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Microprobe Analysis of REE Minerals Using Empirical Correction Factors

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Abstract

Empirical correction factors (α-factors) have been determined in the rare earth oxide system. These, together with extrapolated and theoretical α-factors, have been used for analysis of xenotimes, apatites, monazites, and synthetic rare earth oxide mixtures. The standards used are fused pure rare earth oxides. The precision and accuracy obtained, while capable of improvement, are satisfactory for most petrological and mineralogical applications. The empirical α-factors are considered to give better analytical results for yttrium than theoretical α-factors.

Introduction

Knowledge of the distribution of the rare earth elements (REE) between coexisting minerals is potentially of great importance to our understanding of REE geochemistry and crystal chemistry. The electron microprobe has proved itself indispensable in studies of coexisting minerals of many types, but has not yet found widespread use in the analysis of REE minerals. This has been due in part to a general lack of suitable standards. Natural REE minerals are commonly very inhomogeneous even within single grains, and small amounts of other REE mineral impurities can drastically alter the concentrations of individual REE in the multigranular samples used by other analytical methods.

We have prepared microprobe standards for REE analysis by melting the individual pure oxides. Using these, and binary and ternary mixtures of REE oxides, we have determined empirical correction factors (α-factors) for the REE, as described by Ziebold and Ogilvie (1964) and Bence and Albee (1968). These factors, which are suitable for microprobes with 52.5° takeoff angles at 20 kV acceleration voltage, have contributed to generally better analytical results for xenotimes and fused REE oxide mixtures than were obtained using only the α-factors calculated from theoretical considerations by Albee and Ray (1970).

Determination of α-Factors

Two ARL-EMX microprobes have been used, one in the Physics Institute of the Norwegian Technical University, Trondheim, and the other in the Central Institute for Industrial Research, Oslo. All analyses were carried out at 20 kV accelerating voltage, with beam currents varying from 0.3 to 0.5 μ amperes.

Samples were mounted in epoxy cores set in 1/4″ brass plugs, and were given a thin carbon coating.

Because of the limitations of time, and because calculated α-factors (Albee and Ray, 1970, supplemented by specially calculated factors provided by A. L. Albee) could serve as a base for extrapolations where necessary, we selected mainly the most important binary and ternary rare earth oxide systems (those involving the most abundant rare earths in natural minerals, as well as some involving adjacent rare earths) for empirical evaluation of α-factors.

The mixtures used for α-factor evaluation were made from pure oxides (purity > 99.9 percent), which had been dried for ~5 minutes in a platinum crucible at a temperature of ~900°C, using a Meeker burner. Sample homogenization was assured by grinding to dryness 4–5 times under ethyl alcohol in an agate mortar. Afterwards the powder was dried in air at ~65°C for 15–20 minutes.

Before melting, the powder was pressed into 150–250 mg pellets. The melting was performed in an electric arc furnace (at the Institute for Mineralogy and Geology, University of Uppsala), in which the arc from a tungsten rod strikes the sample as it rests in a depression on a thin (1–2 mm) copper plate that is water-cooled from below. The melting of the sample is observed through a glass port. The temperature is step-wise variable by means of a rheostat. The atmosphere was pure dry argon at a pressure of 300-500 mm Hg. Cooling of the samples after arcing seems to be rapid, from ~2500°C to 20°C in 5–10 sec.

Altogether, glasses of 18 binary and 66 ternary mixtures, and 15 pure oxide glasses, have been synthetized for evaluation of α-factors. A list of these mixtures is available on request. Three major problems have been met with during this preparation: (1) evaporation of Si during melting, (2) inhomogeneous glasses, (3) hygroscopism.

Si evaporation during melting was established by melting three splits of the same composition for 5, 10 and 15 seconds and counting these for Si and rare earths on the microprobe. The count rates for Si decreased, and those for the REE increased, with increasing melting time. Some Si-containing mixtures were also very inhomogeneous. These problems add an extra uncertainty to α-factors for Si radiation in rare earth oxides and for rare earth radiations in SiO_2. The corresponding α-factors of Albee and Ray (1970) are therefore considered to be superior and are used in Table 1. In some cases, SiO_2-REE ternary mixtures have been used to measure α-factors in the REE-oxide binary system, with satisfactory results.

Grossly inhomogeneous glasses were occasionally produced, and these have been rejected as bases for α-factor evaluation. This was true for all CaO-containing mixtures and some of the Si-containing ones. Some of the CaO-rich mixtures apparently separated into an almost pure CaO phase and a REE oxide phase. The same feature, but not so pronounced, was also observed in most of the Si-bearing mixtures. It is not known whether this represents nucleation of several crystalline phases during the cooling or simply reflects inhomogeneities due to the larger grain size of the original CaO and SiO_2 powders relative to those of the REE oxides. Segregation because of crystallization is definitely possible because X-ray powder photographs of some fused REE oxides showed them to be crystalline.

Inhomogeneities are frequently encountered. The general types are small (μm-sized) areas very enriched in one of the components, larger areas with small and gradual changes in composition, and transitions between these two types. Whether a mixture was usable for α-factor calculation or not was judged by taking into account the amounts of the separated phases and the degree of difference in composition.

CaO, La_2O_3, PrO_2, and Nd_2O_3, as well as mixtures with large amounts of one or more of these oxides, proved to be quite hygroscopic. Probe mounts of La_2O_3, PrO_2, and Nd_2O_3 swell out of their holders within a few hours when stored in air. When they are stored in a dessicator this reaction is 30–40 times slower, indicating that no significant water is taken up by the rest of the REE oxides when they are stored in dessicators. Even when these are stored for 2 months in air, their count rates remain constant

TABLE 1. α-Factors Used for Analysis of Xenotimes, Monazites, Apatites and Synthetic Mixtures
20 KeV Accelerating Voltage, 52.5° Takeoff Angle

Radiation										Oxide										
	SiO_2	P_2O_5	CaO	Y_2O_3	La_2O_3	CeO_2	Ce_2O_3	PrO_2	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3
Si Kα	1.00	1.00	1.10	.96	1.61	1.79	1.68	1.87	1.75	1.81	1.93	1.79	1.83	1.65	1.68	1.56	1.60	1.66	1.69	1.74
P "	1.53	1.00	1.06	.94	1.42	1.54	1.47	1.62	1.53	1.57	1.66	1.71	1.75	1.81	1.67	1.72	1.77	1.60	1.63	1.52
Ca "	1.12	1.12	1.00	1.14	.88	.86	.89	.89	.91	.91	.92	.93	.93	.94	.94	.95	.96	.97	.97	.98
Y Lα	1.66	1.11	1.17	1.00	1.29	1.41	1.38	1.62	1.58	1.84	1.89	1.86	1.83	1.98	1.93	2.09	1.81	1.97	1.81	1.80
La "	1.36	1.33	1.44	1.09	1.00	.95	1.01	.91	.98	.93	.97	1.03	1.09	1.04	.98	.98	.98	.98	.98	.98
Ce "	1.35	1.32	1.41	1.09	.99	1.00	1.00	.96	1.02	1.17	.99	.94	.90	.93	.97	.93	.90	.96	1.02	.96
Pr "	1.34	1.31	1.39	1.10	.89	.94	1.00	1.00	1.00	1.16	.99	.99	.98	.97	.97	.97	.96	.97	.97	.98
Nd "	1.36	1.32	1.39	1.10	.95	.89	.97	1.01	1.08	1.00	.99	.98	.97	.95	.94	.95	.94	.94	.94	.94
Sm "	1.38	1.34	1.40	1.11	1.33	.87	.95	.99	1.08	1.12	1.00	.97	.82	1.09	.96	.94	.94	.94	.93	.93
Eu "	1.38	1.36	1.39	1.13	1.14	1.10	1.15	.97	1.04	1.04	1.03	1.00	.74	.97	.98	.99	1.00	.97	.96	.96
Gd "	1.42	1.37	1.41	1.15	1.15	1.05	1.11	1.07	1.13	1.01	.99	.97	1.00	1.01	1.03	1.01	.99	.97	.96	.95
Tb "	1.42	1.38	1.41	1.13	1.19	1.12	1.17	1.07	1.13	1.13	1.03	1.02	1.01	1.00	.99	.90	.94	.94	.94	.94
Dy "	1.44	1.40	1.42	1.14	1.19	1.03	1.10	1.30	1.32	1.13	.97	.97	.95	.97	1.00	.97	.97	.97	.97	.97
Ho "	1.45	1.40	1.43	1.13	1.28	1.24	1.27	1.24	1.27	1.24	1.24	1.16	1.13	1.12	1.13	1.00	1.12	1.05	1.05	1.05
Er "	1.46	1.41	1.43	1.13	1.17	1.06	1.13	1.19	1.23	1.31	1.17	1.10	1.05	1.06	1.07	1.08	1.00	.98	.95	.95
Tm "	1.46	1.42	1.43	1.15	1.16	1.11	1.17	1.12	1.18	1.18	1.11	1.11	1.02	1.02	1.01	1.00	1.00	1.00	.97	.97
Yb "	1.49	1.43	1.45	1.17	1.03	1.04	1.11	1.05	1.12	1.06	1.09	1.10	1.11	1.00	.88	.94	.99	.98	1.00	1.05
Lu "	1.49	1.43	1.45	1.17	1.11	1.06	1.13	1.08	1.15	1.14	1.11	1.11	1.07	1.06	.98	.97	.97	.95	.96	1.00

---- Theoretical α-factors (Albee & Ray (1970); others supplied by A. L. Albee).
____ Empirical α-factors. Those in Ce_2O_3 and Pr_2O_3 are calculated from the ones in CeO_2 and PrO_2 by extrapolating in the binary systems Ce-O and Pr-O.
α-factors for Ce and Pr in O are from Albee & Ray.
Others are extrapolated, partly from the trend of Albee & Ray.

within 2 percent. Special care has, however, been taken in most cases to avoid water takeup, including polishing only under oil and frequent repolishing.

Since α-factors were not measured for all binary REE oxide systems, extrapolations had to be made between the empirically determined ones. Between empirical α-factors, linear extrapolations have been done, taking into consideration both the trend of the calculated factors and the overall trend in the empirical ones. The α-factors were measured in replicate (2–4 times), with a reproducibility better than ± 9 percent.

The empirically determined, extrapolated, and theoretically calculated α-factors (Albee and Ray, 1970) for rare earth lines in rare earth oxides (except Y_2O_3) are shown in Figures 1a, b, and c, and in Table 1.

The α-factors for P radiation and in P_2O_5 have been taken from Albee and Ray (1970) because of the volatility of P_2O_5 and because well-analyzed minerals suitable for evaluation of these α-factors are not available.

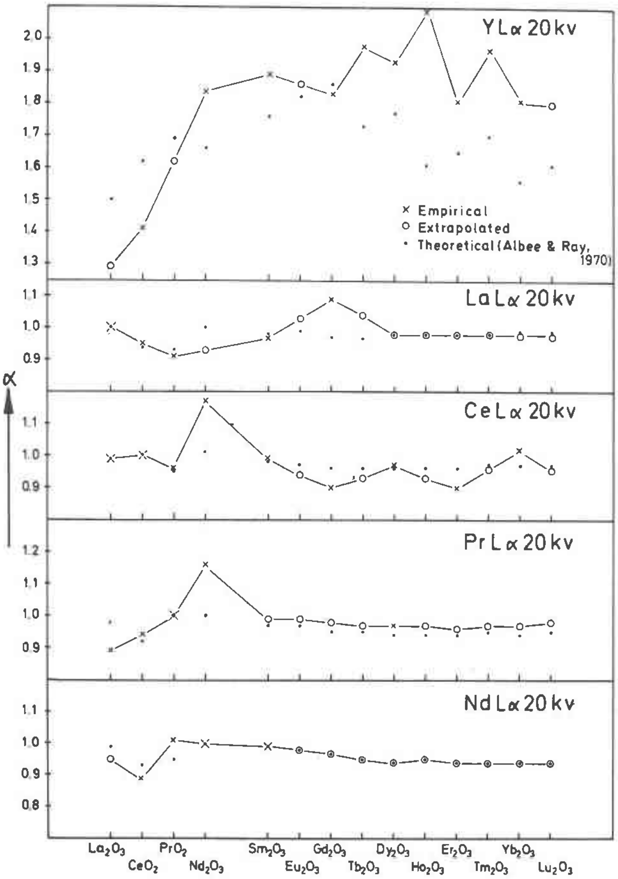

FIG. 1a. Empirically determined, extrapolated, and theoretically calculated α-factors for Y-Nd radiation in rare earth oxides (except Y_2O_3).

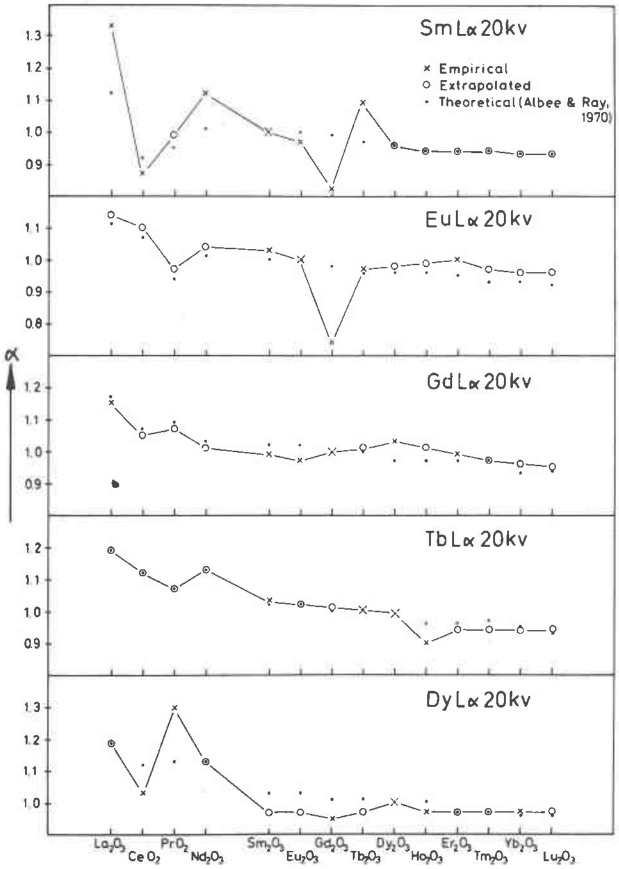

FIG. 1b. Empirically determined, extrapolated, and theroretically calculated α-factors for Sm-Dy radiation in rare earth oxides (except Y_2O_3).

The agreements and differences between the factors of Albee and Ray (1970) and those determined here will be discussed in the section on precision and accuracy.

Peak and Background Interferences

The amount of interference in both peak and background positions has been established as follows. In a pure oxide or an oxide mixture free from the element undergoing interference, the interfering element is counted in the interfering 2θ-position and in the 2θ-position for the radiation line used in analyzing the unknowns ($L\alpha^1_{1,2}$-lines for REE). From the ratio of these two net counts, one obtains the fraction of those counts collected on the interfering element's $L\alpha^1_{1,2}$-line, which should be subtracted from (or added to) the interfered element's $L\alpha^1_{1,2}$-line (or background) in the unknown.

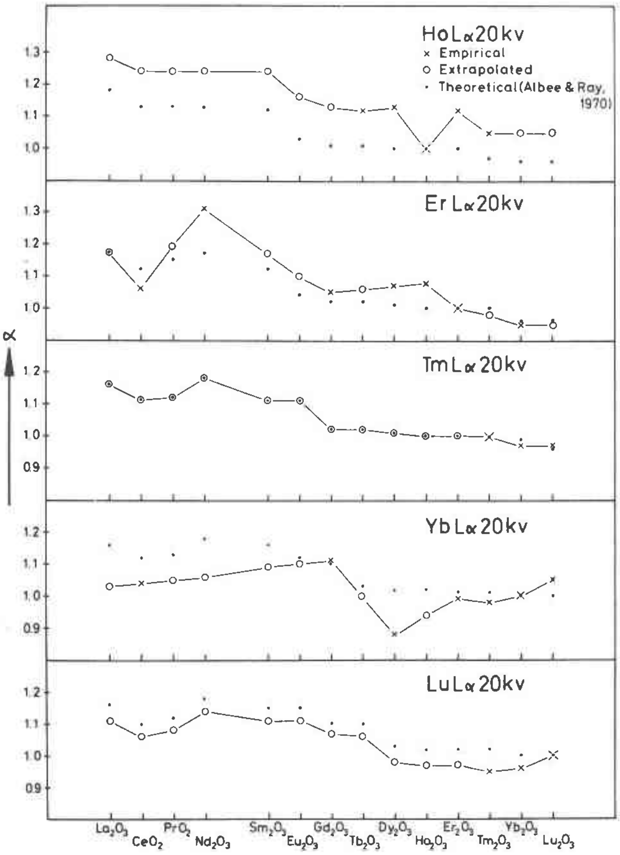

FIG. 1c. Empirically determined, extrapolated, and theoretically calculated α-factors for Ho-Lu radiation in rare earth oxides (except Y_2O_3).

Example: Gd interference on Ho peak (at constant accelerating voltage)

in pure Gd_2O_3

$$\left(\frac{\text{Net counts}_{\text{Gd}L\beta_1^1\ \text{pos. Ho}L\alpha_{1,2}^1}}{\text{Net counts}_{\text{Gd}L\alpha_{1,2}^1}}\right)\cdot 100$$

in unknown

$$\equiv\left(\frac{\text{Net counts}_{\text{Gd}L\beta_1^1\ \text{pos. Ho}L\alpha_{1,2}^1}}{\text{Net counts}_{\text{Gd}L\alpha_{1,2}^1}}\right)\cdot 100$$

$\equiv$ correction factor (%)

$GdL\beta^1_1$ pos. $HoL\alpha^1_{1,2}$ is counted with the same discriminator setup as used for $HoL\alpha^1_{1,2}$ in the unknown. The correction factors for our microprobe are shown in Table 2. The very large corrections associated with the analysis of Pr, Eu, Gd, and especially Ho are obvious sources of error in mineral analyses.

Standards

The standards used in the electron microprobe analyses are shown in Table 3.

For La, Pr, and Nd, the pure oxides were mixed with CeO_2 to decrease the problem of hygroscopism. These binary standards are not a wholly satisfactory solution, but are a large improvement over the pure oxides.

For the natural minerals, Ce and Pr are reported as the trivalent oxide (see further discussion of this in the section on precision and accuracy). This requires the use of β-factors (Bence and Albee, 1968), because the standards used are the tetravalent oxides. The standards are regarded as being composed of $CeO_{1\,1/2}$ + ½O and $PrO_{1\,1/2}$ + ½O, respectively, and corresponding β-factors have been calculated using the α-factors for O given by Albee and Ray (1970).

Chips from transparent yellow crystals of Durango apatite have been used as standard for F, P, and Ca. According to Young *et al* (1969), the composition of the clear yellow crystals is very constant, and their analyses are therefore used in this work. β-factors for Ca and P in Durango apatite have been calculated using only Ca, P, F, and REE, because of the lack of empirical α-factors for the rest of the elements reported in the analyses and because of the small amounts present. α-factors for Ca and P in F are, however, taken from Albee and Ray (1970).

The ratio of fluorine counts on the standard apatite to those on the unknown has been used to estimate wt percent F.

Analytical Testing of the Method

For evaluation of the analytical precision, a xenotime (84) has been analyzed 8 different times (all analyses are from the same area, $\sim 30 \times 30\,\mu$, carefully checked for homogeneity) over a period of *ca* 6 months. Table 4 gives the arithmetic means, standard deviations, and relative standard deviations for these 8 analyses. Calculations of the ϵ expected from counting statistics are extremely complex, due to the necessity of including the statistical error accumulated at *each* counting. These calculations have been done for selected analyses; they demonstrate that > 60 percent of the ϵ quoted in Table 4 is due to inconsistencies in procedure, instrumental instability, or other non-statistical sources. The errors cited in

Table 4 are therefore believed to give a true picture of the *obtained* precision for an analytical series, as contrasted to the better precision that would be calculated from counting statistics.

The analytical data for replicate analysis of an apatite are presented in Table 4. Each analysis has been reduced from the averaged counts on different grains taken out of approximately 1/4 cm³ apatite, having very few inclusions of rare earth minerals. The ϵ values presented must be considered with care. The poor precision for the rare earths results because their concentrations are close to the limit of detection for these elements with the instrumental setup used.

Accuracy

Factors affecting the accuracy are: (1) takeup of water by the standards, (2) wrongly assumed oxidation states, (3) errors in α-factors, (4) systematic instrument errors, (5) systematic operator errors. As discussed above, steps have been taken to eliminate absorption of water by the standards and the oxide mixtures used in α-factor determination.

According to Gschneidner (1973) all rare earths will occur as the stable trivalent oxide except for Ce, Pr, and Tb, which form CeO_2, Pr_6O_{11}, and Tb_4O_7 when heated in air at 800–1000°C. The Meeker burner provides temperatures in this range; the oxides have thus most probably been in the states suggested by Gschneidner before being melted with the electric arc. Reduction during this melting process could occur through oxidation of the copper base plate. A complicating factor would be introduced if the redox conditions in the oven are not constant. Such a possibility can neither be confirmed nor rejected.

TABLE 2. Peak/Background Interferences and Correction Factors Used in This Work

Element inter- ferred	Peak posi- tion*	Interferring radiation line	Correc- tion factor %	Back- ground posi- tion*	Interferring radiation line	Correc- tion factor %
Pr	2.4630	La$L\beta^1_1$	12.72			
Nd	2.3704	Ce$L\beta^1_1$	0.90			
Sm	2.1998	Ce$L\beta^1_{2'1s}$	1.90			
Eu	2.1209	Pr$L\beta^1_{2'1s}$	20.33			
Gd	2.0468	Ce$L\gamma^1_1$	11.79			
"	"	La$L\gamma^1_2$	2.80			
Tb				1.9475	Sm$L\beta^1_1$	0.91
Ho	1.8450	Gd$L\beta^1_1$	42.10			
Er	1.7843	Tb$L\beta^1_1$ }	3.00			
"		Tb$L\beta^1_4$ }				
Tm	1.7268	Sm$L\gamma^1_1$	8.66	1.7558	Gd$L\beta^1_{2'1s}$	1.32
				"	Dy$L\beta^1_1$ }	0.42
				"	Dy$L\beta^1_4$ }	
Yb				1.6919	Tb$L\beta^1_{2'1s}$	3.66
Lu	1.6195	Dy$L\beta^1_{2'1s}$	8.98	1.5705	Ho$L\beta^1_{2'1s}$	9.58

* LiF geared wavelength values from White et al. (1970)

TABLE 3. Standards Used for Analyzing Synthetic Mixtures and Natural Minerals

Element/oxide to be analysed	Standard
F	Durango apat. (3.54% F)
P_2O_5	- " - (40.86% P_2O_5)
CaO	- " - (54.13% CaO)
La_2O_3	La_2O_3/CeO_2 (20% La_2O_3)
Ce_2O_3	CeO_2 (95.35% Ce_2O_3)
PrO_2	PrO_2/CeO_2 (20% PrO_2)
Pr_2O_3	- " - (19.07% Pr_2O_3)
Nd_2O_3	Nd_2O_3/CeO_2 (20% Nd_2O_3)

Pure oxides were used as standards for Si, Y, and all other REE.
All % are wt.%

X-ray powder photographs of some of the fused rare earth oxides reveal that Ce occurs as crystalline CeO_2. The oxide of Pr fits neither Pr_6O_{11}, Pr_2O_3, nor a mixture of these. The Eu oxide shows a composite pattern which is essentially that of monoclinic Eu_2O_3 with a few additional lines. Terbium shows a pattern very similar to that of Eu and is therefore considered to occur mainly in the 3^+ state.

In the minerals analyzed here, the oxidation state for the rare earths is reported as 3^+. According to Ahrens (1964), Ce can occur as 3^+ and 4^+ and Eu as 2^+ and 3^+. Since no Ce is detected in the xenotimes and hardly any in the apatites, the problem of the oxidation state of Ce in compounds and minerals can be neglected for these two. The same argument holds for Pr and Eu.

In the case of monazites (see Åmli, 1975), part of the Ce might occur in the 4^+ state to rectify the charge imbalance caused by substitution of Si for P. The possible reduction of Eu can be neglected, since it is not detected in the monazites. Pr could cause problems due to a wrongly assumed oxidation state in the standard and thus indirectly through erroneous α-factors.

To check the accuracy of the α-factors and the analytical procedures, we have analyzed mixtures of known composition. In Table 5 are presented analyses of two synthetic mixtures (J3 and D5) composed essentially of REE oxides. The arithmetic mean of each mixture is therefore used in this discus-

TABLE 4. Analytical Data on Natural REE Minerals

	Xenotime 84 (aver. 8 anal.)*					Apatite 85 (aver. 3 anal.)			
	$\bar{x}$ wt.%	s	ε %	Atom.** prop.		$\bar{x}$ wt.%	s	ε %	Atom.*** prop.
F	nd	-	-	-		2.92	0.4172	14.0	0.7934
SiO_2	0.31	0.1119	36.10	0.0106	1.0000	0.49	-	-	0.0423
P_2O_5	34.37	0.1781	0.52	0.9894		40.67	0.5930	1.4	2.9577
CaO	nd	-	-	-		54.47	0.4712	0.8	5.0136
Y_2O_3	44.03	0.3201	0.72	0.7966	1.0141	0.71	0.0254	3.5	0.0325
La_2O_3	nd	-	-	-		nd	-	-	-
Ce_2O_3	nd	-	-	-		0.10	0.0234	23.0	0.0030
Pr_2O_3	nd	-	-	-		nd	-	-	-
Nd_2O_3	0.17	0.0192	11.29	0.0020		0.12	0.0141	11.0	0.0037
Sm_2O_3	0.49	0.0220	4.49	0.0057		0.05	0.0127	25.0	0.0014
Eu_2O_3	0.07	0.0217	31.00	0.0008		nd	-	-	-
Gd_2O_3	2.69	0.0812	3.02	0.0304		0.10	0.0141	14.0	0.0028
Tb_2O_3	0.58	0.0479	8.26	0.0065		nd	-	-	-
Dy_2O_3	4.93	0.0728	1.48	0.0539		0.11	0.0380	34.0	0.0030
Ho_2O_3	1.27	0.1110	8.74	0.0136		nd	-	-	-
Er_2O_3	4.05	0.0785	1.94	0.0433		0.04	0.0212	53.0	0.0010
Tm_2O_3	0.70	0.0593	8.47	0.0073		nd	-	-	-
Yb_2O_3	4.36	0.1575	3.61	0.0451		0.08	0.0254	31.0	0.0020
Lu_2O_3	0.87	0.1289	14.82	0.0089		nd	-	-	-
$O \equiv F$						1.23			
Sum	98.89					98.63			

nd - not detected

* 5 anal. for Nd ** Norm. to (P+Si)=1: Formula = $REE_{1.014}(P,Si)_{1.000}$

*** Norm. to (P+Si)=3: Formula = $(Ca,REE)_{5.063}(P,Si)_{3.000}F_{0.793}$

INAA analyses of Xenotime 84: Sm_2O_3, 0.52%; Tb_2O_3, 0.66%; Lu_2O_3, 0.71%.

sion. For J3 the agreement between the analytical result and the nominal composition is good for the heavy REE. D5 shows essentially the same result, but here local inhomogeneity has caused some odd results for Lu and has thus affected the average value. Tm is somewhat high in both. Agreement is good for the light rare earths except for La, Pr, Nd, and Sm. This could be related to the problems caused by the hygroscopic character of especially the La, Pr, and Nd oxides, although as stated above this was considered to be a rather small problem. It could also be an oxidation state problem or a combination of both.

The counting data for J3 and D5 were also reduced using only Albee and Ray's α-factors; these results are also shown in Table 5. For both J3 and D5 the most pronounced difference from the nominal composition is in the Y content. This result is easily understood in light of the respective α-factors for Y*Lα* radiation in the rare earths (Fig. 1a). From the results for Y in J3 and D5, it is concluded that Albee and Ray's α-factors for Y*Lα* radiation in the rare earths are generally too low. Interpretations of the other differences are more difficult. Further testing of the method, based on analyses of simpler oxide mixtures, will probably lead to refinement of Table 1.

For the minerals, the analytical sums and structural formulae give indications of the accuracy. For the xenotimes (Table 4) the analytical sums are generally a little low, and atomic proportions of rare earths are a little high relative to (P + Si). For the apatite the analytical sums are satisfactory, but atomic proportions of Ca plus REE are again somewhat high relative to (P + Si). These results may reflect errors in the Ca and P values used for the Durango apatite, or errors in Albee and Ray's α-factors for REE in CaO and P_2O_5 and *vice versa*.

Normalizations of REE abundances to those in chondrites give some idea of the accuracy of the analyses. It is frequently observed that rare earth patterns for most geological materials are smooth (except for Eu) when normalized in this way. Figure 2 shows xenotime, monazite, and apatite analyses normalized to chondrites. For xenotime 84, the pattern is rather smooth and implies the absence of large analytical errors. For apatite 85 the pattern for the REE detected is also smooth; only Er falls off the curve. The reason for this systematically low Er value is not known. The good agreement for Er seen in Table 5 indicates, however, that this error is not proportional to the Er content.

The pattern for the two monazites indicates high Pr values, as also is seen in the analysis of D5 in Table 5. This high Pr value is probably due mainly to error in the α-factor for Pr radiation in Nd_2O_3 (Fig. 1a). Furthermore, Eu and Tb values are clearly erroneous, since they are reported as not detected in the analysis, and should definitely be detectable according to the normalization pattern, even with a very large negative anomaly for Eu. Ho shows a positive anomaly in 69–1.5 and is not detected in 69–1.3, indicating possibly both systematic and random errors. Er and Yb values are hard to interpret. The odd results for the heavier REE in monazites are most probably explainable in terms of counting statistics and possible errors in the stripping method used for peak and background interferences (Table 3).

TABLE 5. Comparison of Analytical Results for Two Synthetic REE-Oxide Mixtures

	J3 (aver. 5 anal.)			D5 (aver. 4 anal.)		
	This work	Albee & Ray	True comp.	This work	Albee & Ray	True comp.
Y_2O_3	67.92	65.47	68.00	59.80	57.85	60.00
La_2O_3	0.07	0.07	0.10	1.79	1.89	2.00
CeO_2	0.22	0.23	0.20	2.95	3.06	3.00
PrO_2	0.08	0.09	0.10	0.56	0.58	0.40
Nd_2O_3	0.36	0.36	0.30	1.86	1.88	2.00
Sm_2O_3	1.43	1.46	1.50	2.68	2.72	3.00
Eu_2O_3	0.09	0.09	0.10	0.59	0.59	0.60
Gd_2O_3	4.69	4.67	4.50	3.15	3.14	3.00
Tb_2O_3	1.13	1.15	1.20	1.90	1.92	2.00
Dy_2O_3	8.05	8.16	8.00	10.09	10.23	10.00
Ho_2O_3	1.58	1.57	1.50	2.11	2.07	2.00
Er_2O_3	5.74	5.82	5.70	5.18	5.22	5.00
Tm_2O_3	1.48	1.50	1.30	0.82	0.83	0.60
Yb_2O_3	5.00	5.12	5.00	3.00	3.10	3.00
Lu_2O_3	1.63	1.66	1.60	2.32	2.37	2.00
SrO	0.90*	0.90*	0.90	-	-	-
Fe_2O_3	-	-	-	0.80*	0.80*	0.80
ThO_2	-	-	-	0.40*	0.40*	0.40
UO_3	-	-	-	0.20*	0.20*	0.20
Sum	100.37	98.32	100.00	100.20	98.85	100.00

* Assumed values.

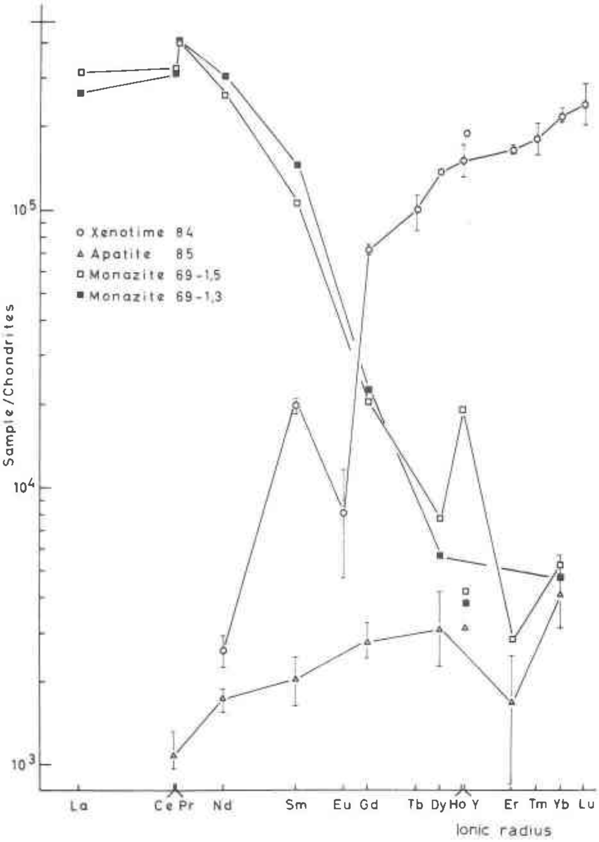

FIG. 2. Average of 8 analyses of xenotime 84, average of three analyses of apatite 85, plus analyses of monazite 69–1.5 and 69–1.3 (see Table 4 and Åmli (1975, Table 2), normalized to chondrites. The bars give the variations in the analytical results. Chondrite REE abundances are from Haskin *et al* (1966); ionic radii for REE^{3+} in 8-coordination are from Shannon and Prewitt (1969).

An instrumental neutron activation analysis (INAA) of material from xenotime crystal 84 was carried out with the help of K.G. Finstad (Min.-Geol. Museum). Reproducible data were obtained only for La, Sm, Tb, and Lu (Table 4). They are comparable to the probe analyses; deviations could be due to variations in the composition of the material analyzed by the two methods. Material from the rim of the crystal (likely to be present in the material subjected to INAA) would give higher values for the light rare earths and lower values for the heavy rare earths, as is observed.

Conclusion

The empirically determined α-factors, combined with those derived by Albee and Ray (1970), allow analysis of apatites, xenotimes, and monazites using pure REE oxides as standards. The precision and accuracy obtained, while capable of improvement, are satisfactory for most petrological and mineralogical applications.

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