O ₃	3.72	3.64-3.83	0.08	Dy	0.052
Tb ₂ O ₃	0.19	0.18-0.20	0.01	Tb	0.003
Gd ₂ O ₃	0.26	0.24-0.29	0.02	Gd	0.004
Y ₂ O ₃	8.75	8.28-9.12	0.35	Y	0.202
				Σ cat.	1.000
P ₂ O ₅	27.25	26.78-27.70	0.38	P	1.001
	95.75				98.27

YB1: mean of three determinations on one of the grains characterized by X-ray diffraction.

YB2: composition of a grain embedded in silicate matrix.

* calculated on the basis of 4 atoms of oxygen apfu (atoms per formula unit).

U, Th, Eu, Sm, Nd, Pr, Ce, La, Zr, Fe, Si and F below detection limits.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA FOR XENOTIME-(Yb)

	lobs	d_{obs} (\AA)	d_{calc} (\AA)	hkl
	7	4.515	4.520	0 1 1
	10	3.437	3.433	0 2 0
	3	2.730	2.734	1 2 1
	8	2.556	2.553	1 1 2
	2	2.430	2.427	2 2 0
	1	2.259	2.260	0 2 2
	3	2.138	2.139	0 3 1
	2	1.920	1.921	0 1 3
	2	1.815	1.815	2 3 1
	5	1.760	1.759	1 3 2
	1	1.718	1.717	0 4 0
	1	1.678	1.677	1 2 3
	0.5	1.602	1.605	1 4 1*
	1	1.537	1.535	2 4 0*
	0.5	1.505	1.507	0 3 3*
			1.501	0 0 4*
	1	1.424	1.425	3 3 2
	1	1.376	1.380	2 3 3*
			1.375	0 2 4*
	1	1.337	1.339	3 4 1*
	1	1.278	1.280	1 4 3*
			1.277	2 2 4*
	1	1.228	1.229	1 5 2

* Diffraction maxima not used for unit-cell refinement. 114.6 mm Debye-Scherrer camera with Gandolfi attachment, $CuK\alpha$ radiation, visually estimated intensities; a 6.866(2), c 6.004(3) \AA (not corrected for film shrinkage, no internal standard)

relation with associated minerals or the overall degree of fractionation of the parent pegmatite. Furthermore, gadolinite, which occurs in relative abundance in one of the SHL dikes, has Y strongly dominant over Yb and the other HREEs, as is also the case in the widespread almandine and spessartine. Voloshin & Pakhomovskii (1986) and Belolipetskii & Voloshin (1996) also noted high variability of the ratio Y/Yb in xenotime from granitic pegmatites containing amazonitic K-feldspar from the Kola Peninsula, in Russia, a variability broadly commensurate with that observed in the Shatford Lake group. Despite a greater diversity of associated minerals, these authors also could not correlate the Y/Yb value with any other variable of the parent pegmatites.

In both the Shatford Lake and Kola localities, variation in the concentrations of complexing agents such as fluorine (not readily detectable in the xenotime-bearing mineral assemblages) in the magma may have played a role in determining the Y/Yb values. Grammacioli & Pezzotta (1997) and Pezzotta *et al.* (1999) proposed such a control, particularly well-expressed for Gd, Tb, and Dy, and best quantified by Y/Dy for a variety of (Y + HREE)-bearing minerals in general, and for gadolinite-(Y) from Baveno, Italy, in particular. Substantial differences in stability constants among fluoride complexes of Y and of HREEs may lead to significant differences in partitioning of these elements between the magma and the precipitating solid phases.

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