

ANALYSIS OF RARE EARTHS IN EUDIALYTE
OF SEAL LAKE, LABRADOR BY MEANS OF
X-RAY FLUORESCENCE SPECTROSCOPY

by

DUNCAN R. SMITH

A Thesis

Submitted to the Department of Geology
in Partial Fulfilment of the Requirements
for the Degree
Bachelor of Science

McMaster University

April 1969

TABLE OF CONTENTS

	<u>Page</u>
Acknowledgements	
Abstract	1
Introduction	2
General Geology of Seal Lake Area	3
Eudialyte Occurrences	4
Preparation of the Eudialyte for Chemical Analysis	6
Preliminary Preparation	6
Mineral Separation	6
Purity of Concentrate	8
Chemical Treatment	9
Procedure A - XRF Analysis of Mineral Powder	9
Procedure B - Ion Exchange Extraction for XRF Analysis	9
Efficiency of the Ion Exchange Technique	11
Preparation of Standards	11
Analytical Procedure	13
Instrumental Parameters	13
Counting Procedure	13
Absorption Corrections	13
Analytical Results	16
Major Chemical Analysis	16
X-ray Fluorescence Analysis	16
Discussion	20
Conclusions	29
Bibliography	32

LIST OF TABLES

		<u>Page</u>
Table I	Parameter Variation Required to Achieve Mineral Separation	7
Table II	Parameter Variations for XRF Analysis	15
Table III	Comparison of Analyses of Differing Eudialytes	17
Table IV	Rare Earth Analyses by X-ray Fluorescence	19
Table V	X-ray Diffraction Powder Traces of Eudialyte	21
Table VI	Chondrite and Shale Normalized Rare Earth Abundances in Eudialyte of Seal Lake, Labrador	22
Table VII	Comparison of Rare Earth Fractionation in Differing Eudialytes	25

LIST OF FIGURES

		<u>Page</u>
Figure I	Plot of Normalized Rare Earth Abundances Versus Ionic Radii	23

ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. R. H. McNutt who supervised the entire project, giving unselfishly of his time, knowledge of instrumental and chemical techniques and constructive criticisms both throughout the year and during the various stages of writing the manuscript. Gratitude is also expressed to Dr. A. P. Beavan, and staff of British Newfoundland Exploration Limited for allowing the author time to collect samples and for providing reports of the Seal Lake Area. Gratitude is also expressed to Dr. W. E. Hale of the Department of Geology, University of New Brunswick, for discussion in the field and to Mr. Brian Michelin who assisted the author in collecting samples. Mr. J. Muysson did the major chemical analysis and Mr. F. Tebay did the x-ray powder diffraction trace.

ABSTRACT

The mineral eudialyte from Seal Lake, Labrador, was analyzed by means of x-ray fluorescence analysis for the rare earths La, Ce, Pr, Nd, Sm, Gd, Y and also for the element Zr. Samples were prepared by two methods: a) whole mineral powder being compressed into pellets, and b) the dissolved mineral being put through an ionic exchange process to eliminate interfering ions before compressing into pellets for analysis. The results are compared with published data on other eudialyte occurrences.

INTRODUCTION

During the summer of 1968, while working for British Newfoundland Exploration Ltd., the author and assistants noticed a deep red mineral within the outcropping bedrock. The mineral was tentatively identified as eudialyte, and specimens were flown out for positive identification. During the late summer, a few days were spent in the area, collecting samples and attempting to extend zones of mineralization. Although no accurate mapping was undertaken, the author gained sufficient knowledge of the area to place the eudialyte in its geological environment.

This thesis is a partial investigation of the mineral's chemical properties with emphasis on its Rare Earth content and fractionation.

GENERAL GEOLOGY OF SEAL LAKE AREA

The Seal Lake area is located approximately 125 miles north-west of Goose Bay, Labrador, in the Grenville Precambrian province.

The Seal Lake Group which is the youngest rock in the area, is a sedimentary unit composed mainly of quartzites, shales and slates and is intruded conformably by many diabase sills. It overlies unconformably on the Letitia Lake Group which consists essentially of quartz-feldspar porphyry, conglomerates, acid volcanics and amphibolite gneisses.

Structurally, the Seal Lake Group and Letitia Lake Group are folded in a large northeast-southwest trending syncline abuted against large masses of granite on the south and anorthosite in the north. The south limb of the syncline dips more steeply than the north, on occasion becoming overturned, and much of the Letitia Lake series has been faulted out especially on the southeast edge of the syncline. For a more detailed account of Geology in this area, see Evans et al, 1962.

Eudialyte Occurrences

The eudialyte occurs in association with a long narrow band of amphibolite-actinolite gneiss within the Letitia Lake series on the northeast side of the syncline.

The band is bounded on both sides by a quartz-feldspar porphyry of variable composition and texture; some bands containing abundant, large, well-formed feldspar phenocrysts in a massive felsic matrix whereas other bands are well foliated and contain elongated quartz and feldspar phenocrysts.

The basement complex, consisting of a large grey-coloured hornblende granite "massif", outcrops approximately one-half mile from the gneiss at its closest approach.

The gneiss itself is composed mainly of amphibolite (arfvedsonite and actinolite) and a Na-feldspar and has very complex banding, structural and mineralogical relationships. There is much flow folding and ptygmatic folding with the gneissosity locally being extremely variable, as are band width and composition. Gabbroic fractions and "pegmatitic" veining of similar composition occur locally throughout the gneiss, probably due to partial anatexis during extreme metamorphism.

In nearly all the cases, the eudialyte appears to be associated with these large grained gabbroic and

pegmatitic fractions. Approximately seven zones of eudialyte mineralization were noticed in the gneiss with the mineral occurring both as disseminations within the country rock and as "veins" up to 12 inches wide and traceable up to 300 feet along strike before disappearing beneath the locally abundant overburden. The veins have a eudialyte content as high as 75% and disseminate into the country rock on either side of the vein. They are generally conformable with the gneissosity of the country rock and in at least one instance have been tectonically folded.

A majority of the occurrences are megascopically on strike with each other and it seems reasonable to assume that they form a continuous zone of mineralization.

PREPARATION OF THE EUDIALYTE FOR CHEMICAL ANALYSIS

Preliminary Preparation

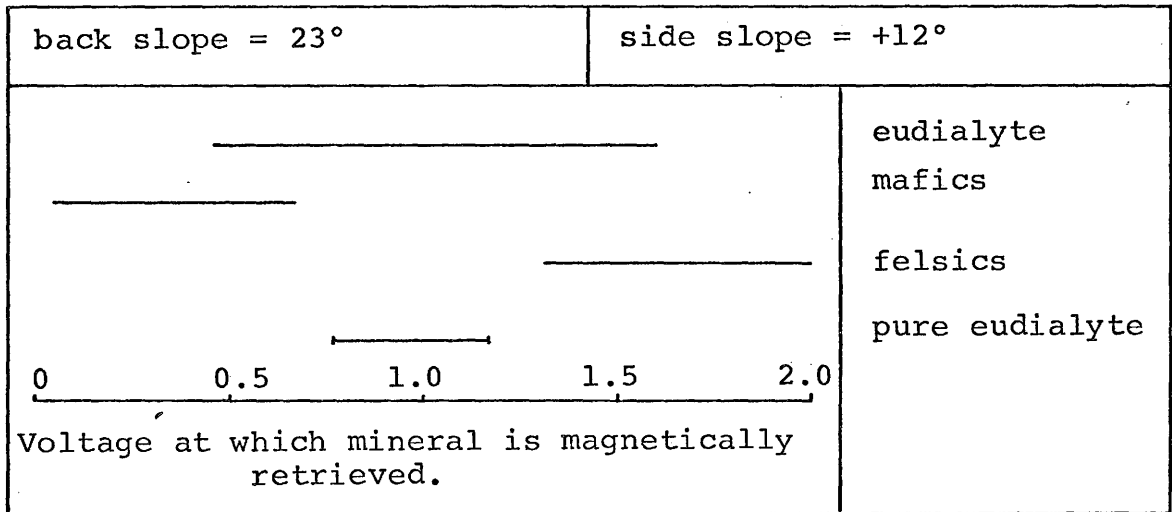
The eudialyte rock specimen was hand broken with a hammer, placed in a Spex shatterbox, and ground for 75 seconds. The rock powder was then put through brass sieves, retaining the 100-200 mesh fraction, discarding the fraction greater than 200 mesh and returning the remainder to the shatterbox, where the procedure was repeated. The 100-200 mesh fraction was then rinsed several times in distilled water, (to remove any dust clinging to the rock particles) rinsed once in acetone, dried in an oven at 75°C and stored in plastic containers.

Mineral Separation

Mineral separation was accomplished by use of a Franz Isodynamic separator. Basically, three fractions were taken off: a felsic fraction, containing mainly feldspar, the eudialyte fraction, and a mafic fraction, containing mainly arfvedsonite with minor actinolite. Parameters varied on the separator to achieve complete separation may be seen in Table I. Pure eudialyte was taken off between 0.65 volts and 1.1 volts. This fraction was put through the separator twice in order to ensure purity.

TABLE I

PARAMETER VARIATION REQUIRED TO ACHIEVE MINERAL SEPARATION



Purity of Concentrate

A microscope slide was prepared for each of the eudialyte and feldspar fractions. On each slide, the mineral was covered by an immersion oil of approximately the same index of refraction as the mineral.

A point count over 1000 grains indicated the eudialyte and feldspar to be 98.1% and 97.3% pure, respectively, with the impurities in the eudialyte being mainly arfvedsonite.

CHEMICAL TREATMENT OF SAMPLES

Two different approaches were instituted in analysis of Rare Earth in this mineral. As each entails different procedures, each shall be discussed separately.

Procedure A - XRF Analysis of Mineral Powder

The purified mineral was ground in a Spex ball grinder for fifteen minutes and subsequently hand ground in a mortar for ten minutes. Three samples of approximately three grams each were accurately weighed on a mettler balance and then pelletized under twenty-five tons pressure in a Spex press, using a binder in the rock powder and powdered boric acid as the backing. The three samples were then placed in a dessicator to await analysis.

Procedure B - Ion Exchange Extraction for XRF Analysis

The mineral sample was put through on ionic exchange column in order to isolate the rare earths for analysis. This was done in order to reduce the absorption effects of the mineral matrix and to eliminate certain elements (particularly Fe) whose lines (specifically $FeK\alpha_1$ and $FeK\beta_1$) interfere with the various Rare Earth lines. The procedure

is as follows.

Approximately 0.3 gms. of the pure mineral was weighed out on a five place mettler balance, placed in a teflon dish and dissolved in 15 ml. concentrated HF and 3 ml vycor doubly distilled HClO_4 . The sample was evaporated to fuming HClO_4 in a steam bath and then converted to chlorides using 30 ml vycor doubly distilled HCl. It was again evaporated to incipient dryness, taken up in 15 ml 0.5 M HCl and quantitatively transferred (rinsing with 0.5 M HCl) into an anion exchange column containing Dowex 50-8X resin (a hydrogen ion exchanger). The resin had been previously prepared by rinsing in distilled water and decanting off all the fines. It was put into a column 30 cm in height and 1 cm in diameter and flushed with 300 ml 2 M HCl and then 300 ml 0.5 HCl.

After absorption of the sample into the column, it was eluted with 300 ml 2 M HCl at a rate of 2 ml per minute in order to remove most of the major constituents of the sample. Following this, an elution was carried out with 500 ml of 6 M HCl bringing off the Rare Earths and any uranium and thorium. This volume was evaporated to dryness and taken up in 50 ml 0.5 M HCl. Approximately 8 grams of Dowex 50-8X resin was then added to this, allowed to sit for 2 hours with occasional stirring, filtered off, rinsed with distilled water and dried under

an infra-red heat lamp. The resin was then crushed in the ball grinder for 35 minutes and pelletized with a powdered boric acid backing as described previously. The above procedure was done in triplicate.

Efficiency of the Ion Exchange Technique

Elution rates of the Rare Earths were determined by eluting through the column a sample of eudialyte of approximately 0.3 grams spiked with tracers of radio-active La^{140} and Yb^{175} . Since Yb is the first Rare Earth to come off the column and La is the last, it was possible to draw up elution curves for the Rare Earth elements. The three samples were run under the same conditions using the same concentration and quantities of reagents where possible.

A check was also run of the sample when the Rare Earths were taken up in the resin. Vials containing samples of the resin, filtrate, and a blank were monitored on the counter. The filtrate and the blank had exactly the same peak pattern, indicating at least a 99.9% transfer of the Rare Earths into the resin.

Preparation of Standards

The rare earth standards used in the XRF analysis had been prepared previously by Barker and McNutt. They

mixed accurately weighed amounts of the rare earth oxides, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy (Johnson and Mathey Specpure) in a powdered boric acid matrix and compressed them into pellets under 25 tons pressure.

A second standard was prepared by the author containing Y and Zr in order to analyze for these elements since they had been noticed qualitatively on the XRF spectrograph.

ANALYTICAL PROCEDURE

XRF Spectroscopy

(a) Instrumental parameters

A Phillips manual, vacuum x-ray fluorescence spectrograph was used for this analysis. It was provided with a spinner which allowed all pellets to be rotated in the paths of the x-ray beam to help minimize sample inhomogeneity. Instrumental parameters which were varied throughout the analytical procedure are summarized in Table II.

(b) Counting procedure

All analyses were performed recording both fixed time and fixed count, a fixed count of 200,000 counts being imposed on the sample when a fixed time of 20 seconds resulted in the number of counts being in excess of 200,000. Each sample was counted in triplicate for the same values and was always seen against a standard to ensure a minimum of drift in the spectrograph.

(c) Absorption Corrections

In comparing the samples with the standards,

absorption coefficient corrections were applied to both the standards and the samples in order to correct for matrix effect (Jenkins and DeVries, 1966). Upon applying secondary absorption coefficient corrections to each standard pellet for all rare lines of interest, a linear relationship between peak intensity and concentration was obtained. One of these standards was then compared against the samples to determine their concentration.

In order to determine the mass absorption coefficient of the Dowex resin matrix (used in Procedure B), two standards were prepared, each containing the same concentration of La. In one sample, the matrix was powdered Boric acid whereas in the other sample the matrix was a similar weight of Dowex resin. From an analysis of these two pellets, the relative mass absorption coefficient of Dowex resin could be found.

TABLE II
PARAMETER VARIATIONS FOR XRF ANALYSIS

ELEMENT	X-RAY LINE	PEAK POSITION (2θ)	kV	mA	COUNTER	VACUUM	CRYSTAL	PULSE HEIGHT ANALYSIS
La	$L\alpha_1$	82.86	50	30	FPC 1.55 kV	yes	LiF_1^*	Window = 300
Ce	α_1	78.97	50	30	FPC 1.55 kV	yes	LiF_1	L.L. = 100
Pr	$L\alpha_1$	75.39	50	30	FPC 1.55 kV	yes	LiF_1	"
Nd	$L\beta_1$	59.45	50	30	FPC 1.55 kV	yes	LiF_1	"
Eu	$L\beta_1$	56.94	50	30	FPC 1.55 kV	yes	LiF_1	"
Gd	$L\beta_1$	54.59	50	30	FPC 1.55 kV	yes	LiF_1	"
Dy	$L\alpha_1$	56.58	50	30	FPC 1.55 kV	yes	LiF_1	"
Y	$K\alpha_1$	32.12	40	14	SC 0.93 kV	no	LiF_2^{**}	None
Zr	$K\alpha_1$	33.93	40	14	SC 0.93 kV	no	LiF_2	None

* $LiF_1 = LiF$ (200) $2d = 4.028 \text{ \AA}$

** $LiF_2 = LiF$ (220) $2d = 2.898 \text{ \AA}$

ANALYTICAL RESULTS

1) Major Chemical Analysis

A major element chemical analysis was performed in the McMaster University Rock Analysis Laboratory (analyst: Mr. J. Muysson). Analytical results are given Table III along with several analyses of eudialyte from the literature (Vlasov et al, 1966a, Vlasov, 1966b).

2) X-ray Fluorescence Analysis

Table IV lists the triplicate analysis for the rare earths La, Ce, Pr, Nd, Sm, Eu, Gd, Y and also for Zr as they were calculated from Procedures A and B for x-ray fluorescence analysis.

TABLE III
COMPARISON OF ANALYSES OF DIFFERING EUDIALYTES

Oxide	(1)	(2)	(3)	(4)	Number of ions in formula	(5)	mol proportion	Number of ions in formula
SiO ₂	45.98	49.95	48.62	49.65	Si = 5.89	50.69	0.8593	Si = 5.341
TiO ₂	0.28	0.90	0.19	0.35	Ti Zr Fe ³⁺ } 1.05	0.08	0.001	Al = 0.000
Al ₂ O ₃	0.28	n.d.	trace	Fe ²⁺ } Mn Mg Ca Sr RE } 4.89		trace	0.000	Ti = 0.0062
Fe ₂ O ₃	0.07	0.90	1.88			0.34	0.0157	Zr = 0.675
FeO	2.68	2.78	6.08	1.98	Fe ²⁺ } Mn Mg Ca Sr RE } 4.89	5.59	0.0738	Fe ³⁺ = 0.195
MnO	3.49	1.75	1.34	2.33		0.50	0.0024	Fe ²⁺ = 0.459
MgO	0.18	0.22	0.27	0.09	Ca Sr RE } 4.89	0.00		Mn = 0.15
CaO	10.62	11.60	10.86	8.79		10.10	0.2197	Ca = 1.37
Na ₂ O	11.16	12.33	13.75	13.58	Na k } 1.99	13.40	0.2162	Na = 2.65
K ₂ O	1.36	0.84	0.33	0.64		0.38	0.004	K = 0.05
ZrO ₂	11.94	13.15	13.98	13.73	OH Cl } 1.99	13.34	0.1086	Sr = 0.01
H ₂ O ⁺	1.37	1.44	} 1.20	2.05		2.51	0.1283	RE = 0.11
H ₂ O ⁻	0.16	0.16		0.32	O } 16.18	0.02		OH = 1.59
CO ₂	2.51	n.d.				0.00		Cl = 0.14
SrO	0.44	0.13		trace	0.13	0.001	O = 16	
ΣRE		0.81	2.56	2.38	2.56	0.009		
S	0.08	n.d.		n.d.	0.00			
Cl	0.42	1.43	0.93	1.84	0.97	0.021		
O ≡ Cl		0.32	0.20	0.41	0.22	0 = 2.896		
Total	93.02	98.07	99.91	99.20		100.39		

n.d. = not detected

analyst: J. Muysson

TABLE III (cont'd)

- (1) Eudialyte Kola Pen. (Dorfman, 1964)
- (2) Mesodialyte Lovozero Massif (Vlasov, 1966a)
- (3) Eudialyte Greenland (Vlasov, 1966b)
- (4) Eudialyte Lovozero Massif (Vlasov, 1966a)
- (5) Eudialyte Seal Lake Labrador (this study)

Structural Formula of Eudialyte (5)

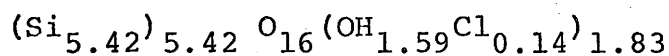
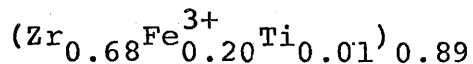
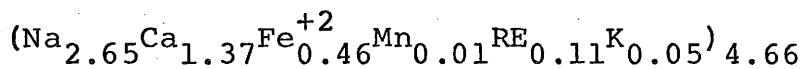


TABLE IV
RARE EARTH ANALYSIS BY X-RAY FLUORESCENCE

Sample	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Eu (ppm)	Gd (ppm)	Y (ppm)	Zr (%)
* DRS-1	1060	5250	432	1620				18,500	13.36
DRS-2	1010	5215	418	1620				17,600	13.47
DRS-3	1000	5225	435	1015				17,900	13.22
** Dowex-1	980	4900	355	1530	425	n.d.	470		
Dowex-2	970	4730	370	1570	410	n.d.	485		
Dowex-2	950	4960	365	1590	430	n.d.	480		

n.d. = below sensitivity

* DRS samples prepared by Procedure A

** Dowex samples prepared by Procedure B

DISCUSSION

The mineral that has been here termed eudialyte is in reality a member of a solid solution series of Zn bearing metasilicates between the sodium end member eudialyte and the potassium end member eucolite (Vlasov, 1966a). An x-ray diffraction powder trace was made of the mineral in order to positively identify it. In Table V, the peak positions of this mineral are compared against the peak positions of the standard eudialyte in the A.S.T.M. files, and it may be seen that peak positions agree very well. It may be noted here that peak intensities were not in very good agreement but this is probably due to a preferred orientation of the powdered mineral.

In thin section, the mineral occurs as subhedral to anhedral rounded grains, 2-3 mm in diameter and has no preferred orientation. The mineral is uniaxial positive, anisotropic, high relief with birefringence being low first-order and has a random fracture pattern with no cleavage. There does not appear to be any reaction between the eudialyte and the mafics (mainly arfvedsonite with some actinolite) or between the eudialyte and the felsics (mainly Na-feldspar displaying an occasional Carlsbad twin, and very minor nepheline(?)).

TABLE V
X-RAY DIFFRACTION POWDER TRACES OF EUDIALYTE

Line	Eudialyte ¹	Eudialyte ²
1	7.19	7.19
2	6.46	6.48
3	6.07	6.07
4	5.72	5.74
5	4.31	4.34
6	4.12	4.14
7	3.98	4.00
8	3.80	3.82
9	3.56	3.57
10	3.42	3.42
11	3.22	3.20
12	2.98	2.99
13	2.85	2.87
14	2.64	2.61
15	2.53	2.53
16	2.47	2.47
17	2.39	2.39
18	2.35	2.34
19	2.26	2.28
20	2.16	2.16

technician: F. Tebay

¹ Eudialyte, this study

² Eudialyte, A.S.T.M. file

TABLE VI
 CHRONDITE AND SHALE NORMALIZED RARE EARTH ABUNDANCE
 IN EUDIALYTE OF SEAL LAKE, LABRADOR

mineral element	La (ppm)	Ce (ppm)	Pr (ppm)	Nd (ppm)	Sm (ppm)	Gd (ppm)	Y (ppm)
Eudialyte this study (conc.)	1020	5230	430	1635	430	475	18,000
Concentration (av.) of 20 chondrites	0.30	0.84	0.12	0.58	0.21	0.32	1.8
Chondrite normalized conc. of Eudialyte	3400	6226	3583	2818	2047	1484	10,000
Av. concentration 40 N. American shales	39	76	10.3	37	7.0	6.1	35
Shale normalized conc. of Eudialyte	26.1	69	41.7	44.2	61.4	77.9	514
wt.% RE taking $\Sigma 6\text{REE} =$ 100 ppm	11.06	56.7	4.66	17.73	4.71	5.15	

In Table III the major element composition of the mineral is tabulated with similar analyses of various eudialyte-group minerals from Greenland (Vlasov, 1966b) and the U.S.S.R. (Vlasov et al, 1966a, Vlasov, 1966b). It is seen that the major chemical composition is most similar to the eudialyte from Greenland (which occurs in a nepheline syenite) especially in the oxides FeO, CaO, Na₂O and ZrO₂. In SiO₂ content, however, it is more similar to the mesodialyte from the Lovozero Plateau.

In Table VI the rare earth concentrations in the mineral, have been normalized against the average rare earth concentrations in chondrites (Haskin and Schmitt, 1967) and also against average rare earth concentrations in North American shale (Haskin and Schmitt, 1967). This has been plotted in Figure I against trivalent rare earth ionic radius. If one considers Yttrium as one of the rare earths it is seen that there may possibly be a tendency towards enrichment of the Y-earth (Tb-Lu+Y) in comparison to the Ce-earth (La-Gd). This is based solely on the Yttrium content in the mineral. In Figure I it may be seen that Y is similar in radius to Dy and is usually plotted with Dy and would tend to behave similarly to it.

In Table VII we have compared the wt% of the Rare Earth (with $\Sigma \text{La} + \text{Ce} + \text{Pr} + \text{Nd} + \text{Sm} + \text{Gd} = 100$) of several eudialyte group minerals, including the one under study.

TABLE VII
COMPARISON OF RARE-EARTH FRACTIONATION
IN DIFFERING EUDIALYTES

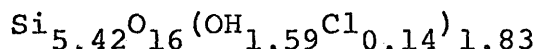
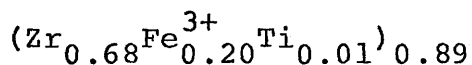
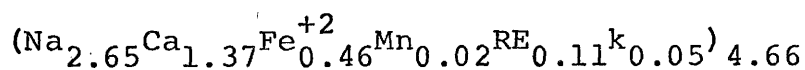
Rare Earth	Wt.% REE with $\Sigma 6\text{REE} = 100\%$			
	(1)	(2)	(3)	(4)
Lanthanum	11.06	16.7	31.5	20.2
Cerium	56.7	42.5	51.4	45.1
Praseodymium	4.66	6.53	3.27	6.53
Neodymium	17.73	20.5	10.52	21.7
Samarium	4.71	6.83	1.63	3.57
Gadolinium	5.15	6.83	1.52	2.79
TOTAL	100	100	100	100

- (1) Eudialyte: this study
 (2) Eudialyte: Lovozero Massif (Vlasov, 1966a)
 (3) Eudialyte: Yenisei Ridge, Tatarka (Vlasov, 1966b)
 (4) Eudialyte: Lovozero Massif (Vlasov, 1966b)

It is obvious from the Table that for the rare earths that have been calculated, the eudialyte under study appears to fractionate the Rare Earths in much the same manner as the eudialyte of the Lovozero Plateau. Concerning the eudialyte of the Lovozero Plateau, Vlasov, 1966a, states (p. 301)

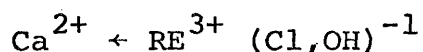
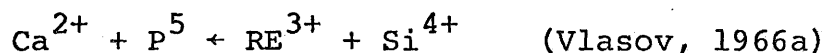
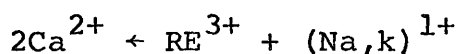
"Unlike most of the rare-earth elements in the massif, the minerals of the eudialyte-eucolite group have a high tenor for the yttrium sub-group of rare earths, particularly Yttrium itself."

The ideal formula for eudialyte is given by Vlasov (1966a) as $(\text{Na,Ca})_5 \text{ZrSi}_6\text{O}_{16}(\text{OH,Cl})_2$ although this formula tends to differ in different texts. A structural formula based on $18(\text{O,OH})$ has been constructed for the mineral under study by the method of Deer, Howie and Zussman (1966) and is as follows:



It is assumed that the trivalent rare earth ions substitute for Ca^{2+} within the crystal structure of eudialyte. When the RE^{3+} ion replaces the Ca^{2+} ion, a valency deficiency arises which may be compensated for by

the replacing of calcium by sodium and hydroxyl by silicon in the anion section of the molecule.



A semiquantitative analysis was made of the purified felsic fraction of the whole rocks (mostly Na-feldspar) which indicated a very low concentration of rare earths in the felsic fraction. This may be due to abundance of calcium in the eudialyte.

Goldschmidt (1954) observed segregation of heavy rare earths, especially ytterbium in zirconates containing Zr^{4+} . This is understandable since the ionic radius of Yb^{3+} ($r = 0.86 \text{ \AA}$) is closer to that of Zr^{4+} ($r = 0.79 \text{ \AA}$) than any other rare earth.

Eudialyte is somewhat different from many rare earth bearing minerals in that it appears to concentrate the rare earths of smaller ionic radius. Vlasov (1966a) indicates that this may be due to the presence of zirconium in the mineral, the rare earth yttrium (Y) being incorporated into the crystalline structures by isomorphously replacing Zr. Upon replacement of zirconium by yttrium electrostatic neutrality is achieved by the simultaneous incorporation

in the mineral structures of higher valency cations.

Vlasov (1966a) does not indicate this in the calculation of his structural formula.

CONCLUSIONS

Analysis of the mineral eudialyte by means of x-ray fluorescence spectroscopy and other "rapid methods" has led to several conclusions.

- 1) The two methods of XRF analysis (Procedures A and B) are in good agreement with each other. Procedure B (the ion exchange procedure) is slightly lower in RE concentrations than comparable RE concentrations in the whole mineral samples. This may be due not to the efficiency of the technique but rather to lack of an accurate absorption correction for the dowex resin matrix. The ion exchange technique has the advantage of removing any interfering elements from the sample before analysis but is more time consuming than the other method.
- 2) The rare earths appear to be present in eudialyte in higher proportions than in the felsic fraction of the host rock. This was determined qualitatively on the x-ray fluorescence spectrograph and is probably due to the abundance of Ca^{2+} in the mineral. Chemical analysis of arfvedsonite which occurs with eudialyte in the Lovozero Massiv (Vlasov, 1966a) does not show any incorporation of REE into the arfvedsonite structure.

XRF analysis should be undertaken for the mafic fraction of the Seal Lake rock in order to determine if REE distribution pattern follows the same course.

- 3) On the basis of Yttrium concentration in this mineral, it would appear that it tends to concentrate the Yttrium-earths (Tb to Lu+Y). This is in agreement with Vlasov (1966a) who feels that this type of fractionation may be due to the presence of zirconium in the mineral. Present data is insufficient to verify this and future work should be carried out to determine concentrations of the remaining rare earths.
- 4) The high Cl, OH, CO₂ content of the mineral indicates that it was formed in the presence of a volatile phase. Vlasov (1966a) feels that the high volatile content of the eudialyte of the Lovozero massif indicates that the zirconium may have concentrated as chlorides with the mineral forming in a vapour-rich hydrothermal phase in the early stages of the formation of the massif. Geologic relations in the Seal Lake area are too vague to make any conclusions of this nature.
- 5) A more sensitive analysis could be made on the samples prepared by Procedure B (ionic exchange) if less dowex resin was used as a matrix in the sample. Care must be taken that sufficient resin is present

to allow for quantitative uptake of the rare earth.
An increase in amount of mineral used per sample
would tend to achieve the same result.

BIBLIOGRAPHY

- Adler, I. 1966. X-ray Emission Spectrography in Geology. Elsevier Publishing Co., New York.
- Blokhin, M. A. 1965. Methods of X-ray Spectroscopic Research. Pergamon Press, New York.
- Dorfman, M. 1959. New Data on Minerals of Yukspor in the Khibina Tundra. *Am. Min.* 44, p. 909.
- Dorfman, M., Lokhin, V., Burora, T. 1964. Barsonovite, a New Mineral. *Am. Min.* 49, p. 1152.
- Evans, E. L., Dujardin, R. A. 1962. A Unique Beryllium Deposit in the Vicinity of Ten Mile Lake, Seal Lake Area, Labrador. *Geol. Assoc. of Can. Proc.* 13, p. 45.
- Goldschmidt, V. M. 1954. *Geochemistry*. Clarendon Press, Oxford.
- Haskin, L., Frey, F., Schmitt, R., Smith, R. 1966. Meteoritic Solar and Terrestrial Rare-Earth Distributions. *Researches in Geochemistry*, Vol. II. Wiley and Sons Ltd., New York.
- Jenkins, R., DeVries, J. L. 1967. *Practical X-ray Spectrometry*. Springer Verlag, New York.
- Mason, B. 1966. *Principles of Geochemistry*. Wiley and Sons, Ltd., New York.
- Nickel, E. and Charette, D. Barylite from Seal Lake, Labrador. Dept. of Mines and Tech. Survey. Investigation Report: Mines Branch, IR 69-9.
- Vlasov, K., Kuzmenko, M., Eskova, E. 1966. *The Lovozero Alkali Massif*. Hafner Publishing Co., New York.
- _____. 1966. *Mineralogy of Rare Elements*. Oldebourne Press, Ltd., London.
- _____. 1966. *Geochemistry of Rare Elements*. Oldebourne Press, Ltd., London.

Zelikman, A., Krein, O., Samsonov, . 1964. Metallurgy
of Rare Metals: Isreal Program for Scientific
Translations, Jerusalem.