XENOTIME FROM ST. SIMÉON, CHARLEVOIX COUNTY, QUEBEC[1]

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ABSTRACT

An occurrence of xenotime from St. Siméon, Charlevoix County, Quebec, is described. Physical properties are ω = 1.724 (faint yellow), ϵ = 1.810 (colourless), S.G. = 4.69. Unit cell; a = 6.89, c = 6.03 Å, c/a = 0.875. Spectrographic analysis showed Y_2O_3 = 49.9, ThO_2 = 1.73, UO_2 = 2.75 wt. %, and SiO_2, Gd, Dy in the range 1–5%. Xenotime occurs here as a minor, fine-grained accessory in gneissic rocks and is probably of pegmatitic origin.

Introduction

During the 1955 field season the writer was engaged in mapping radioactive deposits in the Province of Quebec for the Quebec Department of Mines. Several hand specimens collected in the vicinity of St.Siméon, Charlevoix County, were found to show up to 20X normal radioactive background. The source of the radioactivity appeared to be a yellow translucent mineral present in small grains, which was subsequently identified by an *x*-ray powder photograph to be xenotime. Spectrographic analysis of a sample of the pure mineral showed that it contained appreciable quantities of both thorium and uranium and further work was carried out to establish its composition and physical properties. Xenotime is probably not an uncommon accessory constituent of Precambrian rocks in Canada but in view of the sparse literature concerning this mineral, especially for this country, it seemed worthwhile putting on record the properties of the specimen.

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General Geology and Petrography

The village of St. Siméon is on the north shore of the St. Lawrence River about twenty miles west of the mouth of the Saguenay River. The

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bedrock of the region is of Precambrian age and is in the Grenville sub-province. The principal rock-types exposed are mica schist and gneiss, hornblende schist and gneiss, garnet gneiss, granite gneiss, granite and pegmatite. The geology of the region has been described by Miller (1951). Xenotime-bearing rocks were found by the writer at two localities, on land staked by the Corporation d'Uranium de St. Siméon. Both lie in Lot 15, Range I S.W., Callières Township.

The first locality is about two miles east of St. Siméon along Provincial Highway No. 15, about 500 ft. north of a house belonging to M. Lebret, on the east side of the road. At this point, near the border of a field, are several outcrops of granitic gneiss which show radioactivity up to 20X background. The rock is coarse-grained, is rather variable in composition, but consists chiefly of oligoclase and quartz, with some biotite and chlorite, the latter on shear planes. The rock is pink to white in colour and has a faint gneissosity. Close examination with a hand lens shows numerous yellow translucent grains which are xenotime. These grains are usually rounded but in the vicinity of small shear planes numerous euhedral crystals were observed, showing a rather flat bipyramid. There is a strong tendency for the grains of xenotime to be associated with biotite.

The other locality, about 1500 ft. away on the opposite side of the highway, is a ridge of bare rock consisting of sills of coarse biotite-plagioclase augen-gneiss or granite, intercalated in a coarse biotite-garnet gneiss. The plagioclase is albite or sodic oligoclase, and forms large "eyes" of a yellowish-green colour. Crystals of garnet range up to about ¾ inch in diameter and in places make up over 50% of the rock. Both rock-types have sporadic medium radioactivity due to the same wide distribution of minute grains of xenotime. As before, the mineral occurs in yellow translucent grains and is invariably intergrown with garnet or biotite. No euhedral grains were observed here.

In both the above localities xenotime makes up less than 1% of the rock, apart from a few aggregations where up to 5% may be present in discontinuous lenses up to ½ inch thick.

Xenotime has also been recorded in samples taken from Lot 9, R III S.W. by C. A. Brouillard and Syndicate. The writer visited this locality but was unable to locate any samples containing xenotime.

In thin section the xenotime appears as subhedral to rounded grains, up to 0.5 mm. long. The relief is high and irregular fractures are visible on prismatic grains, whereas rectangular cleavage-traces are visible on basal sections. The mineral is either colourless or very pale lemon yellow with faint dichroism, and appears quite fresh. In thin sections of normal thickness the interference colours may be as high as third order yellow-green in prismatic sections. Basal sections give an accurately uniaxial

TABLE 1. REFRACTIVE INDICES AND DENSITY OF XENOTIME

ω	ϵ	ϵ-ω	S.G.	Source
1.724	1.810	.086	4.69	This paper (pleochroism: *O*, faint yellow; *E*, colourless)
1.721	1.816	.095	4.46–5.106	Quoted by Palache, Berman & Frondel (1951)
1.720	1.827	.107		Hutton (1947)

positive interference figure. As mentioned above the xenotime occurs in association with garnet, where it occurs as inclusions surrounded by radial fracture cracks, or biotite where it commonly forms the cores of pleochroic haloes.

The refractive indices were determined in Na light by conventional immersion methods and are recorded in Table I along with other figures from the literature. The specific gravity was determined using a pycnometer, the figure recorded being the mean of several determinations using both water and toluene. Considerable difficulty was experienced in freeing the powder from air bubbles and it was necessary to immerse the partially-filled pycnometer in boiling water for long periods.

Separation Methods

Hand specimens of the xenotime-bearing rocks were crushed to between 100 and 150 mesh size, discarding the fines. Since xenotime is slightly paramagnetic it was found possible to obtain a concentrate of garnet, biotite and xenotime with the Frantz Isodynamic Separator. This was further concentrated by adjusting the current and tilt on the Separator to obtain a fraction rich in xenotime but also containing a small amount of biotite. This concentrate was separated in tetrabromoethane, the xenotime sinking whereas the biotite floated. The resulting powder was practically pure xenotime, containing less than 1% of other mineral grains. Part of the powder was retained for optical and specific gravity determinations and the rest was crushed to a fine powder for spectrographic analysis. About 1 gram of xenotime was obtained from several hundred grams of rock. The writer is indebted to Roy H. Filby for carrying out the above separation.

X-ray Powder Data

The xenotime specimen was not metamict and gave a good powder photograph. North-American Philips Co. Inc. equipment was used: camera radius 57.54 mm., Cu$K\alpha$ radiation using a Ni filter. The spacings (corrected for film shrinkage) and intensity estimates (visual) are given in Table 2, together with data from the A.S.T.M. *X*-ray Powder Data

File, Card No. 5–0454, on xenotime from Tvedestrand, Norway, examined by J. E. T. Horne, Geological Museum, London (no other reference given). The agreement is very close except in the low-angle region where the present results are somewhat less than Horne's; also no reflection with a spacing of 1.217 Å was detected in the St. Siméon sample.

The unit cell of xenotime was first determined by Vegard (1927) giving $a = 9.735$, $c = 6.013$ Å, space-group $I4_1/amd$. The determination by Horne gave the indices of the first 14 reflections and the cell-size $a = 6.89$, $c = 6.04$ Å. It was found impossible to index the reflections from the St. Siméon specimen using Vegard's a-value but Horne's figures were suitable. Indices are given in Table 2, including that for Horne's reflection at 1.217 Å which was not visible in the writer's photographs. These indices are consistent with the space-group $I4_1/amd$. Using back-reflections and correcting from Cu $K\alpha$ to Cu $K\alpha_1$ the cell dimensions were calculated to be $a = 6.98$ and $c = 6.03$ Å, with $c/a = 0.875$. Palache,

TABLE 2. XENOTIME, YPO_4: X-RAY POWDER DATA
Tetragonal, D_{4h}^{19}–$I4_1/amd$: $a = 6.98$, $c = 6.03$; $Z = 4$

This paper			Horne	
I/I_1	d Å	hkl	I/I_1	d Å
60	4.48	101	30	4.53
100	3.40	200	100	3.43
10	2.71	211	20	2.74
80	2.54	112	60	2.55
20	2.43	220	40	2.43
10	2.25	202	10	2.26
40	2.14	301	50	2.14
20	1.92	103	20	1.923
20	1.82	321	50	1.818
70	1.76	312	70	1.762
20	1.72	400	50	1.718
10	1.68	213	10	1.680
5	1.61	411	10	1.606
10	1.54	420	40	1.538
5	1.511	303, 004	10	1.510
20	1.430	332	30	1.427
20	1.383	204 323	30	1.378
5	1.346	431 501	30	1.342
30	1.282	224	30	1.280
30	1.234	512	40	1.231
—	—	440	10	1.217
10	1.151	600	30	1.148
10	1.136	404, 433, 503	20	1.134
10	1.099	532	30	1.099
5	1.089	620	30	1.089
20	1.076	424	30	1.076
5	1.017	631	10	1.012
10	.984	116	10	.984
15	.955	640	20	.956
5	.948	444	10	.948
20	.928	712, 552	40	.927
20	.914	316, 604, 633	20	.913
10	.884	703	20	.884
10	.868	406, 732	20	.867

Using Cu $K\alpha = 1.5418$ Å

Berman & Frondel (1951, p. 689) give $a = 6.88$ and $c = 6.03$ kX. Assuming 4 formula units to the unit cell the writer's figures give a calculated density of 4.267.

Spectrographic Analysis

Semi-quantitative analysis was made by visual comparison methods for 41 elements, using the G series of standards prepared by Spex Industries Inc., New York. Following this Y, Th and U were determined by quantitative methods, using the Stallwood air-jet (1954). Owing to the unusual composition of xenotime some difficulty was experienced in setting up artificial standards for preparing the working curves. After several trials a standard mixture was made up containing 50% Y, 5% Th, 5% U, using the oxides Y_2O_3, ThO_2, UO_2, made up in a base of sodium metaphosphate, $NaPO_3$. Additional standards were made by diluting the first standard with appropriate amounts of $NaPO_3$. The sample for

TABLE 3. SPECTROGRAPHIC METHOD OF ANALYSIS FOR XENOTIME

Spectrograph	Jarrell-Ash 21-foot Wadsworth grating instrument: dispersion 5 Å/mm. (first order)
Power Source	ARL DC Power Source
Electrodes	⅛in. graphite rod (National Carbon Co., Regular Grade), lower electrode (anode) crater 1.5 by 6 mm.
Air jet	¼ psi pressure
Arc gap	9 mm.
Voltage	240 v. D.C. (open circuit)
Current	9–10 amp.
Slit	4.5 mm. length; 20 μ width.
Step-sector	Step-ratio log $I/I_0 = 0.2$
Optical system	Arc focused on slit by cylindrical quartz lens (axis vertical) focal length 67 mm.; arc focused on spectrograph mirror by a cylindrical quartz lens (axis horizontal), focal length 450 mm., placed at the slit.
Sample for arcing	Mixture of standard (or unknown) $+NaPO_3+CaCO_3+$graphite powder in ratio 1:1:4:4. Electrodes filled with about 10 mg. mixture then sintered at 500° C. for 30 minutes.
Exposure	50 seconds
Plates	Eastman-Kodak Company No. III-F
Processing	3 minutes development in D19 at 22° C., followed by 10-second stop bath, 10-minute fix and 20-minute wash
Plate Calibration	Fe arc recorded on each plate and calibration curve drawn by the 2-step method
Densitometer	ARL instrument: 0 and 100 positions adjusted before every reading for added precision: background corrections applied
Spectral lines	Y 4251.205 Å
	Th 4391.114
	Th 4282.044
	U 4241.669
	Ca 4456.620 (internal standard)

arcing consisted of standard+$NaPO_3$+$CaCO_3$+graphite in the proportions of 1:1:4:4. During analysis of the xenotime the powder was mixed with $NaPO_3$, $CaCO_3$, and graphite, in the same proportions. In this manner the influence of varying matrix upon spectral line intensity was minimized. A total of 11 replicate analysis was made of the xenotime. Further details of the analytical methods are tabulated in Table 3. The results were computed by regression analysis using the methods of Shaw & Bankier (1954).

The composition of the analyzed specimen is given in Table 4 along with some figures from the literature. Computation of the standard deviations for Y, Th and U gave 6.3, 14.4 and 10.0 % respectively, in terms of amount present. Spectrographic determination of major element proportions of such refractory elements is notoriously difficult and the precision is therefore satisfactory. No assessment of systematic error is possible, but since the compositions of standards and analyzed sample were very similar and since each was considerably diluted before analysis with the same matrix it is unlikely that this error is significant.

TABLE 4. ANALYSIS OF XENOTIME IN WT. %

Element or oxide	This paper	Literature*	
		Range	No. of Analyses
Y_2O_3	49.9		
Y earth oxides		30.23–67.78	12
ThO_2	1.73	tr – 3.33	5
UO_2	2.75	3.17– 4.13	3
P_2O_5 (theoretical)	38.6		
Total	93.98		
SiO_2	1–5	.24– 4.32	6
Gd	1–5		
Dy	1–5		
CeO_2	nd	.32–11.03	5
Nd, Sm, Fe, Pb, Zr	.1–1		
Mg, Al	.01–.1		
Ca, Ni, Cu, Sb, Bi	tr < .01		
La, Ce, K, Na	nd < .1		
Be, As, Pt, Mn, Ge, Sn, Ga, Mo, V, Li, Ag, Zn, Ti, Pd, Sc, Cr, Ba, Sr	nd < .01		

tr trace
nd sought but not detected
*Taken from Dana (1892) and from Palache, Berman & Frondel (1951).

Discussion

The rocks in which the xenotime occurs are partly sedimentary, partly igneous, and the origin of the mineral poses a problem. It is unlikely that its present manner of occurrence is due to simple metamorphism of a heavy accessory mineral suite in the original sediments, since there is a tendency for euhedral shape in some cases and an association with shear-planes. It is possible that it was an original heavy accessory, since mobilized and redistributed during plutonic metamorphism. The average shale has been reported to contain 28.1 ppm. (Minami, 1935) and 45 ppm. (Shaw, 1954) yttrium, and in shales this will probably be of non-detrital origin. The latter figure may be rather high (ibid., p. 1173) and 35 ppm. Y will be taken as the best estimate. Using the analysis reported here this amount of Y would account for about 100 ppm. or .01% wt. % xenotime in metamorphosed shales. The rocks under discussion contain from 10x to 500x this amount.

It therefore seems probable that the mineral has formed from substances introduced from elsewhere. Pegmatites carrying fergusonite, uraninite and allanite are present in the vicinity and it is likely that these and the xenotime are of cognate origin.

During recent years extensive prospecting for radioactive minerals has been carried out in the St. Siméon area and many radioactive localities have been found, both by ground examination and air-borne scintillometer survey. The xenotime described here contains moderate amounts of uranium and thorium, and, if widely disseminated, may give misleading encouragement to the prospector. A rich concentration of course would be valuable.

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