A STUDY OF ALLUVIAL MONAZITE FROM MALAYA[1]

B. H. Flinter, *Geological Survey, Federation of Malaya;* J. R. Butler, *Department of Geology, Imperial College, London;* and G. M. Harral, *Overseas Geological Surveys, London.*

Abstract

Sixteen samples of alluvial monazite from Malaya have been analyzed for their rare earth, thorium, uranium, calcium, and silicon contents, and an attempt is made to find some correlation between composition and specific gravity, mass magnetic susceptibility and interplanar spacing. Compositionally, three of the samples, all from columbite-producing areas, are unusual, one being especially rich in Eu, one in Gd, and one in U and Dy.

Introduction

Monazite is of widespread occurrence in the alluvial deposits of Malaya and is a major by-product of tin-mining. This is the first time the rare earth distribution of Malayan monazite has been examined in detail, and the study was made as an initial step towards the evaluation of the mineral's commercial possibilities. Emphasis was thus placed on the alluvial deposits along the west coast of the country where mining operations are concentrated. The geographic distribution of the samples examined is shown in Table 5.

Determination of the individual rare earths was done at the Imperial College of Science & Technology, London, by J. R. Butler, whereas all the chemical assays were carried out at the geochemical laboratories of the Geological Survey of Malaya under the supervision of G. M. Harral.

Preparation of the Material

In order to enhance the practical value of this study, the samples used were made to approximate as closely as possible to the material that could be extracted commercially. From experience of Malayan alluvial monazite, commercial extraction can be duplicated by using a Frantz Isodynamic electromagnetic separator with a setting of 25° for the side slope and 15° for the forward slope, and extracting the material within the range 0.8 to 1.0 amps., *i.e.* all material magnetic at 0.7 amps and nonmagnetic at 1.0 amps was discarded. This also removed any xenotime which is more magnetic. At least 99.6% of the monazite was extracted within the range 0.8–1.0 amps for all the samples except Nos. 2, 8, 9, 10, and 15. In samples 2, 9, 10, and 15, 0.8%, 3.5%, 2.0%, and 8.6% respectively were attracted at 0.7 amps, while in samples 8 and 10, 2.1% and 2.3% respectively were not attracted at 1.0 amps.

The retained fraction was then cleaned by hand-picking under a stereo-

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microscope, all material containing inclusions being discarded. The cleaned sample was then split in two, half being used for chemical analysis and half being used for the other tests.

General Description of the Samples

As all the samples studied are detrital, their derivation cannot be categorically stated. It is almost certain that most, if not all, are derived from cassiterite-bearing granite, the major rock type in Malaya. Probable exceptions are samples No. 1a, No. 15 and possibly No. 1. These may be derived from pegmatites which occur within the two localities in closer proximity than any granite mass. However, in appearance, No. 15 does not resemble known pegmatitic monazite from the same area, and Nos. 1 and 1a look even less like it.

Apart from No. 14 which was obtained from the heavy mineral suite of a beach sand, all the samples come from areas which are being actively mined for cassiterite. Nos. 1 and 1a were obtained from a single alluvial concentrate and, with No. 15, occur in columbite-producing areas.

In form, all the samples were fairly similar, being moderately well-rounded discrete crystals or parts of crystals. No. 1a was appreciably less rounded and had better developed crystal faces than the others. No. 14 was the most irregular, much of the material being fairly angular. Nos. 1 and 15 were slightly more angular than the remainder.

No. 14 was also the most variable in size, the material ranging from 0.1 to 0.4 mm. No. 10 had a similar size range but was mainly 0.3 mm. The remainder ranged from 0.2 to 0.6 mm; samples 1, 1a, 3, 6, and 12 were slightly coarser than the rest.

In color, all except No. 1a were similar, varying from a clear, deep canary yellow for fresh material, through cloudy-white translucent material, to completely opaque, cream-colored material with a resinous luster as the rare earth oxides became progressively more oxidized. In bulk the altered material imparted a pale greenish tinge. In a few cases only, oxidation gave rise to a dark gray or black coloration. Nos. 1 and 9 were almost completely fresh, being a clear deep yellow, the former having a pale salmon tinge. Nos. 3, 8, and 11 were completely transformed to opaque, cream-colored material. The remainder had varying proportions of oxidation. No. 1a was strikingly distinctive in color, being an intense, clear apple-green. Green monazite is known in quantity only from the Semeling area in Kedah, although traces of a much paler green monazite were noted in samples 5 and 10.

The associated minerals are:

Nos. 1 & 1a. Columbite, cassiterite, garnet (mainly pink to orange almandine, very minor pale yellow spessartite), tourmaline, gahnite, magnetite and minor amounts

of wolframite (?), Ta/Nb-rutile, chromite and fergusonite. In the separated fraction of No. 1, inclusions of gahnite were fairly common but columbite was less abundant. In No. 1a, inclusions were abundant, the majority being columbite which was irregular in shape and randomly distributed. A few crystals of tourmaline were also noted as inclusions. A most interesting feature was the fairly common intergrowth of the monazite with crystals of a beige-colored, opaque, resinous variety of zircon. A few typical examples are shown in Fig. 1.

No. 2.   Cassiterite, zircon, ilmenite, iron oxides, xenotime, Ta/Nb-rutile, tourmaline, columbite, and minor amounts of allanite and euxenite. The clear monazite was free of inclusions. The translucent resinous (oxidized) monazite con-
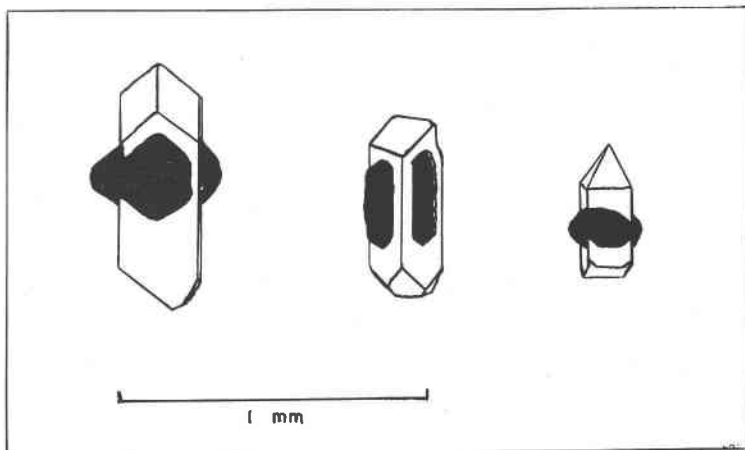

FIG. 1. Intergrowths of monazite (dark) and zircon in sample 1a.

tained a fair amount of inclusions, these being cassiterite, Ta/Nb-rutile and columbite.

No. 3.   Cassiterite, zircon, ilmenite, iron oxides, tourmaline, xenotime, Ta/Nb-rutile and a minor amount of columbite. Inclusions of Ta/Nb-rutile were present.

No. 4.   Similar to No. 3, but with epidote and minor allanite additionally present, and Ta/Nb-rutile very abundant. Inclusions of cassiterite and Ta/Nb-rutile were rare.

No. 5.   Similar to No. 3 with some anatase additionally present. An appreciable amount of columbite occurred.

No. 6.   Mainly ilmenite and Ta/Nb-rutile, with less zircon and cassiterite. Some inclusions of Ta/Nb-rutile were present.

No. 7.   Xenotime, ilmenite, cassiterite, and zircon. Some grains contained inclusions of ilmenite.

No. 8.   Similar to No. 3 except for the absence of columbite.

No. 9.   Similar to No. 3. Inclusions were very rare.

No. 10.   Similar to No. 9.

No. 11.   Similar to No. 3, except that there were fewer inclusions.

No. 12.   Similar to No. 3. Inclusions were absent.

No. 13.   Similar to No. 3 with a minor amount of gahnite additionally present. Inclusions of Ta/Nb-rutile occurred in minor amounts.

No. 14.   Mainly xenotime and ilmenite, with minor amounts of tourmaline, columbite, allanite, Ta/Nb-rutile, cassiterite, and zircon. The separated fraction was very pure, only very minor amounts of finely disseminated opaque inclusions occurring.

No. 15.   Columbite, cassiterite, Ta/Nb-rutile, gahnite, garnet (pink almandine), zircon, pyrite, and tanteuxenite. In the magnetically separated fraction, incluclusions of Ta/Nb-rutile and cassiterite were fairly abundant.

ANALYTICAL METHODS

Total rare earths, SiO_2 and CaO were determined gravimetrically; so was ThO_2 (by the double hexamine method of Ismail and Harwood, 1937). Ce was determined titometrically on a solution of the rare earth oxides after oxidizing Ce^{3+} to Ce^{4+} with ammonium persulphate. U was determined colorimetrically after the method of Guest and Zimmerman (1955). Individual lanthanons were determined spectrographically using the chemically separated rare earth oxides (Butler, 1957a). Possible interference due to the coincidence of Ca4435.68 Å with Eu4435.53 Å was ruled out by confirming the absence of the stronger Ca line at 4434.96 Å. Y was determined in the rare earth oxides by an x-ray fluorescent method with added Sr as an internal standard to Y.

Repeat specific gravity determinations were made on a Berman balance using the powder basket method with CCl_4; and the results are ± 0.01.

DISTRIBUTION OF THE RARE EARTHS

Rare earth distribution has been studied more in monazite than in any other rare earth mineral and the general abundance pattern is now fairly well known. Results have been correlated with the work of Carron *et al.* (1958) who found that laboratory orthophosphates of La, Ce, Pr, Nd, Sm and Eu each had a monazite type structure whereas those of Ho, Er, Tm, Yb, Lu and Y had a xenotime type structure; (Gd, Tb) PO_4 (with Gd:Tb about unity) crystallized as the monazite phase but with minor amounts of the xenotime phase; (Tb, Dy) PO_4 (with Tb:Dy about unity) crystallized as the xenotime phase but with minor amounts of the monazite phase. High contents of Y and the heavy lanthanons are not, therefore, to be expected in monazites.

There is much natural variation in the relative abundances of Y and the light lanthanons in monazite even though the vast majority of those analyzed are from granites, granite pegmatites or alluvial deposits derived therefrom. Wylie (1950) Vainshtein *et al.* (1955, 1956a, 1956b) and Seminov and Barinskii (1958) give data for the light lanthanons and

Murata et al. (1953, 1957, 1958) give data for Y and the light lanthanons down to Gd. Recently, Heinrich et al. (1960) have studied 14 pegmatitic monazites for La, Ce, Pr, Nd, Sm, Gd and Y and show that: (i) paragenetically identical monazites from a single pegmatite can be remarkably similar in their rare earth composition (ii) paragenetically identical monazites from different pegmatites from the same districts may have characteristic (regional) rare earth distributions.

In order to see how the data for the Malayan monazites (Tables 1 and 2) compare with those for other monazites, it is convenient to consider the range and variation in concentrations of pairs of lanthanons. Table 3 shows ratios for Ce/La, Ce/Nd, La/Nd, and Nd/Sm from the various sources indicated. Ionic radii for La^{3+}, Ce^{3+}, Nd^{3+}, and Sm^{3+} are, (Ahrens 1952), 1.14 Å, 1.07 Å, 1.04 Å, and 1.00 Å respectively. It might be expected, therefore, that more variation would be obtained for the ratio La/Nd (with a difference in ionic radii of about 10%) than for the ratio Ce/La, Ce/Nd or Nd/Sm (with differences in ionic radii of about 7, 3, and 4% respectively). In monazites derived from granites or granite pegmatites, the 12-fold variation in La/Nd is conspicuously higher than the $3\frac{1}{2}$-fold variation in Ce/La and the $4\frac{1}{2}$-fold variation in Ce/Nd. Variation in Nd/Sm is, however, at least 7-fold. Sm varies from about 14 to about 1 at. % in the total rare earths in monazites, a much larger variation than for La, Ce or Nd, and it is probably not as suitable a size for the monazite structure as La, Ce, and Nd for the conditions under which monazite crystallizes from pegmatites and granites. La, Ce, and Nd are collectively more essential to monazites than Sm, and it may be supposed that Sm variations in monazite reflect more closely the variations in concentrations in Sm^{3+} in the fluid from which the monazites crystallize than do variations in La, Ce and Nd. (The low variation in the Pr content in the rare earths of monazites established by Murata et al. (1953, 1957) would indicate that the size of $Pr^{3+}-1.06$ Å—is eminent for monazites crystallized from acid rocks). Sm can, of course, exist as Sm^{3+} or Sm^{2+} and the larger Sm^{2+} (ionic radius about 1.2 Å) would certainly not be incorporated in the monazite structure.

It will be seen from Table 3 that the Malayan monazites have average values for Ce/La, Ce/Nd, and Nd/Sm very close to those obtained for pegmatitic and granitic monazites by other authors. None of the Malayan samples approach, compositionally, the most La-enriched monazite (from Kazakhstan) recorded by Vainshtein (1956b). On the other hand, the Malayan monazites are distinct from the three cited monazites occurring in association with carbonate, bastnaesite and pyrite (Table 3). The monazite from the pyrite-apatite vein (Murata et al., 1957) has, for instance, equal atomic proportions of La and Ce (Ross et al., 1958),

TABLE 1. ANALYTICAL RESULTS

Sample No.	Chemical Analyses. Weight % Oxides														M.M.S. Current Strength[3] (amps)			S.G.
	Ce_2O_3[1]	Ce_2O_3[2]	La_2O_3	Pr_2O_3	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_2O_3	Y_2O_3	ThO_2	U_3O_8	CaO	SiO_2	0.8	0.9	1.0	
1	26.7	26.4	14.0	2.7	12.2	2.09	0.6	1.00	—	1.04	2.00	0.19	0.82	0.60	36	58	5½	5.14
1a	20.9	20.7	9.7	2.7	10.6	2.77	—	1.07	0.3	2.08	6.09	5.43	1.55	0.64	96½	3½	—	5.19
2	23.9	25.8	11.2	2.6	15.4	3.85	—	1.3	—	1.44	6.67	0.40	0.92	1.04	55½	40½	4	5.16
3	26.5	27.0	12.4	2.7	12.8	3.20	—	1.23	—	1.46	6.09	0.28	1.20	1.44	78½	21½	—	5.10
4	26.2	26.6	12.0	2.6	12.1	2.03	—	0.97	—	1.77	7.33	0.35	1.22	1.40	44	54½	1½	5.18
5	25.5	25.8	12.8	2.6	12.0	2.5	—	1.23	—	1.70	6.98	0.32	0.65	1.34	21	78½	½	5.14
6	26.5	27.7	13.3	3.0	12.4	2.11	0.13	1.01	—	1.60	6.24	0.31	0.35	1.12	42	53½	4½	5.12
7	28.4	29.0	14.2	2.8	12.8	2.16	—	0.49	—	1.42	4.44	0.23	0.70	1.34	8	87½	4½	5.06
8	28.4	29.6	14.4	2.8	12.8	2.1	—	0.49	—	1.24	4.58	0.38	0.81	1.60	10½	82	7½	5.07
9	25.8	26.2	13.7	2.6	12.1	2.01	0.13	0.45	—	1.32	7.51	0.31	1.25	1.28	35½	36	28½	5.13
10	27.1	28.4	14.3[4]	2.7	12.9	2.14	—	1.02	—	1.28[4]	4.33	0.27	0.50	1.22	35½	53	11½	5.16
11	26.5	27.2	13.4	2.7	12.1	2.1	—	1.27	—	1.74	6.42	0.72	1.02	1.54	20½	68½	11	5.12
12	25.9	26.4	13.3	2.6	11.9	2.6	—	1.25	—	1.78	7.07	0.37	1.37	1.32	65½	16½	18	5.14
13	25.9	26.8	12.2	2.7	12.5	2.83	—	1.99	—	1.91	6.33	0.41	0.92	1.68	29½	48½	22	5.09
14	28.5	28.7	14.3	2.8	12.2	2.17	—	1.04	—	1.34	4.91	0.26	1.00	1.12	1	57	42	5.07
15	23.2	23.5	9.1	2.6	14.1	4.27	—	3.33	—	2.41	6.49	0.50	1.25	0.98	86	10½	3½	5.23

[1] Spectrographically.
[2] Chemically.
[3] Side slope 25°, forward slope 15°.
[4] La_2O_3 12.7% & Y_2O_3 1.1% by radioactivation analysis (J. A. W. Dalziel, pers. comm.)

TABLE 2. ATOMIC PERCENTAGES OF RARE EARTHS IN TOTAL RARE EARTHS

	1	1A	2	3	4	5	6	7	8	9	10	11	12	13	14	15	†
La	23.3	19.1	18.8	20.6	20.6	21.9	22.0	22.8	23.3	23.6	23.3	22.4	22.4	20.4	23.0	15.4	5
Ce	44.2	41.0	40.2	43.8	45.5	43.4	44.2	45.6	45.6	44.3	44.0	44.0	43.4	43.0	45.6	39.0	5
Pr	4.4	5.3	4.4	4.4	4.4	4.4	4.9	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	4.4	25
Nd	19.8	20.3	25.2	20.7	20.2	20.0	20.0	19.9	20.0	20.3	20.4	19.7	19.5	20.2	19.1	23.3	5
Sm	bb	5.1	6.1	5.0	bb	4.0	bb	bb	3.1	bb	bb	bb	4.0	4.4	bb	6.8	10
Eu	0.9	*	*	*	*	*	0.2	*	*	0.2	*	*	*	*	*	*	25
Gd	1.5	1.9	1.9	1.9	1.5	1.9	1.5	0.7	0.7	0.7	1.5	1.9	1.9	3.0	1.5	5.1	10
Y	2.5	5.9	3.5	3.5	4.4	4.2	3.8	3.3	2.9	3.3	3.0	4.2	4.3	4.6	3.1	5.9	5

bb indicates Sm between 2.8 and 3.8 at. %.
* indicates Eu below 0.13% and not detected.
Dy is approximately 1.5% in No. 1a otherwise it is below detection limit of 0.6%.
Tb is approximately at detection limit of 0.5% in No. 1a.
Er, Yb and Lu are not detected and are below 0.5, 0.2 and 0.1% throughout.
No data for Ho and Tm.
† indicates per cent standard deviation.

TABLE 3. CONCENTRATION RATIOS OF SOME LIGHT LANTHANON PAIRS IN MONAZITES

Environment of monazite & Number of samples analyzed	Ce/La	Ce/Nd	La/Nd	Nd/Sm	Reference
Granite; average of 44	1.8	2.5	1.4	6.3	Vainshtein et al. (1955)
Granite; 5	1.8	2.4	1.3	6.2	Vainshtein et al. (1955)
Granite; 2	2.1	2.4	1.2	5.9	Murata et al. (1953, 1957)
Granite pegmatite; 24	2.0	2.3	1.2	5.1	Vainshtein et al. (1955)
Granite pegmatite; 10	2.0	2.15	1.05	4.5	Vainshtein et al. (1956a)
Granite pegmatite; 11	2.2	2.1	0.95	4.3	Murata et al. (1953, 1957)
Granite pegmatite; 31	2.1	2.4	1.2	3.1	Murata et al. (1958)
Granite pegmatite; 14	3.1	2.0	0.67	5.3	Heinrich et al. (1960)
Malaya; 16	2.1	2.1	1.1		
La-rich-monazite, granite pegmatite, Kounral, Kazakhstan, U.S.S.R.	1.3	5.5	4.2	10	Vainshtein et al. (1956b)
Nd-rich monazite, granite pegmatite, Jamestown, Colo., U.S.A.	3.2	1.3	0.4	8.5	Murata et al. (1957)
Sm-rich La-poor monazite, Brown Derby No. 1 pegmatite, Gunnison Colo., U.S.A.	4.6	1.6	0.34	1.43	Heinrich et al. (1960)
Range for monazites in acid rocks	1.3-4.6 (3½-fold)	1.2-5.5 (4½-fold)	0.34-4.2 (12-fold)	1.4-over 10 (over 7-fold)	All cited above and Richartz (1961)
Range for monazites from Malaya	1.9-2.5	1.6-2.4	0.7-1.2	3.5-6.5	
Carbonate vein; 1	1.3	5.2	3.9	over 10	Vainshtein et al. (1955)
Calcite-bastnaesite vein; 1	1.8	4.47	2.48	10.8	Murata et al. (1953)
Pyrite-apatite vein; 1	1.00	4.4	4.4	10	Rose et al. (1958)

and the ratios Ce/Nd and La/Nd are conspicuously higher than are normal for monazites from acid rocks. Borovsky and Gerasimovsky (1945) do record Ce/La at 0.91 for one out of 7 monazites from granites; however, the samples are from widespread localities with Ce/La averaging as low as 1.3, and it is believed that La has been systematically underestimated. Murata *et al.* have indicated a compositional criterion in considering monazites of different parageneses. They calculated the sum of the atomic percentages of La, Ce, and Pr in the total rare earths of monazites and found values between 58 and 80 at. % for monazites associated with acid igneous rocks or acid pegmatites. The ratio Ce/(Nd+Y) (atomic) was shown to decrease as the La+Ce+Pr sum increased. Heinrich *et al.* (1960) found values down to 51 at. % for pegmatitic monazites. In the two monazites associated with alkali rocks, La+Ce+Pr was 87 at. %. Most of the Russian data are not accurately amenable to this treatment as Y is seldom reported, but in monazite from alkali granite pegmatite, Tommat, Yakutiya, U.S.S.R. (Seminov and Barinskii, 1958), La+Ce+Pr is 81 at. % in total lanthanons, and any Y would reduce this value on a total rare earth basis.

In the monazite selected for La enrichment (from Kazakhstan) La +Ce+Pr amounts to 90.1% (presumably atomic %) and Y would have to be 13 at. % in the total rare earths to bring the value for La+Ce+Pr down to 80 at. %. In the lanthanons of the La-enriched monazite, Dy, Er and Yb are not reported and are presumably below 0.2%. It seems certain that Y would be appreciably less than 9 at. % which is the highest value for Y recorded in monazites to date. The use of the sum of La+Ce +Pr, therefore, has limitations, and more data on monazites from quartz-free igneous rocks or alkali rocks are needed before a paragenesis outside acid rocks can be proved from rare earth contents and distribution alone.

Most of the Malayan monazites have the sum of the atomic percentages of La, Ce, and Pr in total rare earths between 69 and 73%; their Ce/(Nd+Y) ratios vary between 1.73 and 2.05. The exceptions are Nos. 1a, 2, and 15 which have La+Ce+Pr values of 65.4, 63.4, and 58.8 and Ce/(Nd+Y) ratios of 1.56, 1.40, and 1.34. These three monazites may, therefore, be of pegmatitic origin.

The Y contents of the Malayan monazites are comparable with those reported by other authors. They range from 2.5 to 5.9 at. % and average 3.8 at. % compared with the range of less than 0.3 to 9.1 at. % and average of 3.9 at. % found by Murata *et al.* (1953, 1957). However, when the contents of Eu and the heavy lanthanons, Gd and Dy, are considered, then three of the Malayan monazites stand out as unusual.

In the Malayan samples monazite No. 1 contains easily the highest concentration of Eu; it is nearly 1 at. % in the total lanthanons. Eu is

rarely recorded in the literature. Borovsky and Gerasimovsky (1945) found up to 1.5% Eu in the (chemically separated) yttrium group of four monazites; this might be equivalent to as much as 0.2% Eu in the total rare earths and is comparable to the amount found in the Malayan samples No. 6 and No. 9. Semenov and Barinskii (1958) found 0.1% Eu in lanthanons of two monazites but Murata *et al.* (1957) did not record it even in their most Nd-rich monazite; Vainshtein *et al.* make no reference to Eu in any of the many monazites that they have examined, and Heinrich *et al.* (1960) did not report on Eu for their Sm-rich or other monazites. Not much is known about the geochemistry of Eu. It differs from all the other rare earths, except Sm and Yb, in being able to assume the divalent state and this has been advanced as an explanation for its scarcity in rare earth assemblages. Eu^{2+} has a size rather larger than 1.2 Å and might, therefore, be expected to be camouflaged in Sr^{2+}, Pb^{2+} or even Ba^{2+} minerals. Low concentrations of Eu have, in fact, been found in Sr minerals like strontianite, but less Eu (below 0.05%) has been found in strontianite from Kangankunde, Nyasaland, than in the associated monazite (with approximately 0.2–0.3% Eu_2O_3 in the total rare earth oxides). Eu does not seem to have been seriously sought in minerals like anglesite, cerussite, barytes or witherite; nevertheless, it is fair to observe that Eu must be one of the rarest elements that is entirely lithophile and non-radioactive. Monazite No. 1, therefore, is a very Eu-rich mineral, and in the manufacture of the metal or compounds of Eu, it would be a most valuable raw material. Many monazites from which Eu is commercially extracted have Eu running at only 1 or 2 per cent of the Sm content (J. Clinch, pers. comm.).

Monazite No. 15 contains abnormally high Gd—5.1 at. %—almost twice as high as in the other Malayan samples. Murata *et al.* (1953, 1957) recorded 4 at. % in a pegmatitic monazite with just over 8 at. % Y (in the rare earths); they show others with up to 9 at. % Y but less than 4 at. % Gd and there is no correlation between Gd and Y. Heinrich *et al.* (1960) record 4.9 at. % Gd and 4.4 at. % Y in their Sm-rich monazite. Most monazites for which Gd and Y have been determined show Y exceeding Gd but the ratio Y/Gd can be as low as 0.5. Monazite No. 15 has the highest of both Y and Gd of the Malayan minerals but these elements do not vary sympathetically. The reason for high Gd in No. 15 is probably its availability during crystallization of the monazite, favorable temperature and rate of crystallization rather than major element compositional controlling factors as there is nothing exceptional about the overall composition (Table 1). RE_2O_3 and ThO_2 have values paralleled by several of the other Malayan monazites in which Gd is quite low. CaO is fairly high, but it is just as high in No. 9 and No. 12 where Gd is average

or below average; neither does Ca vary with Gd or Sm more sensibly. SiO_2 is quite low in No. 15 and also in the unusual monazite No. 1a; but SiO_2 is also low in No. 1 which shows no startling properties amongst the lanthanons.

Monazite No. 1a is unusual in containing approximately 1.3 at. % Dy (and just detectable Tb) in the total rare earths; in all the other Malayan monazites it is below 0.8 at. %. However, Dy is not often determined in monazites, and 1.3 at. % need not be regarded as an extreme limit of Dy content in the rare earth oxides of monazite. Vainshtein *et al.* (1956a) detect Dy in 13 out of 56 monazites, but they give no figures, and their limit of detection, although not stated, would seem to be below 1%. $DyPO_4$ crystallizes in the xenotime class, but presence of xenotime intermixed with monazite No. 1a is ruled out as a cause of the high Dy content as Yb is below about 0.1% in the separated rare earth oxides. Xenotime contamination is also unlikely in view of the low Y content in the monazite and the absence of any lines in the x-ray patterns. The major element constitution of this Dy-enriched monazite is interesting in its U content. U is no less than about 6%. This is at the expense of a reduction in total RE_2O_3 and not a reduction in ThO_2. (Indeed ThO_2 is also about 6%.) In rare earth minerals where substantial U occupies rare earth lattice positions, the heavy lanthanons tend to preponderate. Thus members of the euxenite-polycrase series and the samarskite-yttrocolumbite series (or the yttrocolumbite-yttrotantalite series) have rare earth assemblages characterized by dominant Y and high Dy and/or Er and/or Yb (Butler, 1958); generally, these minerals have $U > Th$ if U exceeds a few wt. %. In the series aeschynite-priorite, however, there is some evidence that Th is high in aeschynite (where Ce earths predominate) and U is high in priorite (where Y-earths predominate). The reexamination of lyndochite and the remarks on the distribution of the rare earths in davidite are relevant here (Butler, 1957b, 1961; Butler and Hall, 1960). Further, Semenov and Barinskii (1958) have shown that thorite and thorianite are rich in the light lanthanons whereas uraninite is rich in the heavy lanthanons (and presumably Y also). In monazites, then, the presence of Th in varying amounts does not act as a control or a restraint on rare earth assemblages; the light lanthanons can all produce the monazite structure perfectly well and the reason for lack of correlation between Th and rare earth distribution is apparent. The presence in monazite of the smaller sized U^{4+} however, does tend to facilitate uptake of the heavier lanthanons. U^{4+}, has a radius of 0.97 Å compared with 0.97 Å for Gd, 0.92 Å for Dy^{3+} and 1.02 Å for Th^{4+}.

In the light of these observations, it will be of interest to see if future work shows that Th content in xenotime has a greater effect in changing typical rare earth distribution patterns than has U.

PHYSICAL PROPERTIES

Specific gravity: According to Palache *et al.* (1951, p. 693) and Frondel (1958, p. 157) the specific gravity of monazite ranges from 4.6 to 5.4, lying mostly within the values 5.0 and 5.2. They further state that the specific gravity "increases with content of Th." The atomic weights of Th and U (232 & 238) appreciably exceed those of the lanthanons (162 for Dy to 139 for La) and Y (89) and some correlation between ThO_2 (plus U_3O_8) content and specific gravity of monazite is to be expected. The Malayan samples, which vary from 5.06 (No. 7) to 5.23 (No. 15), show that the statement above, that the specific gravity increases with Th content, is an over-simplification. Sample No. 1a, with a total of 11.52% U and Th oxides, has a lower specific gravity (5.19) than sample No. 15, in which the specific gravity is 5.23 and the U and Th oxides total less than 7%. The specific gravity of the Malayan monazites is best correlated with the ratio of "light" to "heavy" oxides *i.e.* Y+La+Ce +Pr:Nd+Sm+Gd+Th+U (wt. % oxides). When plotted graphically, however, sample Nos. 1, 4, and 10 are rather off the main trend of increasing specific gravity with decreasing values of the oxides ratio, and there is no obvious explanation. Karkhanavala and Shankar (1954) found, on heating, an increase in specific gravity of a monazite due to the monazite being metamict. The specific gravities of the Malayan monazites were re-determined after heating at 1150° C. for five hours but, although they all increased between 0.04 and 0.10 above the original values, the general trend and anomalies remained the same. In some of the samples heating produced a change in color, the most striking being No. 1a which changed from bright apple-green to a dull green with a dull rust-brown coating, and No. 1 which changed from clear yellow to a bright clear red.

Mass magnetic susceptibility: Richartz (1961) has recently studied magnetic fractions of a monazite from Brazil in which the susceptibility ranged from near that of ilmenite to near that of (associated) zircon. The variation in magnetic properties was well correlated with a change in composition of rare earths; Fe in the monazite was below 0.1% and the elements Mg, Ca, Ti, Mn, Cu, and Eu were present as traces only. The atomic percentages of the individual rare earths in total rare earths changed for the six successively less magnetic fractions as follows: La from 19.7 to 28.8%, Ce from 41.3 to 50.3%, Nd from 21.4 to 11.9%, Sm from 5.6 to 1.5%, Gd from 3.9 to 2.8%, and Y from 3.5 to below 1%. The oxides of these elements show contrasting susceptibilities; La_2O_3 +Y_2O_3 are diamagnetic, Ce_2O_3, Nd_2O_3, and Sm_2O_3 are weakly to moderately paramagnetic, Gd_2O_3 is strongly paramagnetic, and Dy_2O_3 very strongly paramagnetic.

The variation in mass magnetic susceptibility of the Malayan monazites is large. The relationship between magnetic susceptibility and rare earth composition of these monazites, although not clear-cut, follows broadly Richartz's findings. Monazite No. 1a, with its unusually high Dy content, is clearly the most magnetic; the high U content (5%, being the only sample with more than 1% U_3O_8) may also be a contributing factor, but it is not likely to have as great an effect as the Dy. Slightly less magnetic is monazite No. 15 which has the highest Gd content. Both these monazites are considerably poorer in diamagnetic La than the others. At the opposite end of the scale are samples 14, 7, and 8. These are, together with Nos. 1 and 10, highest in La. Nos. 8 and 13 are also lowest in Gd.

The Malayan samples indicate that similarity in mass magnetic susceptibility does not necessarily mean similarity in composition. Monazites 7 and 8 are in fact similar in both, but 9 and 10, though similar in susceptibility, are not similar in composition. Nor does the reverse hold: samples 5 and 12 are similar in composition, but differ considerably in susceptibility.

The presence of unsought-for Fe in the samples (except for No. 1a, which had less than $\frac{1}{2}\%$), may be the reason for the lack of a clear-cut relationship, but this is not considered to be the case. It appears far more likely to be owing to the compensating compositional effects of the highly contrasting rare earth elements.

X-ray powder pattern: Powder photographs of eight of the sixteen samples were taken, using a camera of 114.83 mm. diameter with Ni-filtered copper radiation, $CuK\alpha = 1.50450$ Å.

The ionic radii, after Ahrens (1952), of the rare earth elements are centered around 1.05 ± 0.03 Å. Within this range lie Ce (1.07), Pr (1.06), and Nd (1.04), and also Th (1.02). Sm, Gd, and U are slightly smaller at 1.00, 0.97, and 0.97 Å respectively while Y is considerably smaller and La considerably larger at 0.92 and 1.14 Å respectively. This wide range in ionic radius could reasonably be expected to reflect a corresponding variation in the interplanar (d-) spacings of the mineral, and it is logical to assume an increase in the interplanar spacing with a predominance of La and a decrease if the smaller ions (Sm, Gd, U, and Y) predominate.

Molloy (1959) states (p. 517) that variation in rare earth composition does cause a small variation in cell dimensions, but he does not give details. In his conclusions (p. 531) he goes on to say that "the range in individual (hkl) reflections . . . does not yield any simple relation to chemical composition." Richartz (1961) found that the lines of an undifferentiated monazite concentrate were diffuse whereas those of the

fractions separated from it were quite sharp. This he concluded to be due to the greater compositional variation (in the La+Ce/Nd+Sm+Gd+Y ratio) in the undifferentiated concentrate giving rise to a spread of lattice values.

The patterns obtained on the Malayan samples conformed to the general pattern given in the ASTM powder data card 4-0612 and by Frondel (1958, p. 158, after Karkhanavala and Shankar) but the actual values differ. The data for the Malayan samples do, in fact, indicate that for d-values below, and including, the (200) reflection (above which value the

TABLE 4. SYSTEMATIC VARIATIONS OF X-RAY DIFFRACTION SPACINGS (Å)
WITHIN THE RANGE $hkl = 200$ TO 040 CU RADIATION, Ni FILTER $\lambda = 1.50450$ Å

hkl / Sample	200	120	210	012, 112	031	$\bar{2}12$	032, $\bar{1}03$	040
15	3.24	3.05	+	2.83	2.16	1.94	1.85	+
1a	3.26	3.05	2.94	2.82	2.16	1.95	1.85	1.73
13	3.25	3.055	2.95	2.84	2.17	1.95	1.86	1.73
12	3.25	3.06	2.94	2.84	2.18	1.95	1.86	1.73
1	3.25	3.06	2.95	2.83	2.17	1.95	1.86	1.73
14	3.25	3.06	2.94	2.83	2.17	1.95	1.86	1.73
8	3.27	3.06	2.94	2.83	2.18	1.96	1.86	+
7	3.27	3.06	+	2.84	2.18	1.96	1.86	1.74
ASTM 4-0612	3.31	3.09	2.99	2.88	2.19	1.97	1.88	1.75
Frondel (1958)	3.29	3.10	2.98	2.87	2.19	1.97	1.87	1.75

+ Line present but not measured.

accuracy of measurement from photographs is unreliable), a definite trend of variation occurs (see Table 4), particularly for reflections where d = 3.24–3.27, d = 2.16–2.18, and d = 1.94–1.96, and there is a reasonably sympathetic relationship between this variation and the La:(Sm+Gd +U+Y) ratio. Monazite Nos. 15 and 1a, with the lowest d-values (smallest spacings) and the lowest La content, seem to indicate that La has a slightly greater effect than the group of smaller ions. They also confirm the ineffectiveness of Nd, as they contain the highest and lowest Nd content of all the samples.

CONCLUSIONS

Although certain trends are indicated for the properties studied, no simple correlation with composition can be established. The position is unfortunately complicated by the effects of compensating replacements, such as the presence of equal amounts of a large or heavy element and correspondingly small or light element, which counter the indicated

TABLE 5. LIST OF LOCALITIES OF THE SAMPLES STUDIED

No.	State	Locality	G.S.F.M.No.
1	Kedah	Siau Hin Mine, Semeling	E-2/1
1a	Kedah	Siau Hin Mine, Semeling	E-2/1a
2	Perak	Larut Tin Fields Ltd., Taiping	E-8/2
3	Perak	Wah Sung Tin Mine Ltd., Trong	E-8/16
4	Perak	S.K.C. Ltd., (Kinta), Batu Gajah	E-8/4
5	Perak	Tronoh Mines Ltd., Kampar	E-8/7
6	Perak	Hung Soon Kongsi, Bidor	E-8/9
7	Perak	Austral Amalgamated Tin Ltd., Sungkai	E-8/14
8	Pahang	Karak Tin Mine, Karak	E-6/1
9	Selangor	Sg. Way Dredging Ltd., Sg. Way	E-10/2
10	Selangor	Petaling Tin Ltd., Petaling	E-10/1
11	N. Sembilan	Tambah Tin Dredging Co. Ltd., Pertang	E-5/2
12	N. Sembilan	Tongkah Compound No. 2, N.L., Seremban	E-5/3
13	N. Sembilan	Rantau Tin Dredging Co. Ltd., Siliau	E-5/1
14	Malacca	Pulau Besar	E-4/1
15	Johore	Bakri Mining Co., Bakri	E-1/1

trends, giving anomalous results. The indicated effects imposed by the individual elements are as follows:

Ce, La, Nd, Gd, Sm, U, and Th collectively affect the specific gravity; a high value of Ce+La gives a low specific gravity whilst a high value of Nd+Gd+Sm+U+Th gives a high specific gravity.

La, Gd, and Dy affect the mass magnetic susceptibility; U appears to do so. A composition of high Gd+Dy (and possibly U) and low La content gives a high magnetic susceptibility and vice versa.

La has a definite (the most important) effect on the interplanar and unit cell dimensions, increasing them both. A decrease in both is caused by Y, U, Gd and, to a lesser extent, Sm.

Because of its very limited variation, little can be concluded about Pr. It probably has some effect on the specific gravity; and has apparently no effect on the magnetic susceptibility or structural dimensions.

Th, though the most variable has virtually the least effect. It has no effect on the magnetic susceptibility or on the structural dimensions and only affects (increases) the specific gravity in combination with U, Sm, Gd, and Nd.

In addition to its effect on the physical properties, indicated above, a high U content affects the lanthanon distribution in favor of the heavy lanthanons.

prism spectrograph for determining the lanthanons and to Alan Z. Smith (Imperial College) for determining Y by x-ray fluorescence.

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