

Lanthanide Abundances in Coexisting
Skarn Minerals, as Determined by X-ray
Fluorescence Analysis

by

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To my lovely fiancée,

Karen Lee

who made this possible

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Abstract

A method is presented for the determination of trace quantities of the rare earth elements and yttrium in calcareous minerals by X-ray fluorescence analysis. Initial chemical concentration of the rare earths is accomplished by scavenging their insoluble hydroxides on a ferric hydroxide precipitate and serves the further purpose of elimination of matrix absorption effects which dampen sensitivity when the raw minerals are analysed.

Triplicate analyses are given for La, Ce, Sm and Y in a calcite-fluorite-apatite skarn rock and for each of the three minerals of this rock. Apatite and calcite are enriched in all the rare earths investigated relative to the whole rock, while fluorite shows a relative depletion. The apatite is enriched in the rare earths relative to the calcite. Peak height ratios of Nd, Eu, Er, Lu, Gd+Ho and Dy+Tm in each of the separated minerals to the whole rock show the same trends as the quantitative data and also indicate that apatite and fluorite show a stronger affinity for the lanthanides of low atomic number than for those of higher atomic number. The abundances of the rare earths in the apatite show the same dependence on ionic radius as has been noted by other workers. The whole rock and each of the minerals which it contains are enriched in all the rare earths relative to chondrites.

The rare earths have preferentially entered the lattices of those minerals which provide a stronger rare earth-anion bond.

Introduction

This study was undertaken for two general purposes:

- (1) To find a quantitative analytical technique for the determination of the rare earth elements by X-ray fluorescence spectrography; and
- (2) To determine the nature of the distribution of the lanthanides and yttrium between coexisting calcite, fluorite and apatite in a skarn zone.

The Sample Locality

Location:

All samples were collected from outcrop on the property of Cardiff Uranium Mines, in northwestern Cardiff Township, Haliburton County, Ontario. The mine is reached by taking highway 500 south from the town of Wilberforce for 1.5 miles to a dirt road and proceeding one mile east along it to the headframe on the hillside.

Petrology:

Calcite-fluorite-apatite veins lie within a 300 to 500 foot wide band of scapolite and biotite amphibolites and limy paragneiss near its contact with crystalline limestone which underlies the western part of the property. These gneisses are metasomatized and grade into hybrid syenite gneiss which is intruded by syenite and granite pegmatites. The samples taken for analysis were from a calcite-fluorite-apatite vein, three feet from the hybrid syenite gneiss contact on the hillside, 50 yards south-east of the Cardiff headframe.

Samples Collected:

Sections of a 12-inch long apatite crystal from a calcite-fluorite-minor apatite matrix were collected from outcrop, in addition to specimens of the matrix from within 5 inches of the apatite crystal boundary.

Preliminary Treatment of Samples

Mineral Separation Procedure:

- 1) The calcite-fluorite-minor apatite matrix (from now on referred to as the whole rock) was put through the jaw crusher twice, and the pulverizer twice. It was then sieved through brass sieves and the -100, +200 size fraction was rinsed in distilled water and dried twice. The whole rock powder was stored in a sealed plastic container, dried overnight at 90°C in a Pyrex beaker, and placed in a dessicator to cool before weighing.
- 2) Random sections of the apatite crystal were chosen for analysis. Visible fluorite grains were scraped from the outer surface of the apatite with a dissecting needle. After the apatite was crushed twice in the jaw crusher, pulverized twice, and sieved, the -100, +200 size fraction was washed with distilled water, stirred for thirty seconds, and the fines were decanted. The washing, rinsing and decanting sequence was repeated two more times and then the apatite powder was rinsed in acetone once, the fines were decanted with the excess acetone, and the remainder was dried under an infra-red heat lamp. The apatite powder was poured into a 1000 ml. separatory funnel, three-quarters full of tetrabromethane, and allowed to settle. After approximately one hour, almost complete separation into floating calcite and heavy apatite had taken place. The floatent was carefully stirred three times to loosen any trapped particles of apatite, as was the

apatite deposit on the bottom to free any grains of calcite which may have been carried with it. The apatite was tapped from the bottom, rinsed eight times with acetone, dried under an infra-red heat lamp, and stored in a sealed plastic bottle. Prior to weighing, the apatite powder was dried in a Pyrex beaker overnight at 90°C and placed in a dessicator to cool.

- 3) A number of $\frac{1}{2}$ inch to $\frac{3}{4}$ inch fragments were selected from the same whole rock supply as in (1) above, and inspected under the microscope to ensure that no visible apatite grains were chosen. This calcite-fluorite mixture was put through the same crushing, rinsing and separation procedure as described in (2) above, the fluorite sinking to the bottom of the separatory funnel and the calcite remaining on top. Each of these was recovered separately and rinsed, dried, cooled and weighed in a manner identical to that of the apatite in (2) above.

Purity of Concentrates:

A microscope slide was prepared of each of the separated apatite, calcite, and fluorite concentrates, and their purity was determined by mineralogical point-counting. A 1.540 index of refraction oil was used as a mounting medium and 600 to 700 grains were counted in each slide. The results are presented in Table I.

TABLE I. PURITY OF SEPARATED CONCENTRATES

CONCENTRATE	MODAL % FLUORITE	MODAL % CALCITE	MODAL % APATITE
FLUORITE	98.6	1.1	0.3
CALCITE	0.2	99.8	0.0
APATITE	0.1	0.2	99.6

Chemical Procedure

Standards:

The total calcite and the total fluorite recovered in part (3) of the mineral separation procedure above were each weighed to provide an approximate weight percent mineralogical analysis of the whole rock, neglecting the less-than-one-percent apatite. This was found to be 34.4% fluorite and 65.6% calcite.

Only one set of rare earth standards was prepared. This set was used for analyses of apatite, fluorite, calcite and the whole rock. It was decided that a matrix approximating the mineralogical analysis of the whole rock, above, would be used for the standards. Consequently, a 30 gm. mixture consisting of 34.4% laboratory chemical calcium fluoride and 65.6% laboratory chemical calcium carbonate was prepared and ground in a mortar and pestle for 15 minutes.

Milligram quantities of rare earth oxides were weighed precisely to five decimal places into 5.00 gram samples of the above matrix in 400 ml. Pyrex beakers. 7.5 milligrams of Fe_2O_3 was then added to each standard.

Chemical Concentration of the Rare Earths and Yttrium:

Having found the intensities of the characteristic X-ray lines for the rare earth elements to be too weak for quantitative analysis when a pellet of raw rock was examined, it was decided that a method must be found

for the quantitative extraction and concentration of them from their enclosing matrix.

Each standard was dissolved in 100 ml. of concentrated HCl by gentle heating on a hot plate for one hour, using watch glasses as beaker covers. The pH of the solutions was brought to approximately 9 by addition of concentrated NH_4OH from a buret.

A pH meter was standardised against a pH 9.00 buffer solution while the standards cooled to room temperature.

The precipitation of ferric hydroxide with its accompanying coprecipitation of insoluble rare earth hydroxides was continued by dropwise addition of concentrated NH_4OH from a 100 ml. buret to pH 9.80.

Each of the precipitates was filtered through a Whatman "ashless" No. 41 filter paper and rinsed several times with cold distilled water. The filter papers were placed in pre-weighed porcelain crucibles, were charred under an infra-red heat lamp for 45 minutes before being ignited at 850°C for one hour in a furnace, and were then cooled in a dessicator before weighing. The crucibles were weighed before and after emptying the precipitate. Boric acid powder was added to each precipitate to make the total weight 1.4 grams and the resulting mixture was hand-ground in a mortar and pestle for 15 minutes. These mixtures were then pressed into pellets with a boric acid back layer under 20 tons pressure, using a 30 ton press. The pellets were labelled on the back and stored in a dessicator to await X-ray fluorescence analysis.

Treatment of Samples:

Triplicate 5.00 gm. samples of each of the fluorite, calcite, apatite

and whole rock powders were weighed out and treated in precisely the same manner as the above standards.

It was difficult to dissolve all the fluorite in this volume of HCl and it was consequently heated more strongly for a longer period of time and stirred vigorously. More HCl was added when necessary.

It was noted that a large amount of hydroxides other than $\text{Fe}(\text{OH})_3$ were insoluble at this pH, both in the standards and in the samples. This was presumed to be mostly $\text{Ca}(\text{OH})_2$ which was filtered along with the $\text{Fe}(\text{OH})_3$. Much more precipitate was obtained from the apatite samples than from the others, possibly due to the formation of insoluble calcium or ammonium phosphate salts at this pH. Whereas the calcite, fluorite, and the whole rock underwent an enrichment in the rare earths in the X-ray pellets relative to the actual minerals, apatite suffered a dilution in the rare earths. This resulted from the nearly 5 grams of precipitate obtained from the apatites, only a portion of which could be mixed with a boric acid "cement" to form a 1.4 gram pellet, while the entire amount of recovered precipitate in each of the calcite, fluorite, and whole rock samples was mixed with boric acid to form a pellet of the same weight as the apatite pellet. Thus, the apatite pellets are 40% to 50% by weight H_3BO_3 and the others are often 75%-95% H_3BO_3 , while the standards are 25% - 35% H_3BO_3 .

Efficiency of the Scavenging Technique:

Cerium (IV) hydroxide begins to precipitate at pH 1.0. The rare earth (III) hydroxides begin to precipitate at pH 6 with $\text{Lu}(\text{OH})_3$ and end quantitatively with $\text{La}(\text{OH})_3$ at pH 9.0. Thus, precipitation from a solution of pH 9.8 is theoretically quantitative for the rare earth hydroxides in either oxidation state, and the theoretical concentrations of rare earths in

the pellets of the standards as calculated in Table II is based on the assumption that the insoluble lanthanide hydroxides are co-precipitated on the $\text{Fe}(\text{OH})_3 - \text{Ca}(\text{OH})_2$ precipitating mixture and separated from solution with 100% efficiency. If this is not the case, the efficiency of the process is assumed to be the same in both samples and standards since they are very similar to one another in chemistry and since both undergo essentially the same chemical procedure.

No La, Ce, or Y was detected by X-ray fluorescence analysis of the evaporated filtrate left after precipitation of the rare earths from S-6, the standard containing the highest concentrations of these elements, indicating that the scavenging technique accomplishes at least 97% recovery of the lanthanides.

It is readily seen from Table II that, by this procedure, the pellets of the standards are concentrated in the rare earths by a factor of 3.3 to 3.5 over their concentrations in the original matrix. This factor will be the same for the calcite, fluorite, and the whole rock, while the concentration of rare earths in the apatite pellets is only 50% to 66% of that in the actual apatite.

Blanks:

S-1 serves as a blank on the matrix of the standards and on the $\text{HCl-NH}_4\text{OH}$ reagents. In the case of every element analysed, this blank was found to be very small. The X-ray intensity for every rare earth element investigated was found to be only a few counts per second above or below background at the peak positions. In all cases, this value was used as the intensity ordinate for the zero concentration of the calibration curves.

TABLE II. CONCENTRATION RANGE OF THE STANDARDS

OXIDE	STANDARD	S-1	S-2	S-3	S-4	S-5	S-6
La ₂ O ₃	mgm in 5 gm matrix ppm in pellet	0	1.43	3.55	5.67	29.72	60.00
		0	1020	2500	4000	20,700	42,700
CeO ₂	mgm in 5 gm matrix ppm in pellet	0	1.74	3.13	6.40	33.65	63.35
		0	1240	2210	4510	23,400	45,100
Y ₂ O ₃	mgm in 5 gm matrix ppm in pellet	0	0	0	6.73	34.69	66.06
		0	0	0	4750	24,200	47,000
Sm ₂ O ₃	mgm in 5 gm matrix ppm in pellet	0	0	3.25	6.75	0	0
		0	0	2290	4760	0	0
Er ₂ O ₃	mgm in 5 gm matrix ppm in pellet	0	0	3.14	6.36	0	0
		0	0	2220	4480	0	0
Yb ₂ O ₃	mgm in 5 gm matrix ppm in pellet	0	0	3.17	1.20	0	0
		0	0	2240	850	0	0

This blank will be greater than, or equal to, the blank on the laboratory reagents alone and, since the value of the blank on the standards is so low, the blank on the samples is taken to be zero X-ray intensity.

X-Ray Fluorescence Analysis

Instrumental Parameters:

A Philips manual, vacuum, X-ray fluorescence spectrograph was used for all analyses. A Tungsten target tube and a Lithium Fluoride analysing crystal ($2d = 4.028 \text{ \AA}$) were used throughout. Due to the possible hygroscopicity of the precipitate, all analyses were performed under vacuum. A spinner allowed all pellets to be rotated in the path of the X-ray beam to help minimize sample inhomogeneity. Table III summarizes the instrumental parameters for each element.

Background positions were selected such that readings were taken as close to equal distances on either side of the peak positions as was feasible.

Pulse height analysis was required for Ce in order to minimize the intensity of a second order $W L\beta_{17}$ interfering X-ray line. For Sm, pulse height analysis was used to decrease the intensity of very "noisy" background in the vicinity of the peak position.

The flow proportion counter used P10 gas, a 10% methane - 90% argon mixture.

Counting Procedure:

All analyses were performed by recording the time required to accumulate a fixed number of counts. All time determinations at peak and background positions were repeated in triplicate and averaged. 10^4 to 10^5

TABLE III. INSTRUMENTAL CONDITIONS FOR La, Ce, Sm, AND Y

ELEMENT	X-RAY LINE	BACKGROUND POSITIONS ($^{\circ}2\theta$)	PEAK POSITION ($^{\circ}2\theta$)	EXCITING VOLTAGE (Kv)	TUBE CURRENT (Ma)	COUNTER	PULSE HEIGHT ANALYSIS
LANTHANUM	La_1	82.00, 84.30	82.95	50	30	F.P.C 1.62Kv	Not Required
CERIUM	La_1	77.87, 80.45	79.00	50	30	F.P.C 1.62Kv	Window = 250 Lower Level = 325
YTTRIUM	$K\alpha$	23.35, 24.60	23.85	40	20	S.C. 0.96Kv	Not Required
SAMARIUM	$L\beta_1$	59.00, 60.10	59.52	50	30	F.P.C 1.47Kv	Window = 75 Lower Level = 100

counts were accumulated at the background positions, depending on the sample being analysed. Wherever practical, the same number of background counts were accumulated on the samples as on the standards. 10^4 to 2×10^6 counts were accumulated at the peak positions, again depending on the concentration of the sample. Wherever practical, the same number of peak counts were accumulated on the samples as on the standards.

The sensitivity of the X-ray unit to a given element at a given X-ray line was found to vary from day to day. As a result, each triplicate set of samples was run contemporaneously with a calibration curve for the particular element in question in an attempt to ensure that no instrumental "drift" occurred between the times of sample and standard analysis.

Calibration Curves:

Due to the wide concentration range of the prepared standard pellets, a calibration curve prepared from the entire set of standards for any given element on any given day was linear at low concentrations and began to curve toward lower sensitivity at higher concentrations.

It was then decided to run each triplicate sample against a calibration curve consisting of only two points: the standards immediately below and above the sample in concentration. The blank was also run for each calibration curve.

The calibration curves were plotted, the concentrations of the sample pellets were read from them, and these were converted to actual sample concentrations, using the initial sample weight, the weight of the precipitate, and the dilution factor of the precipitate in the boric acid of the X-ray pellet.

Relative Analysis:

The X-ray spectrum of one apatite, one calcite, one fluorite, and one whole rock pellet was traced from $34.00^\circ 2\theta$ to $84.00^\circ 2\theta$ on a strip-chart recorder at $1^\circ 2\theta$ per minute. The Tungsten tube, operated at 50 Kv and 30 ma, was used with the flow proportion counter at 1.47 Kv. No pulse height analysis was used and all other conditions were the same as for quantitative analysis above. The recorder paper was set at a full scale reading of 2×10^3 counts per second.

The net peak heights, proportional to the concentrations of lanthanides in the pellets, were converted into numbers proportional to concentrations in the actual mineral or rock. Thus, the information derived gives relative concentrations of the rare earths from sample to sample rather than a statement of their absolute rare earth contents.

The elements investigated, their X-ray lines, and the corresponding peak positions employed are given in Table IV.

TABLE IV. RARE EARTHS INVESTIGATED BY RELATIVE ANALYSIS

ELEMENT(S)	X-RAY LINE(S)	PEAK POSITION ($^\circ 2\theta$)
NEODYMIUM	Nd $L\beta_1$	65.15
EUROPIUM	Eu $L\alpha_1$	63.00
ERBIUM	Er $L\beta_1$	46.50
LUTETIUM	Lu $L\alpha_1$	47.50
GADOLINIUM + HOLMIUM	Gd $L\beta_1$ + Ho $L\alpha$	54.60
DYSPROSIUM + THULIUM	Dy $L\beta_1$ + Tm $L\alpha_1$	50.30

The Gd line could not be resolved from the Ho line. Nor could Dy be resolved from Tm. In each of these cases, the X-radiation detected at the peak position listed in Table IV was taken to be proportional to the sum of the concentrations of the two elements concerned. It is also possible that part or all of the radiation detected at 63.00° may be due to Zr $K\beta_1$.

Experimental Results

Quantitative Results:

Table V lists triplicate quantitative analyses for La, Ce, Sm and Y in each of the calcite, fluorite, apatite, and whole rock samples and indicates the degree of reproducibility achievable by this technique.

TABLE V. REPRODUCIBILITY OF ANALYSES

ELEMENT SAMPLE	LANTHANUM (ppm)	CERIUM (ppm)	SAMARIUM (ppm)	YTTRIUM (ppm)
CALCITE #1	368	865	72	815
CALCITE #2	309	736	63	778
CALCITE #3	373	886	84	837
FLUORITE #1	140	341	12	338
FLUORITE #2	121	268	12	291
FLUORITE #3	130	309	10	287
APATITE #1	8857	23045	2139	11897
APATITE #2	7870	20252	1865	11213
APATITE #3	7741	17412	1738	9936
WHOLE ROCK #1	226	547	45	652
WHOLE ROCK #2	174	462	36	580
WHOLE ROCK #3	216	517	41	623
COEFF. OF VARIATION	5.87	6.58	6.81	4.24

Table VI shows the average of the triplicate analyses for each element in each sample. These averages are corrected for the impurities of Table I.

TABLE VI. CORRECTED AVERAGE RARE EARTH CONCENTRATIONS

ELEMENT	LANTHANUM(ppm)		CERIUM(ppm)		SAMARIUM(ppm)		YTTRIUM(ppm)	
	AVERAGE	CORRECTED	AVERAGE	CORRECTED	AVERAGE	CORRECTED	AVERAGE	CORRECTED
MINERAL								
CALCITE	350	350	829	830	73	70	810	810
FLUORITE	130	100	306	240	11	5	305	270
APATITE	8156	8190	20236	20300	1914	1920	11015	11100
WHOLE ROCK	205	210	509	510	41	40	618	620

Relative Results:

Table VII shows the results of the relative analysis. Numbers shown are proportional to the concentration of the rare earth element indicated for the sample indicated. Thus, the ratio of the concentrations of any rare earth element listed may be computed for any pair of samples.

TABLE VII. RESULTS OF RELATIVE ANALYSIS

(numbers are proportional to concentrations)

SAMPLE ELEMENT(S)	SAMPLE			
	APATITE	CALCITE	FLUORITE	WHOLE ROCK
NEODYMIUM	189	7.53	1.40	3.74
EUROPIUM	18.3	10.4	n.d.	9.51
ERBIUM	36.2	3.10	n.d.	1.28
LUTETIUM	24.0	1.28	n.d.	0.966
GADOLINIUM + HOLMIUM	84.3	4.57	0.925	2.56
DYSPROSIUM + THULIUM	43.1	1.50	n.d.	1.30

n.d. - not detected

Discussion

The result of dividing the concentration of each rare earth element determined in each of the coexisting minerals by its corresponding concentration in the whole rock is shown in Table VIII.

TABLE VIII. RARE EARTH CONCENTRATION RATIOS OF EACH MINERAL TO THE WHOLE ROCK.

ELEMENT	APATITE	CALCITE	FLUORITE
La	39.0	1.67	0.476
Ce	39.8	1.63	0.471
Sm	48.0	1.75	0.125
Y	17.9	1.31	0.436
Nd	50.6	2.01	0.374
Eu	1.92	1.09	low
Er	28.3	2.42	low
Lu	24.8	1.33	low

Ratios for La, Ce, Sm and Y are based on the corrected means of triplicate quantitative analyses, while those for Nd, Eu, Er and Lu are derived from semi-quantitative peak height ratios. The ratios for each mineral are plotted against the rare earth trivalent ionic radii (Cotton and Wilkinson, 1962) in Figure I.

From Figure I, it is apparent that apatite and calcite are enriched in all the rare earth elements relative to the whole rock, while fluorite is depleted in all of them. Apatite is more greatly enriched in the rare earths than is calcite. While many irregularities appear in these graphs, there is a general trend for both apatite and fluorite to preferentially accept the larger rare earth ions, rather than the smaller ones, into their crystal structures. This effect is not as clearly marked in calcite. Europium is anomalously low in the three minerals, perhaps due to its stability as a divalent ion.

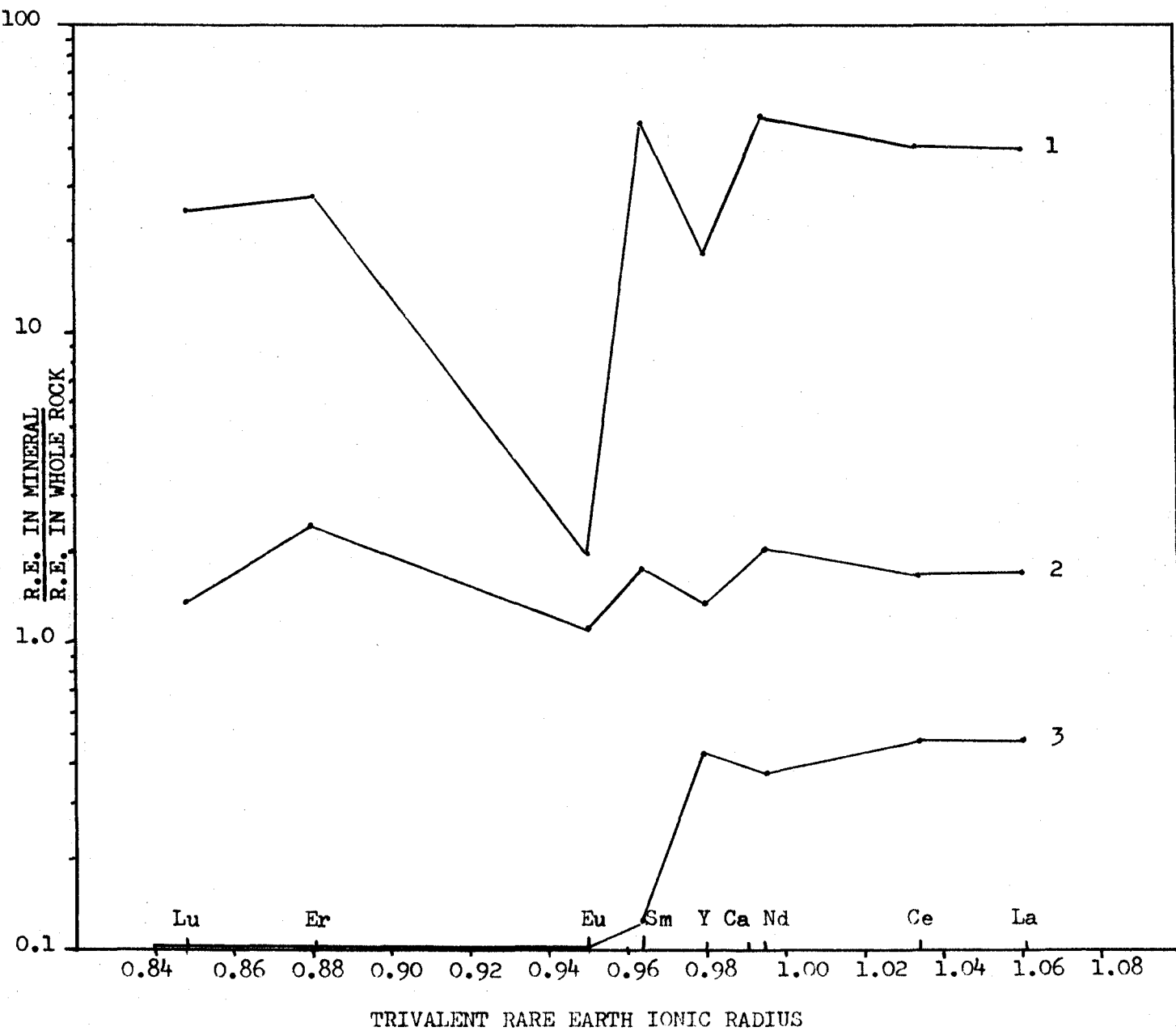
In Table IX are presented the results of dividing the concentration of each rare earth in the whole rock, fluorite, calcite and apatite by its corresponding average concentration in twelve chondrites. These values are taken from Towell (1963), who indicates that the mean relative rare earth abundances of chondrites are representative of the relative rare earth abundances in the earth as a whole.

TABLE IX. CHONDRITE-NORMALIZED RARE EARTH ABUNDANCES IN THE CALCITE, FLUORITE, APATITE, AND THE WHOLE ROCK

ELEMENT	AVGE. CONC. OF 12 CHONDRITES (ppm)	<u>R.E. IN WHOLE ROCK</u>	<u>R.E. IN CALCITE</u>	<u>R.E. IN FLUORITE</u>	<u>R.E. IN APATITE</u>
		R.E. IN CHONDRITES	R.E. IN CHONDRITES	R.E. IN CHONDRITES	R.E. IN CHONDRITES
La	0.32	660	1090	310	25,600
Ce	0.90	570	920	270	22,600
Sm	0.21	190	330	24	9150
Y	1.9	330	430	140	5840

R.E. - concentration of each rare earth element (ppm).

FIGURE I. WHOLE ROCK - NORMALIZED RARE EARTH ABUNDANCES IN APATITE, CALCITE AND FLUORITE, PLOTTED ON A LOGARITHMIC SCALE AS A FUNCTION OF IONIC RADIUS.



1. APATITE

2. CALCITE

3. FLUORITE

R.E. - CONCENTRATION OF EACH RARE EARTH (ppm)

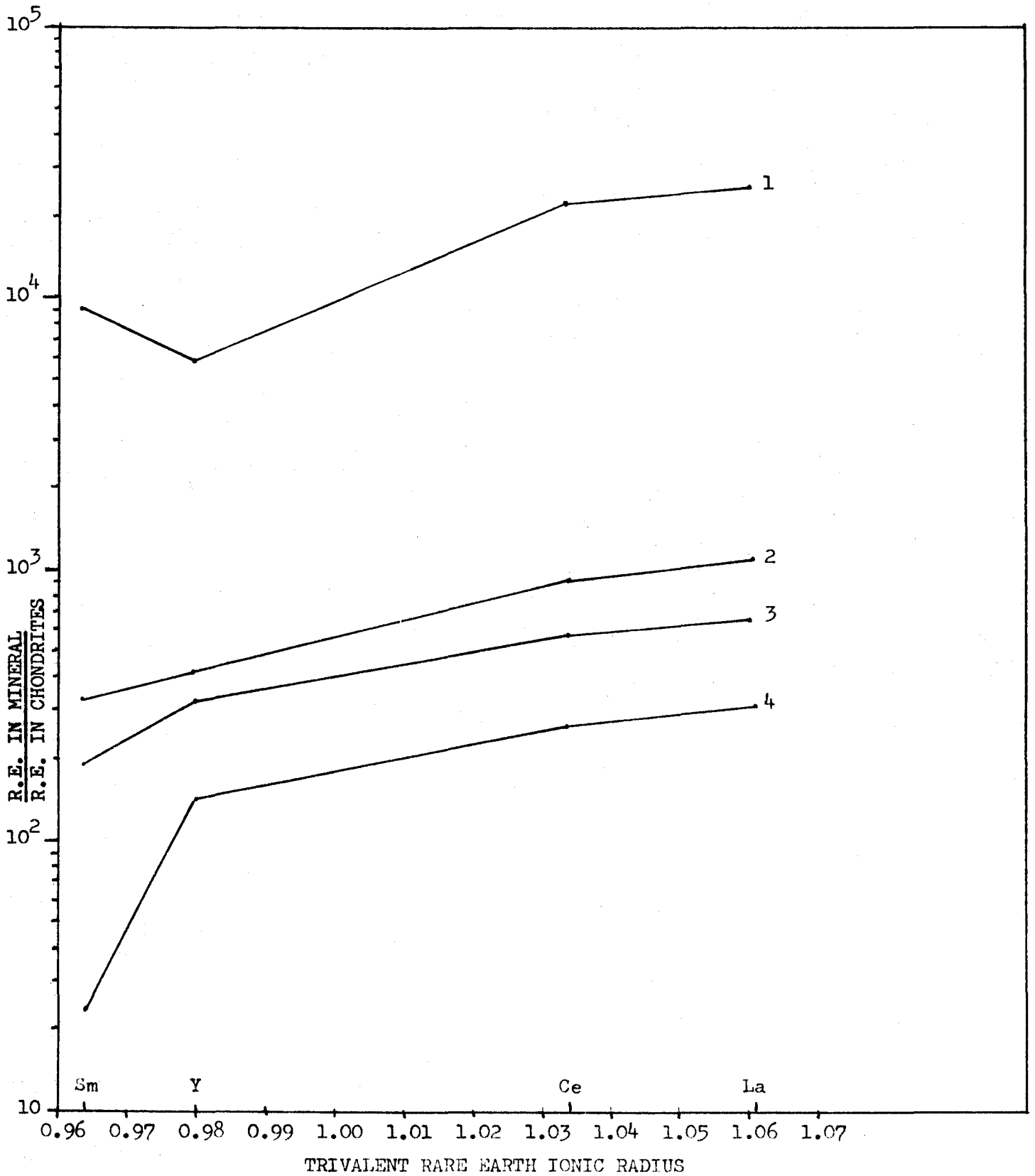
Since absolute rare earth concentrations are not available for Nd, Eu, Er, and Lu in the coexisting skarn minerals, the above calculation cannot be made for these.

The ratios of Table IX are plotted against the trivalent ionic radii of the rare earth elements in Figure II. The resulting graphs show that the distribution of rare earths in the whole rock and in the individual minerals is due to fractionation processes which have acted to enrich these much more in the larger rare earth ions than in the smaller ones relative to the earth's crustal abundances. The enrichment of the apatite and calcite in all the rare earths and the depletion of the fluorite in them relative to the whole rock is again clearly illustrated.

Due to its very high concentration of rare earths, the apatite of this study is particularly interesting. In Table X are given both absolute and chondrite-normalized rare earth concentrations for apatites from the San Marcos gabbro and Bonsall tonalite (Towell, 1963), the arithmetic means of 25 metamorphic apatites and of 21 igneous apatites (Cruft, 1966), and the apatite of this study.

In Figure III, the chondrite-normalized rare earth abundances of the apatites of Table X are plotted against the atomic numbers of the rare earths. Yttrium has been given the atomic number of promethium, since they have almost identical trivalent ionic radii. Although it is extremely enriched in the rare earths relative to the other apatites plotted, the apatite of this study exhibits the same general trend toward decreasing enrichment relative to chondrites with increasing atomic number which other authors have noted. Neumann, Jensen and Brunfelt (1966) have also noted this trend in two igneous apatites of the Lovozero Massif, while

FIGURE II. CHONDRITE - NORMALIZED RARE EARTH ABUNDANCES IN THE APATITE, CALCITE, FLUORITE, AND THE WHOLE ROCK, PLOTTED ON A LOGARITHMIC SCALE AS A FUNCTION OF IONIC RADIUS



- 1. APATITE
- 2. CALCITE
- 3. WHOLE ROCK
- 4. FLUORITE

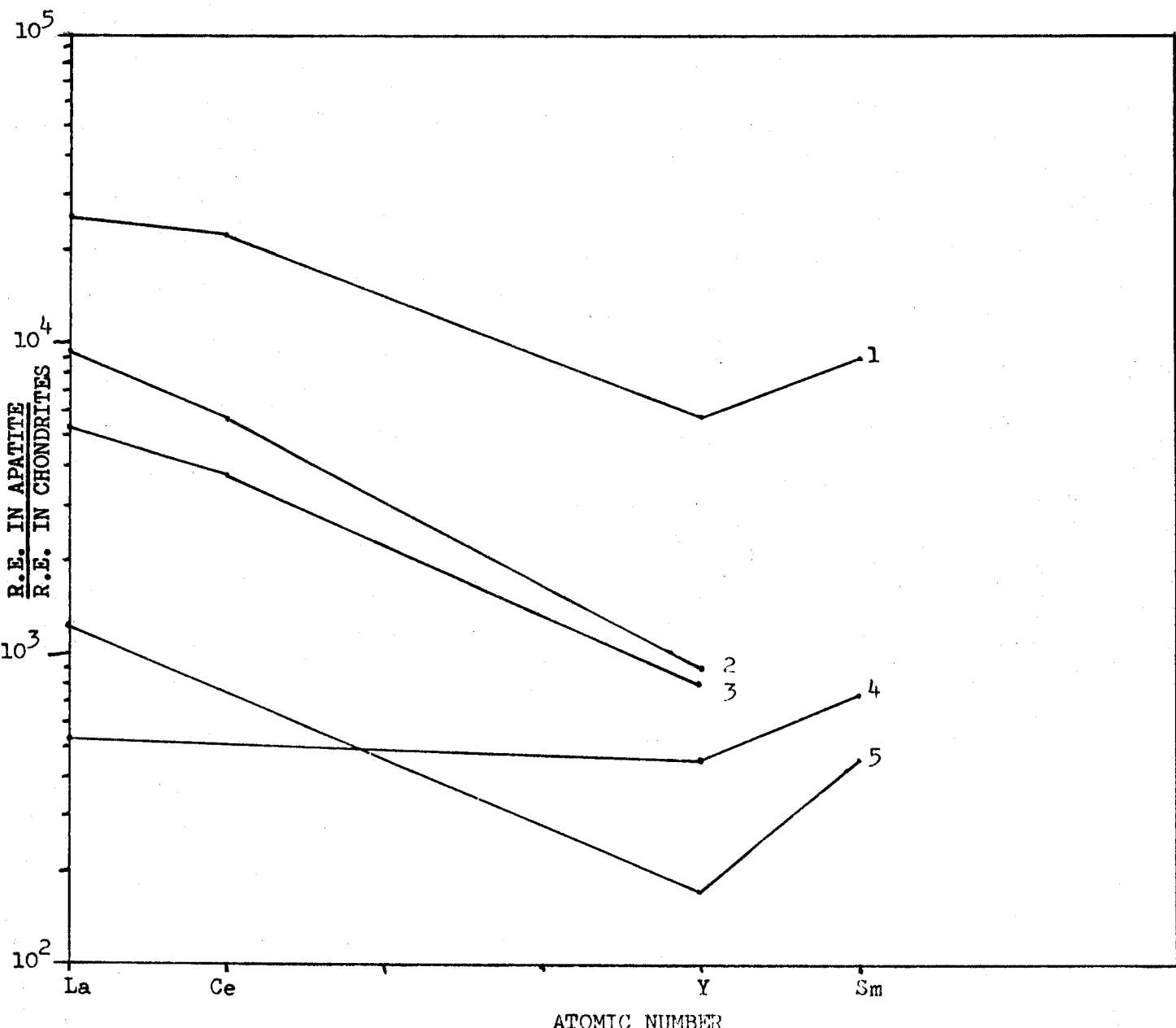
TABLE X. CHONDRITE-NORMALIZED RARE EARTH CONCENTRATIONS OF VARIOUS APATITES.

ELEMENT	APATITE SAN MARCOS GABBRO		APATITE BONSALL TONALITE		AVGE. OF 25 META- MORPHIC APATITES		AVGE. OF 21 IGNEOUS APATITES		APATITE THIS STUDY	
	a	b	a	b	a	b	a	b	a	b
La	392	1230	171	534	3029	9475	1696	5300	8190	25,600
Ce					5117	5680	3391	3765	20,300	22,600
Sm	97	464	157	748					1920	9150
Y	327	172	878	462	1717	904	1523	802	11,100	5840

a. Absolute rare earth concentration (ppm)

b. Chondrite-normalized rare earth concentrations.

FIGURE III. CHONDRITE - NORMALIZED RARE EARTH ABUNDANCES IN
 VARIOUS APATITES, PLOTTED ON A LOGARITHMIC SCALE
 AS A FUNCTION OF ATOMIC NUMBER

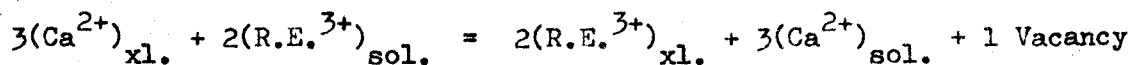


1. CARDIFF TOWNSHIP, ONTARIO
2. ARITHMETIC MEAN OF 25 METAMORPHIC APATITES
3. ARITHMETIC MEAN OF 21 IGNEOUS APATITES
4. BONSAILL TONALITE
5. SAN MARCOS GABBRO

a third from the Ukraine shows the reverse trend, although these writers have normalized their rare earth abundances to a group of basalts, rather than chondrites.

The same data are plotted in Figure IV against trivalent ionic radius. The greater enrichment of all the apatites in the larger rare earth ions is evident.

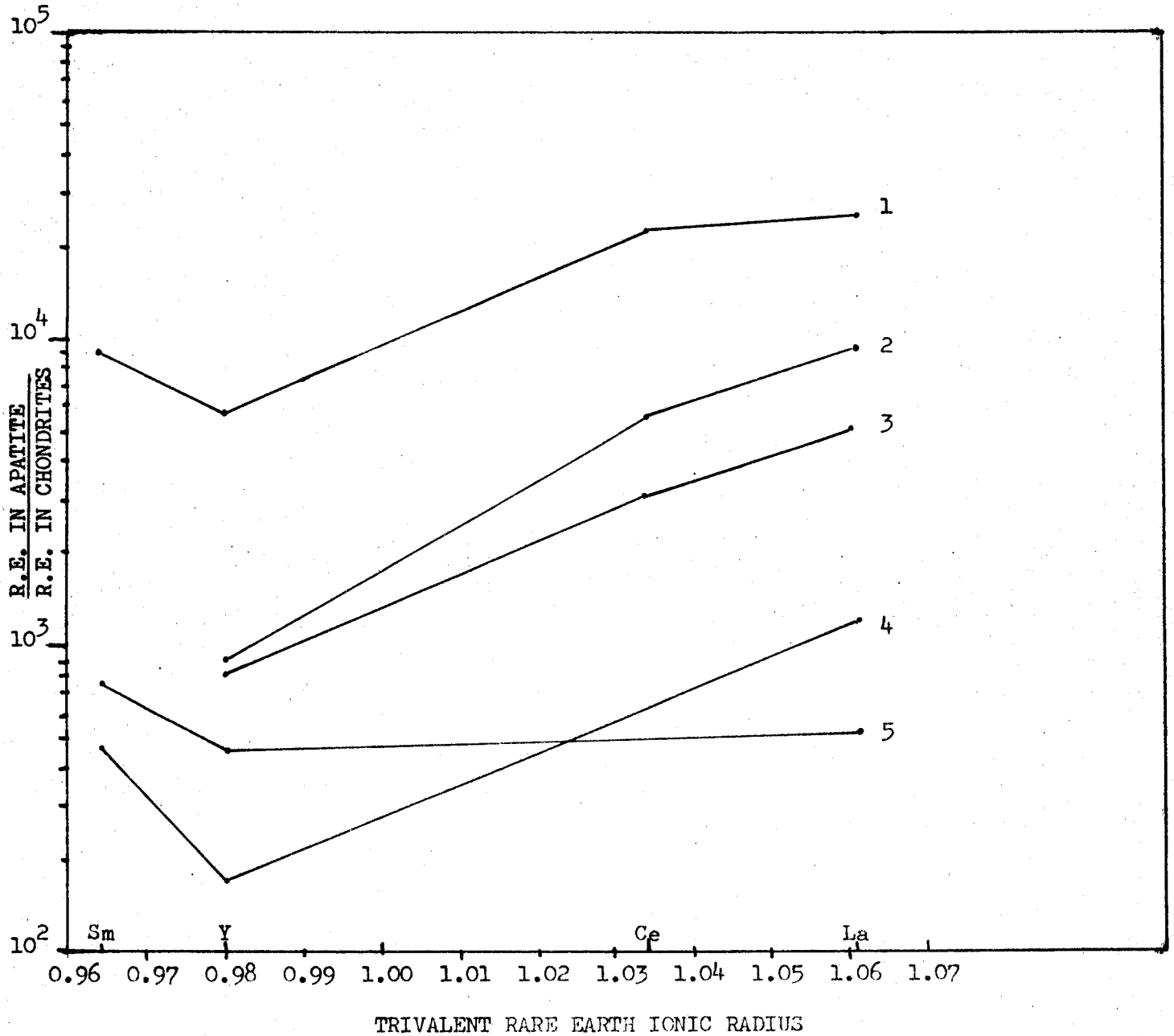
The trivalent rare earth ions substitute for Ca^{2+} in the crystal structures of fluorite, apatite, and calcite, in which they enter lattice sites co-ordinated by fluoride ions or the oxygen atoms of phosphate and carbonate anions respectively. One possible mechanism by which this can occur is:



where a vacancy is produced in the lattice to maintain charge neutrality.

While much of the character of the bond between the rare earths and their co-ordinating atoms is undoubtedly ionic, there is a covalent contribution to it due to a lanthanide ion-anionic induced dipole interaction, in which the cation polarizes the electronic charge clouds of the surrounding anions toward itself. The Gibbs free energy of dissociation decreases from +16.9 Kcal/mole for HPO_4^{2-} to +14.1 Kcal/mole for HCO_3^- to +4.3 Kcal/mole for HF at 25°C in aqueous solution, as calculated from equilibrium constants (Cotton and Wilkinson, 1962). This data indicates that the polarizability of an oxygen atom of a phosphate anion is greater than an oxygen of a carbonate group which, in turn, is far greater than the polarizability of a fluoride ion. Thus, an ion-induced dipole interaction provides a stronger covalent contribution to a bond in a phosphate or carbonate than in a fluoride. Consequently, an increase in the stability

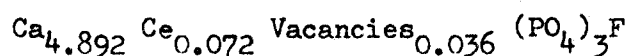
FIGURE IV. CHONDRITE - NORMALIZED RARE EARTH ABUNDANCES IN
 VARIOUS APATITES, PLOTTED ON A LOGARITHMIC SCALE AS
 A FUNCTION OF IONIC RADIUS



1. CARDIFF TOWNSHIP, ONTARIO
2. ARITHMETIC MEAN OF 25 METAMORPHIC APATITES
3. ARITHMETIC MEAN OF 21 IGNEOUS APATITES
4. SAN MARCOS GABBRO
5. BONSTALL TONALITE

of a lanthanide - anion bond is expected in the order: fluorite, calcite, and apatite. The data of Figure I clearly show that the lanthanides have, indeed, preferentially entered the crystal lattices of those minerals in which they form the strongest bonds.

The apatite from Cardiff Township contains over 2% Ce. If this Ce has substituted for Ca via the mechanism suggested above, the ideal fluorapatite formula becomes:

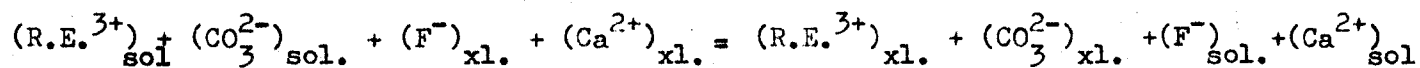


where 0.72% of the calcium sites are vacant. The lanthanide ion - oxygen bonds would have to be of sufficient strength to offset the decrease in the lattice energy of the apatite caused by the creation of a significant number of vacancies.

Other mechanisms in which no vacancies are created are also possible. Two are given below:-



OR



For the latter case, it may be impossible for a large CO_3^{2-} to enter the F^- lattice site which may be quite small.

While the partitioning of the entire rare earth group between the coexisting minerals can be understood by bonding considerations, the reasons why the whole rock and the fluorite and apatite have a stronger affinity for the larger rare earth ions than the smaller ones have not

been explained. The solution to the problem may well lie in the size of the calcium sites in the crystal structures of the minerals.

Conclusions

A study of the feasibility of quantitative analysis for the lanthanides by X-ray fluorescence spectrography and of the distribution of the rare earth elements so determined among coexisting fluorite, calcite, and apatite in a skarn zone in Cardiff Township, Ontario has revealed the following results:

- (1) Preliminary concentration of the rare earths by co-precipitation on a ferric hydroxide scavenger at pH 9.8 provides at least 97% recovery of them.
- (2) The reproducibility of the entire analysis, including the preliminary chemical concentration and the X-ray fluorescence spectrographic counting procedure ranges from a coefficient of variation of 4.24% for Y to 6.81% for Sm.
- (3) The results obtained for the apatite of this study are in excellent agreement with those obtained by various authors for other apatite rare earth analyses.
- (4) The coexisting apatite, calcite, and fluorite, and the whole rock are enriched in the rare earths relative to chondrites.
- (5) The apatite and calcite are enriched in the rare earths relative to the whole rock, while fluorite is depleted in them.
- (6) Apatite is enriched in the rare earths relative to calcite.
- (7) Theoretical considerations indicate that the rare earths have preferentially entered the lattices of those minerals which provide a

stronger rare earth - anion bond.

- (8) The apatite and the fluorite have preferentially accepted the larger rare earth ions, relative to the smaller ones. Calcite does not show this trend.

Suggestions for Further Study

For improvement of analytical data:

- (1) Quantitative analysis for Nd, Er, and Lu is possible by the present technique, using Nd $L\beta_1$, Er $L\beta_1$, and Lu La_1 , respectively.
- (2) It may be possible to excite the K X-ray lines of the lanthanides, La through Dy, by means of a Ag or Cr target tube and a 54 Kv generator. This would lead to an increase in analytical sensitivity over that obtained from the L lines employed in this study. Rare earth elements which were previously undetected due to their very low concentrations may appear due to excitation of their K spectra. The second order K lines of many lanthanides, whose L lines do not appear in the second order, may be analytically useful and will provide greater resolution between closely-spaced rare earth lines than that achievable from first order L lines. The K lines of Ho & Tm will not be excited at 54 Kv, while those of Gd and Dy will. Ag lines interfere with the second order lanthanide K spectrum. Thus, the increased resolution effect must be accomplished with the Cr tube. Furthermore, the Cr and Ag tubes will eliminate W lines which interfere with Yb $L\beta_1$ and Tm $L\beta_1$. No Cr or Ag lines interfere with the first order lanthanide L lines.
- (3) If $Al(OH)_3$ scavenges lanthanide hydroxides efficiently, the addition of Al_2O_3 rather than Fe_2O_3 would minimize the intensity of Fe lines which interfere with the determination of Tb $L\beta_1$ and others.
- (4) A smaller sample size may eliminate the copious Ca precipitates and the

difficulties in dissolving fluorite, but at the same time will severely hinder the determination of the less abundant lanthanides(Sm).

- (5) The use of an analysing crystal of smaller $2d$ than LiF will provide greater resolution between closely-spaced lines, although a loss of intensity relative to that attainable from LiF will occur.

For Further Theoretical Consideration:

- (1) Analysis of the individual minerals, particularly the alkali feldspar, of the syenite; and the fluorite-apatite-free marble far from the syenite contact for rare earths.
- (2) A study of the variation in content of each rare earth in each mineral with distance from the syenite-marble contact.
- (3) Electron probe or autoradiographic techniques would reveal the possible presence of minute inclusions of rare earth minerals in the specimens analysed.

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Appendix: Details of Chemical Reagents and Apparatus

Chemical Reagents:

Acetone - Mallinckrodt analytical reagent grade.

Ammonium Hydroxide - C.I.L. C.P. reagent, concentrated.

Boric Acid - Shawinigan, powdered.

Buffer Solution - Fisher Certified Reagent, pH 9.00

Calcium Carbonate - Analar Analytical Reagent.

Calcium Fluoride - B.D.H., precipitated.

Dessicant - Silica gel.

Ferrous Oxide - Johnson Matthey, "specpure".

Hydrochloric Acid - C.I.L. C.P. Reagent, concentrated.

Rare Earth Oxides - Johnson, Matthey, "specpure".

Tetrabromomethane - Fisher Purified. (density = 2.96 at 20°C).

Apparatus:

Balance - Mettler Gram-Atic, electronic.

Crucibles - porcelain, 1.7 inch outer diameter.

Filter Paper - Whatman "ashless", No. 41.

Furnace - Thermolyne, 1000°C.

Infra-red Heat Lamps - General Electric, mounted on retort stands.

pH Meter - Fisher Accumet Model 310, with a Fisher pH electrode and a Beckman calomel electrode.

Press - Spex, 30 ton.

X-ray Fluorescence Spectrograph - Philips, manual vacuum.