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NATURE, DISTRIBUTION AND CONTENT OF ZIRCONIUM AND NIOBIUM IN A SILICO-CARBONATITE SILL AT ST-MICHEL, MONTREAL ISLAND, QUEBEC

(Report and 2 figures)

H.R. Steacy and J.L. Jambor

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## CONTENTS

Page

Abstract .		iv					
Introductio	on	1					
Acknowled	gments	1					
General features of the sill							
Sampling p	procedure	2					
Analyses f	or zirconium, niobium and strontium	3					
Analy	tical procedure	3					
Analy	tical results	3					
Discussion	1	6					
Reference	S	7					
Table 1 Table 2	Results of X-ray spectrographic analyses for zirconium, niobium and strontium	4					
	Illustrations						
Figure 1.	Photograph of the northeast wall of the quarry at St-Michel, Québec	2					
Figure 2.	Plan showing stations at which samples were collected for analyses	3					

#### ABSTRACT

A silico-carbonatite sill exposed in the Francon (1966) Ltée quarry at St-Michel, Montreal Island, Québec, contains approximately 0.09 per cent  $\text{ZrO}_2$  and 0.11 per cent Nb<sub>2</sub>O<sub>5</sub>. The sill consists predominantly of feldspar and dawsonite. Zirconium is present as zircon and weloganite, the latter occurring megascopically in vesicles and cavities which are a prominent feature of the sill. Niobium is present as pyrochlore which is finely disseminated in the rock matrix.

#### INTRODUCTION

The recently reported occurrence of zirconium as the carbonate, weloganite,  $[Sr_5Zr_2(CO_3)_9.4H_2O]$  by Sabina <u>et al</u>. (1968) is of interest because zirconium is used extensively in nuclear reactors and because Canada has no known commercially exploitable deposits. Also, the carbonate, weloganite, appears chemically to be a more desirable source of zirconium than the silicate, zircon, from which the metal is currently extracted. Zircon, ZrSiO<sub>4</sub>, is a common accessory mineral in igneous and metamorphic rocks, and in sands derived from the weathering of such rocks. Production is presently obtained from beach sands, principally in Australia and the United States, where zircon and other heavy resistant minerals have been pre-concentrated by wave action.

The finding of weloganite led to this present study of the nature, distribution and abundance of zirconium in the sill. As the study progressed niobium was found to be as consistent in its distribution as zirconium and roughly of the same order of magnitude. Accordingly, data for niobium are also given. Analytical data are also presented for strontium, as it is an essential constituent of weloganite. The field work, which involved the collection of samples at 41 stations in the quarry, was carried out by the authors in August, 1968.

#### ACKNOWLEDGMENTS

Grateful acknowledgment is made to Francon (1966) Ltée and to the Miron Company Limited, both of Montreal, for granting permission to collect samples and to publish the data. The authors are indebted to G.R. Lachance for the X-ray fluorescence analyses, and to R.J. Traill for suggesting the study and for critical reading of the manuscript.

#### GENERAL FEATURES OF THE SILL

The weloganite-bearing sill intrudes flat-lying Ordovician limestones at St-Michel, Montreal Island, Québec, where it is exposed in a limestone quarry operated by Francon (1966) Ltée. In August, 1968, the excavated quarry area in which the sill was exposed was approximately 1,300 feet in length and 700 feet in width, the elongation being about N 45°W. Quarry development drillholes beyond the excavated area indicate that the sill covers a known area approximately 3,300 feet by 1,300 feet, the continuation being open in all directions. Drillhole data also indicate a thinning from about eight feet southeast of the excavated area to four feet in the northwest. Within the excavated area the sill averages six feet in thickness. Although some faulting of the sill, with displacements of several feet, and variations in the stratigraphic horizon of emplacement do occur (Fig. 1), the sill can nevertheless be traced completely around the quarried area.

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Figure 1. Photograph of the silico-carbonatite sill exposed on the northeast wall of the quarry at St-Michel, Québec. The light-coloured, six feet thick sill may be seen at the centre of the photograph intruding darker, flat-lying Ordovician limestone. At the left the sill wedges out and reappears at a lower horizon. At right centre, it swings down abruptly to the quarry floor.

The sill is dense, fine grained, light grey to greenish, and contains numerous vesicles and cavities ranging up to several cm in diameter. These are a prominent feature of the sill, occupying several per cent of its volume. They are best developed in the central and upper quarter of the sill, and are commonly elongate parallel to the sill - limestone contacts. Many are partly filled with various minerals, the most abundant being weloganite, quartz, plagioclase, and dawsonite. Lesser amounts of strontianite, barite, calcite, dolomite, siderite, two new barium aluminum carbonates and analcite are also present in the vesicles. Small amounts of other minerals have been reported by Sabina <u>et al.</u> (1968). An interesting feature observed in breaking specimens was the occasional, instantaneous appearance of damp patches on the broken surfaces. These would quickly evaporate and probably represent vesicle-trapped water. Petrographic examination of the sill indicates that it is an unusual silico-carbonatite composed predominantly of feldspar and dawsonite. The petrography will be described in detail in a later paper.

#### SAMPLING PROCEDURE

Specimens were collected at 41 stations along the perimeter of the quarry, for the most part at measured intervals of 100 feet. A plan of the quarry kindly supplied by Francon (1966) Ltée served as a guide in the sampling and as a base map for plotting the sample stations (Fig. 2). The general procedure followed at each sampling station was for the collector to pre-select visually a particular point in the sill at a distance sufficiently removed that details, such as the abundance of weloganite, could be discerned. A single specimen was then taken at that point. When the sill could not be reached a specimen was similarly taken from the talus slope. The specimens so collected ranged from about 75 to 600 cubic inches, the average being perhaps 300 cubic inches.



Figure 2. Plan of northwest excavation of quarry at St-Michel, Québec, showing stations at which samples were collected for analyses. The ramp leads to a higher quarry floor and to the crushers and plant.

#### ANALYSES FOR ZIRCONIUM, NIOBIUM AND STRONTIUM

#### Analytical Procedure

All samples were crushed to minus 1/4 inch, halved, and one of the halves pulverized. By gradually rolling and splitting, a final 20 gram fraction was obtained for analysis. All samples were scanned at 50 KV and 35MA from 18 to 28° 2 $\Theta$  using an X-ray spectrograph with a tungsten target and lithium fluoride crystal. Six samples giving the highest and lowest chart peaks for K $\propto$ Sr, Zr, and Nb were selected, and to these samples 0.1 and 0.2 per cent powdered Nb<sub>2</sub>O<sub>5</sub>, ZrO<sub>2</sub>, and SrO were added. The six samples were counted, background subtracted, and the percentages of the three elements calculated by the "standard addition" method. The remainder of the samples were read on the basis of the results obtained for the six.

#### Analytical Results

The results obtained for the analyses for Zr, Nb and Sr are given in Table 1. Samples F-13, F-14 and F-15 were inadvertently combined during the crushing stage and hence only the composite could be analyzed. This, and the average of the eleven specimens comprising F-17, provide a total of 39 analyses for the three elements from the 41 sample sites. The range and average of the analytical values are given in Table 2. For comparative purposes four large hand specimens from a sill in the nearby quarry operated by Miron Company Limited were also analyzed. The results for these four, labelled M-1 to M-4, are included in Tables 1 and 2.

#### TABLE 1

## Results of X-ray spectrographic analyses for zirconium, niobium and strontium in silico-carbonatite specimens.

Analyst: G.R. Lachance, Geol. Surv. Can.

No.	Descriptive Notes		Weight %	
		$\operatorname{ZrO}_2$	$Nb_2O_5$	$\operatorname{SrO}$
F- 1	single specimen from sill	0.11	0.11	0.2
F- 2	composite of specimens taken from top, centre, and bottom of sill	0.09	0.12	0.17
F- 3	composite from top, centre, and bottom of sill	0.04	0.07	0.13
F- 4	composite from top, centre, and bottom of sill	0.06	0.11	0.14
F- 5	single specimen from sill	0.06	0.11	0.11
F- 6	single specimen from talus	0.07	0.12	0.15
F- 7	single specimen from sill	0.08	0.11	0.17
F- 8	single specimen from sill	0.08	0.13	0.07
F- 9	single specimen from talus	0.05	0.10	0.04
F-10	composite from top, centre, and bottom of sill	0.09	0.11	0.12
F-11	composite of two specimens from sill	0.09	0.10	0.13
F-12	single specimen from talus	0.13	0.13	0.15
F-13	single specimen from talus			
F-14	single specimen from talus			
F-15	single specimen from talus Average of F-13, F-14, F-15	0.09	0.11	0.10
F-16	single specimen from sill	0.07	0.10	0.09
F-17-1 -2 -3 -4 -5	eleven specimens collected at approximately equal intervals, and numbered consecutively, from bottom to top of sill	0.08 0.10 0.10 0.09 0.09	0.09 0.13 0.12 0.12 0.12 0.12	0.05 0.04 0.04 0.04 0.04 0.02
-6		0.10	0.10	0.03

No.	Descriptive Notes	,	Weight %	
		$2rO_2$	$Nb_2O_5$	$\mathbf{SrO}$
F-17-7 -8 -9 -10 -11		0.09 0.14 0.09 0.25 0.21	0.11 0.09 0.09 0.10 0.10	0.03 0.03 0.03 0.04 0.04
F-18	single specimen from talus	0.14	0.11	0.07
F-19	single specimen from sill	0.11	0.11	0.12
F-20	single specimen from sill	0.12	0.11	0.14
F-21	single specimen from sill	0.12	0.09	0.18
F-22	single specimen from talus	0.11	0.10	0.18
F-23	single specimen from talus	0.08	0.12	0.09
F-24	single specimen from talus	0.06	0.11	0.19
F-25	single specimen from sill	0.11	0.11	0.16
F-26	single specimen from sill	0.07	0.12	0.10
<b>F-27</b>	single specimen from sill	0.07	0.11	0.12
F-28	single specimen from sill	0.08	0.13	0.12
F-29	single specimen from sill	0.07	0.12	0.15
F-30	single specimen from sill	0.07	0.08	0.17
F-31	single specimen from sill	0.06	0.12	0.15
F-32	single specimen from sill	0.11	0.11	0.18
F-33	single specimen from sill	0.05	0.12	0.15
F-34	single specimen from sill	0.07	0.12	0.18
<b>F-</b> 35	single specimen from sill	0.10	0.12	0.18
F-36	single specimen from sill	0.09	0.14	0.17
F-37	single specimen from sill	0.15	0.13	0.11
F-38	single specimen from sill	0.12	0.14	0.20
F-39	single specimen from sill	0.17	0.15	0.18
F-40	composite from top, centre, and bottom of sill	0.17	0.12	0.16
F-41	composite of two specimens from sill	0.12	0.11	0.19
M- 1	single specimen, Miron quarry	0.09	0.09	0.02
M- 2	single specimen, Miron quarry	0.04	0.02	0.11
M- 3	single specimen, Miron quarry	0.05	0.08	0.01
M- 4	single specimen, Miron quarry	0.08	0.10	0.03

Samples		$ZrO_2$	$Nb_2O_5$	
F-1 to F-41	Range Average	0.04-0.17 0.09	0.07-0.15 0.11	
M-1 to M-4	Range Average	0.04-0.09	0.02-0.10 0.07	

### Range and average of $\rm ZrO_2$ and $\rm Nb_2O_5$ analyses (weight per cent) from Table 1

TABLE 2

#### DISCUSSION

Because sampling of the sill was not thorough, and because in collecting samples there was a natural tendency to avoid areas of vesicles and cavities, commonly rich in weloganite, the indicated average content of 0.09 per cent  $ZrO_2$  is probably minimal. However, because the niobium-bearing mineral occurs in the silicocarbonatite matrix the indicated average content of 0.11 per cent Nb<sub>2</sub>O<sub>5</sub> is probably a better representative average. These concentrations are higher than the geochemical norms for igneous rocks, the zirconium being approximately four times the norm, and niobium approximately 30 times. The concentration of niobium would appear to be unusually high, but niobium-enriched carbonatites are fairly common; and one, at Oka, Québec, contains Canada's only producer.

Mineralogical studies of the sill show that zirconium is present as weloganite and zircon; niobium is present as pyrochlore; and strontium is present as strontianite and weloganite. A hafnium/zirconium metal ratio of 0.03 was obtained by XRF analyses on a large composite sample of weloganite. Weloganite and zircon are estimated to contribute equally to the zirconium content of the sill. Pyrochlore and zircon were observed only in the compact silico-carbonatite matrix. Pyrochlore occurs as disseminated, tan-coloured octahedra, averaging approximately 70 microns in diameter. Zircon occurs as disseminated, euhedral to subhedral crystals, up to a millimetre in length. On the other hand, weloganite and strontianite occur mainly in vesicles and cavities, as late stage primary minerals. The analyses indicate a fairly uniform distribution of the three elements throughout the sill.

The economic appraisal of a deposit is dependent upon many factors which can be properly assessed only through exhaustive study. However, two factors of prime importance are tonnage and grade. With respect to the latter, and to producing deposits, the concentrations of zirconium and niobium in the silico-carbonatite sill described in this paper are not considered economic at present. The persistence of weloganite and pyrochlore throughout the sill, rather than simply a chance occurrence, suggests that other carbonatites found to be associated with the Monteregian intrusive bodies should be sampled and analyzed for zirconium and niobium. Also, the possibilities of encountering concentrations of zirconium in carbonatites should not be overlooked when examining such deposits in Canada, particularly if they are found to be dawsonite-bearing. To date only two such carbonatites have been found, both in the Montreal area (Sabina <u>et al.</u>, 1968; Stevenson and Stevenson, 1965). This study suggests the possibility that dawsonite-bearing carbonatites may be more widespread in their occurrence.

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