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Dispersed and Not-So-Rare Earths

The relative abundances of these elements reflect the earth's geochemical evolution from primordial matter.

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To teachers of general chemistry, who normally feel pressed by having more material to teach than time in which to teach it, the rare-earth elements are a boon. They constitute almost 15 percent of all the known elements, and their chemistry can be quickly dealt with in a few sentences. The lanthanides are the classic example of a long, or *f*-electron-filling, transition series. They have ground-state or low-excited-state outer electron configurations which result in strongly metallic behavior and preferred oxidation state 3+ for every member of the group. In the lanthanides, the radii of the ions decrease slightly with increasing atomic number (a phenomenon known as the lanthanide contraction), and this (or its causes) is responsible for most of the small differences in chemical behavior which do exist among the lanthanides. Under sufficiently strenuous conditions, some of the rare-earth elements can be oxidized or reduced to the 4+ or 2+ states, but only Ce^{3+} and Eu^{3+} have sufficiently low resistance to be converted to Ce^{4+} and Eu^{++} by natural processes. In this article the rare-earth elements are taken to include the lanthanides and yttrium, whose geochemical behavior closely mocks that of the heavy lanthanides. Scandium, of the same periodic group as yttrium and lanthanum, is not included because its geochemical behavior is considerably different.

Prior to the discovery of ion-exchange and solvent-extraction techniques, the principal methods for separating the members of the rare-earth group from each other were fractional crystallization and fractional precipitation. These are the processes by which natural fractionations among these elements probably occur. The extreme chemical similarity among the rare-earth elements greatly complicated and delayed their discovery (*1*). The first recorded observation of the new "earth" (a difficultly reducible oxide) was made in 1794 by the Finnish chemist Gadolin. It was gradually established that the new earth was not a single element, and various of the rare-earth elements were separated, but over the years claims of the "discovery" of far more individual elements than in fact exist were made and hotly defended. The allowable number of elements for the group was not known until the association of x-rays with atomic number was developed by Moseley, in the second decade of the present century. The last naturally occurring members of the group to be discovered, ytterbium and lutetium, were independently obtained by Urbain and by Welsbach in 1907–08, but some workers, reluctant to accept the consequences of Moseley's generally accepted theory, continued their efforts to split several of the pure elements, on the assumption that they were mixtures. Even after this burst of futile activity had subsided, the still unknown element 61 was sought, and its discovery was reported from time to time, but it was first isolated from the products of uranium fission and named promethium by Marinski and Glendenin. Promethium has no known isotopes of sufficiently long half-life for any to be found in nature. The rare-earth elements were so named because known occurrences were few and it was anticipated that there would not be appreciable amounts of them in nature. In 1908, Eberhard (*2*) showed that they are trace constituents of common rocks. Their abundances in the earth's crust are about the same as those of tin, lead, and cobalt, so they are not really rare but are best referred to as "dispersed," since they are spread thinly throughout the major phases of the lithosphere.

The difficulties encountered in separating the individual members of the rare-earth group from each other in the laboratory led geochemists to expect that, in geochemical processes, these elements would behave as an entity, or coherent group, rather than as a number of individual elements. It was further postulated that, if any group of chemically similar elements could be expected to retain the *relative* abundances characteristic of primordial solar-system matter, it would be the rare-earth elements. This view is at least partially substantiated by the observation that where one member of the rare-earth series is found in nature, the others are also present.

Partial separations, or fractionations, among the members of the rare-earth group were shown to have occurred during the formation of rare-earth minerals, according to the earliest accurate, systematic analyses of these elements by Goldschmidt and Thomassen in 1924 (*3*). The abundance of europium was extremely low as compared with that of terbium and holmium, and Goldschmidt suspected it had been removed from the rest of the rare-earth elements because of reduction to the 2+ state. In 1935, I. Noddack succeeded in analyzing a composite sample of stone meteorites for rare-earth elements (*4*). Since the chondritic meteorites were being increasingly regarded as the material least

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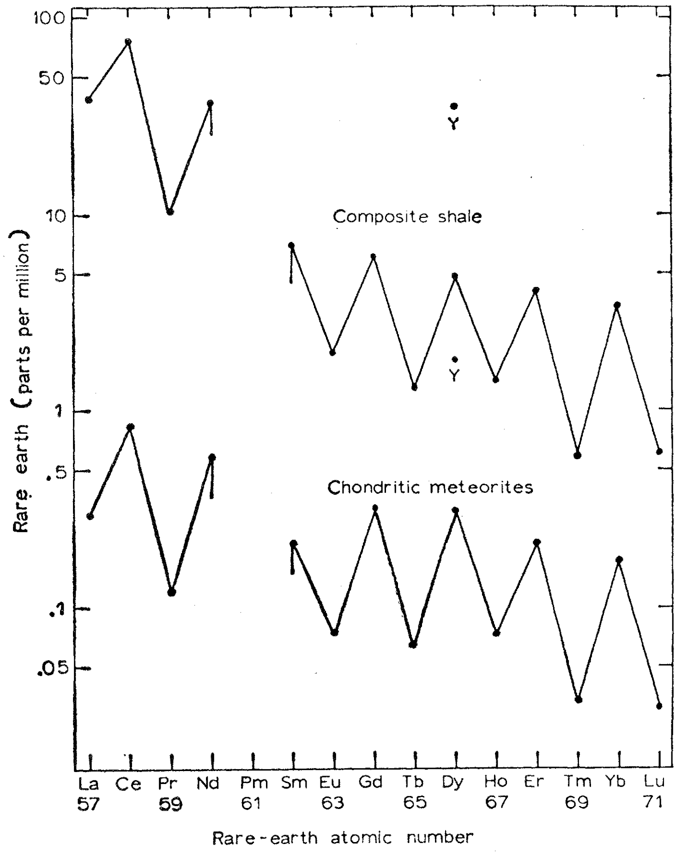
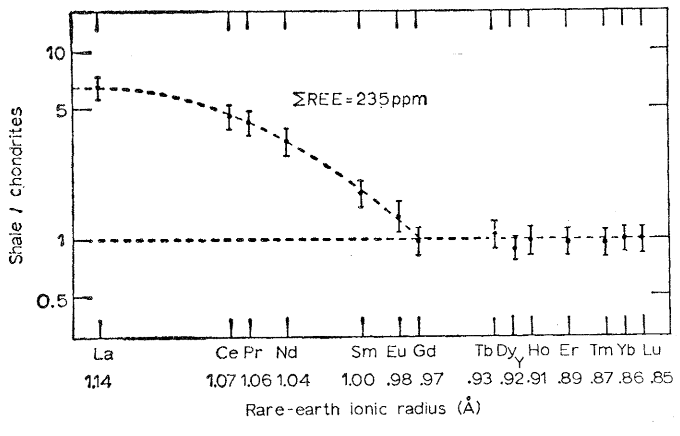
differentiated from primordial solar matter, one would have expected the Noddack values to represent the best guess on the relative abundances of the rare-earth elements in the earth and in other matter. However, Noddack reported more neodymium than cerium, a result entirely inconsistent with measured values for terrestrial rare-earth minerals. Furthermore, in the same year Minami, working in Goldschmidt's laboratory, analyzed three composite samples of shales (*5*). The relative abundances of rare-earths were quite similar in the three shales; cerium was more abundant than neodymium, as expected, and the light rare-earth elements were relatively more abundant in the shales than in the meteorites. Also, the element europium had an abundance similar to the abundances of terbium and holmium, as anticipated for the primordial distribution but not found in the terrestrial minerals. Goldschmidt postulated that the rare-earth elements (europium in particular), while somewhat fractionated during igneous rock crystallization, were remixed by weathering and sedimentation into their average crustal relative abundances (*6*). While it is clear from Goldschmidt's earlier work (*6*) that he was concerned over the difference in the ratios of light-weight to heavy rare-earth elements for the shales and for the chondrites, he eventually concluded that these differences between the meteoritic and the crustal patterns were a result of analytical error (*7*). He chose Minami's results for the distribution of rare-earth elements in shale as the more accurate estimate of the





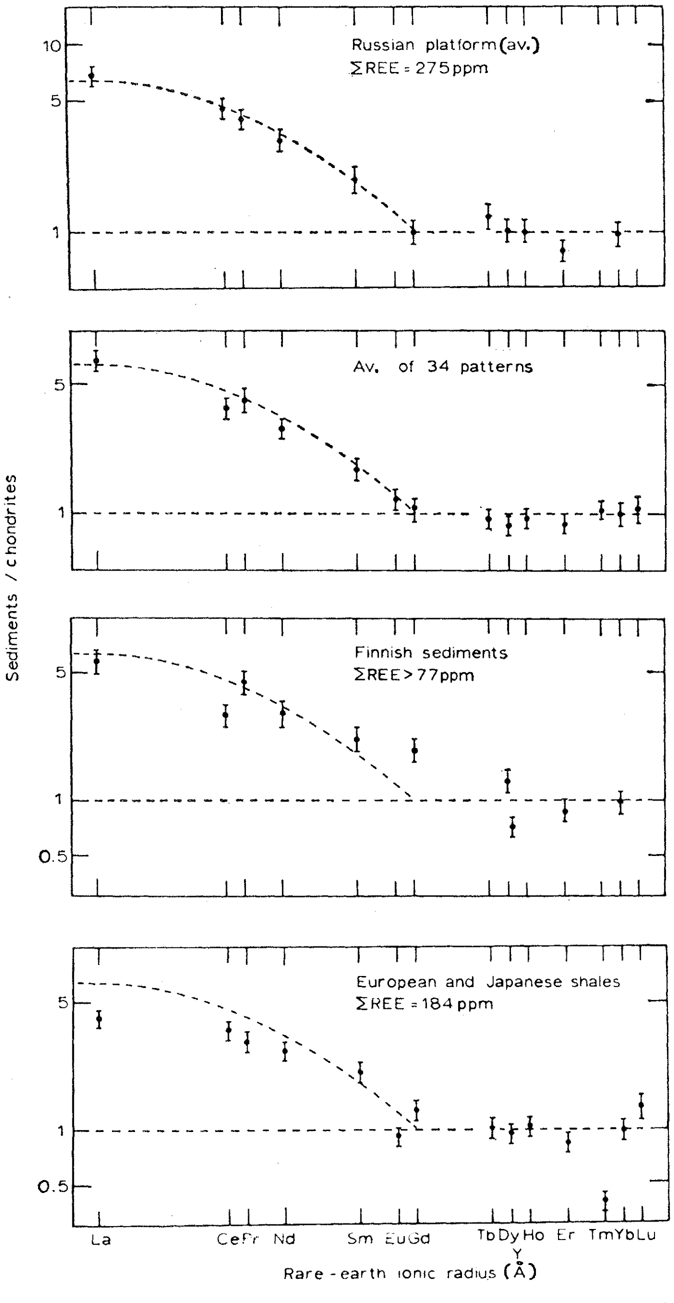


Fig. 1 (top, left). The rare-earth content of a composite sample of 40 North American shales and the average of the rare-earth contents of 20 chondritic meteorites (in parts per million). The abscissa corresponds to the rare-earth atomic number, except for yttrium (Y), which is plotted together with dysprosium. [Average for chondrites from Schmitt *et al.* (*9*)] Fig. 2. (bottom, left). Comparison plot for the North American shale composite (see text); ΣREE, total rare-earth content. Fig. 3 (right). Comparison plots for five sediment composites. In each graph the dashed upper curve represents the North American shales of Fig. 2.

primordial distribution, and stated that no significant difference between the crustal and the primordial distributions of these elements could be expected, because of their strong tendency to behave as a coherent group. These views were accepted by a number of compilers of postulated elemental abundances.

The development of theories and models for nucleosynthesis revived interest in rare-earth abundance patterns. Nuclear properties do not obey the same law of periodicity that chemical properties obey, and accurate knowledge of the primordial relative abundances of rare-earth elements would serve to anchor firmly calculation parameters for the medium- to heavy-element mass region. To this end, Schmitt and his co-workers analyzed three chondritic meteorites in 1960 (*8*). The rare-earth abundance patterns for the three chondrites were identical, and the values were similar, in overall trend, to Noddack's values for meteorites, except for neodymium and cerium. Twenty different chondrites have now been analyzed, with the same result, and this distribution is presumed to be the primordial one (*9*). As Goldschmidt expected, cerium is more abundant than neodymium in meteorites.

In 1962, Haskin and Gehl reported rare-earth analyses, by neutron activation, for ten samples of sedimentary rocks (*10*). They obtained the somewhat surprising result that seven of the ten had rare-earth abundance patterns which were very similar, even though the individual samples included limestone, sandstone, shale, marble, and quartzite. The average pattern was similar to that found by Minami for shales. Thus, the view that the meteoritic and crustal abundance patterns differ was confirmed. The earth's crust, as judged by analysis of sedimentary rocks, is considerably richer than chondrites in all the rare-earth elements. The crustal and chondritic distributions are identical for the heavy rare-earth elements gadolinium to lutetium, but there is a smooth trend toward increasing enrichment of the lighter rare-earth elements samarium to lanthanum in the crust relative to abundances in the chondrites. These results substantiate the belief that the earth and the meteorites were formed from the same homogeneous batch of matter, as had been previously indicated by isotopic similarities. The relative enrichment of the crust in the light rare-earth elements is a plausible consequence of the differentiation of homogeneous primordial matter which led to formation of the earth's mantle and crust (*10, 11*).

With confirmation of the view that meteoritic and crustal patterns of rare-earth abundances differ, a number of questions arose, including the following. Why is there so little difference in rare-earth patterns among diversified sedimentary rock types? How constant, from sediment to sediment, is the distribution? Of what part of the earth or its crust is it a representative average? Did this characteristic crustal pattern result from geochemical processes or from cosmochemical processes prior to the accretion of the earth? What information about geologic processes can be obtained through detailed study of naturally occurring rare-earth patterns and the factors which produce them? Research aimed at answering various parts of these questions has been going on for some time, and is being done by a number of investigators. The prin-

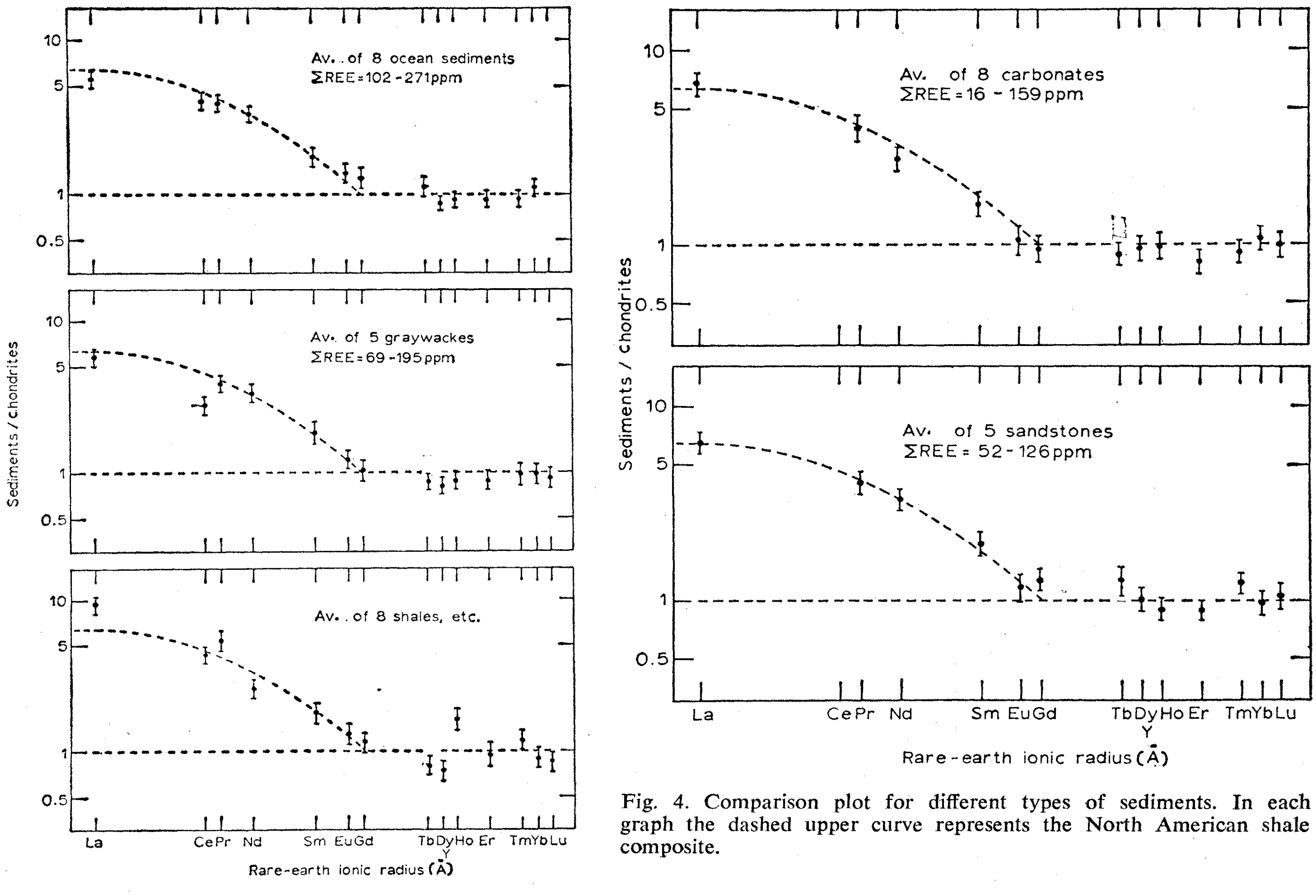


Fig. 4. Comparison plot for different types of sediments. In each graph the dashed upper curve represents the North American shale composite.

cipal contribution of a research group at the University of Wisconsin has been a survey of rare-earth contents and patterns in the most common rock types (*12*). For a comprehensive survey of present knowledge of natural rare-earth patterns, see Goldschmidt (*7*), Rankama and Sahama (*13*), Balashov (*14*), Jensen and Brunfeldt (*15*), Schmitt *et al.* (*16*), and Haskin *et al.* (*17*).

Data Presentation

The averages for the rare-earth contents of 20 chondrites and the rare-earth content of a composite of 40 North American shales are given in Table 1 and, in Fig. 1, are plotted against atomic number (*Z*) of the rare-earth. The differences between the *relative* rare-earth abundances of the two materials (chondrites and shales) becomes apparent only after close inspection of the graph, because the most striking feature of all rare-earth distribution patterns is the alternating high and low abundances of the even- and odd-*Z* rare-earth elements, a consequence of the greater number of stable even-*Z* isotopes which can be formed during nucleosynthesis (the Oddo-Harkins rule). In some past work, important differences among rare-earth patterns have been obscured because of the complexities of such plots. In order to show trends more clearly, the following procedures have been adopted. First, for convenience in obtaining comparable numbers for similar patterns and in calculating averages for several patterns, the values for absolute content of each individual rare-earth element in a particular material are divided by the value for ytterbium content in that material (a procedure known as "ytterbium-normalization"). When graphical illustration to show similarities of differences between two rare-earth patterns is desired, the zig-zag effect associated with the Oddo-Harkins rule can be removed by dividing the values of one distribution, element by element, by those of the other. Identical patterns yield identical individual-element ratios, while differing ratios indicate relative enrichment or depletion. The element ratios can then be plotted against rare-earth atomic number, ionic radius, or some other useful parameter. Ionic radius is a potentially important influence on rare-earth fractionation but may not be a more meaningful parameter than atomic number, since it has been shown that the reciprocals of the rare-earth ionic radii are a linear function of atomic number (*18*). The chondrite and shale rare-earth patterns of Fig. 1 were normalized relative to ytterbium, and the values for individual elements in the shale distribution were divided by corresponding values for the chondrite distribution. The ratios are plotted in Fig. 2, in which the identity of heavy rare-earth elements in the distribution and the trend toward enrichment of the shale in light rare-earth elements are clearly apparent.

Table 1. Rare-earth contents of meteorites and shales (in parts per million).

Rare-earth element	Average of 20 chondritic meteorites*	Composite of 40 North American shales
Y	1.8 ± 0.3	35
La	0.30 ± .06	39
Ce	.84 ± .18	76
Pr	.12 ± .02	10.3
Nd	.58 ± .13	37
Sm	.21 ± .04	7.0
Eu	.074 ± .015	2.0
Gd	.32 ± .07	6.1
Tb	.049 ± .010	1.30
Dy	.31 ± .07	
Ho	.073 ± .014	1.40
Er	.21 ± .04	4.0
Tm	.033 ± .007	0.58
Yb	.17 ± .03	3.4
Lu	.031 ± .005	0.60
All rare-earth elements	5	230

* Data from Schmitt (*9*).

The rare-earth patterns of Figs. 3–14 and 17–20 have been similarly treated, the chondrite pattern having been used as a standard; in each case a dashed line representing the crustal pattern, as shown by the North American shale composite, is included. Several variations of this procedure have been used (*10, 19*).

Sedimentary Rocks

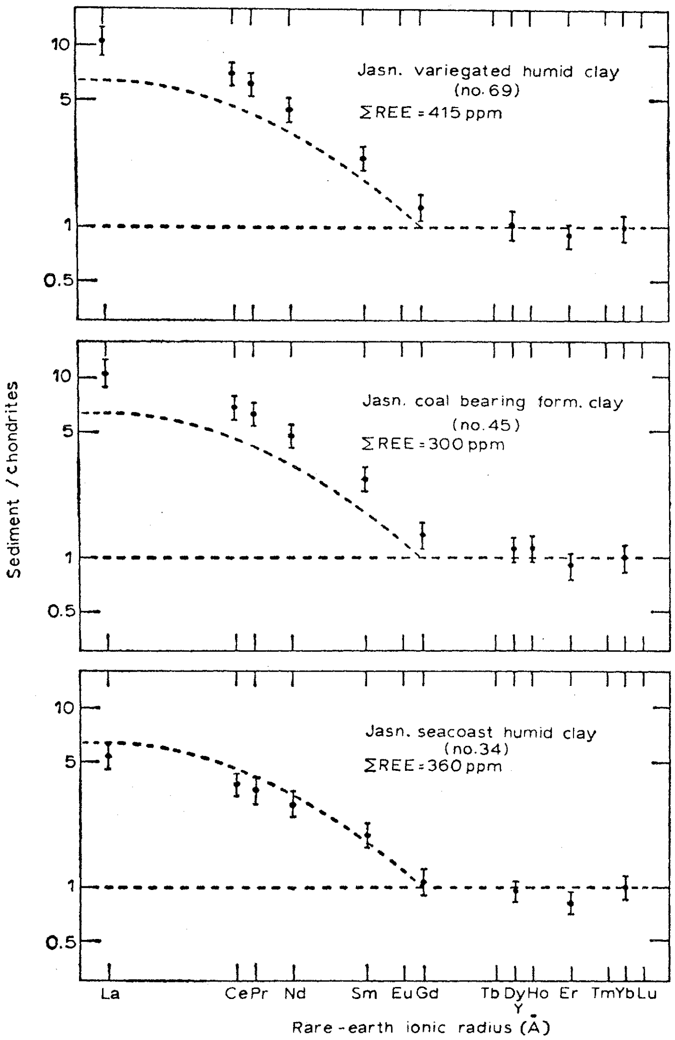
The second question—how similar are rare-earth distributions among diverse sediment types? —can now be fairly well answered. In addition to the composite of 40 North American shales, 34 individual sedimentary rocks have been analyzed, by neutron activation, for rare-earth elements. These rocks include eight carbonates, five sandstones, five graywackes, eight ocean sediments (*20*), and eight shales and related substances. The average of the ytterbium-normalized patterns for the 34 individual sediments is identical, within the limits of experimental uncertainty, to the pattern for the composite of North American shales. Identical to these patterns is that obtained by Balashov *et al.* (*21*) for the Russian platform. This latter correlation is a particularly important one; the American rocks were selected merely because they were readily obtainable, whereas the pattern for the Russian platform is a weighted average for different sediment types from a single, large source area of igneous materials. Figure 3 is a comparison plot for these composites. Thus, it is well established that there is a particular rare-earth pattern characteristic of crustal materials. The results of two earlier determinations of rare-earth patterns in sedimentary rock are included in Fig. 3 (*5, 22*). Both are in qualitative agreement with the more recent results, but there are quantitative differences, both in relative abundance and in absolute content. The differences are probably a consequence of the less sophisticated analytical methods available to Minami and Sahama. A partial redetermination of the constituents of one of the shale composites analyzed by Minami shows that the absolute rare-earth content is greater, and the pattern of relative abundances contains more light rare-earth elements, than had previously been reported (*23*).

It seems nearly incredible that the processes which led to the formation of sediments of such widely differing gross compositions as are represented by limestones, sandstones, and shales could have endowed these rocks with nearly identical relative rare-earth abundances. Yet, the averages of the ytterbium-normalized patterns for four of the five rock types (Fig. 4) are identical, within the analytical uncertainty of ±10 to 15 percent, to the pattern for the composite of North American shales (Fig. 1). This conclusion, based on very few samples of each class of sediment, indicates that systematic differences in rare-earth abundance pattern which are related to sediment composition are very small or nonexistent, and that many further analyses, plus increased analytical precision, will be required to show them.

The group of Fig. 4 which is not statistically identical with the North American shale average is that designated "Ave. of 8 shales, etc.," which includes five shales, a clay, a laterite, and a bauxite. Failure of this group to conform to the average can be attributed to the patterns for two of the shales, one of which has an abnormally high lanthanum content, the other of which has a high content of lanthanum and praseodymium but an extremely low content of cerium and neodymium. The pattern obtained for the latter shale is undoubtedly in error, but *all* sediment analyses performed to date by the Wisconsin workers have been included in the compilation for this "Ave. of 8 shales" group, regardless of suspicious values for individual elements, in order to avoid any arbitrary and unwarranted deletions which might bias the comparison. The rare-earth pattern for the composite of North American shales is adequate evidence of the absence of systematic differences between shales and other sedimentary types, but the possibility of greater variability among shales cannot be ruled out or supported by the average of the eight individual patterns.

Of the 34 individual sediment patterns, only seven are identical to the sediment average within the limits of experimental error. Of these, five are ocean sediments, which may represent broader and better-averaged source areas than land sediments do. But, despite the fact that most of the patterns can be distinguished from the average, the extent of deviation from the average is small. The values for contents of individual rare-earth elements of each sediment were normalized relative to ytterbium, then the values were divided by the corresponding ytterbium-normalized values for chondrites, and the ratios were compared to those for the composite North American shale. Of 412 individual-element ratios, only 15 percent differed from the corresponding composite-shale ratio by as much as 50 percent and only 4 percent differed by as much as 200 percent. Some of these aberrant values are certainly due to experimental error, since they indicate anomalous enrichment or depletion in certain rare-earth elements relative to others when no plausible mechanism in explanation of such differences is known. The percentages given above constitute upper limits for large deviations from the average pattern.

The aberrant values, erroneous or real, are well scattered among the 34 sediment patterns, as 44 percent of these patterns contain at least one element whose ratio differs from that of the corresponding element in the composite shale by 50 percent or more. Finally, it is concluded that most rare-



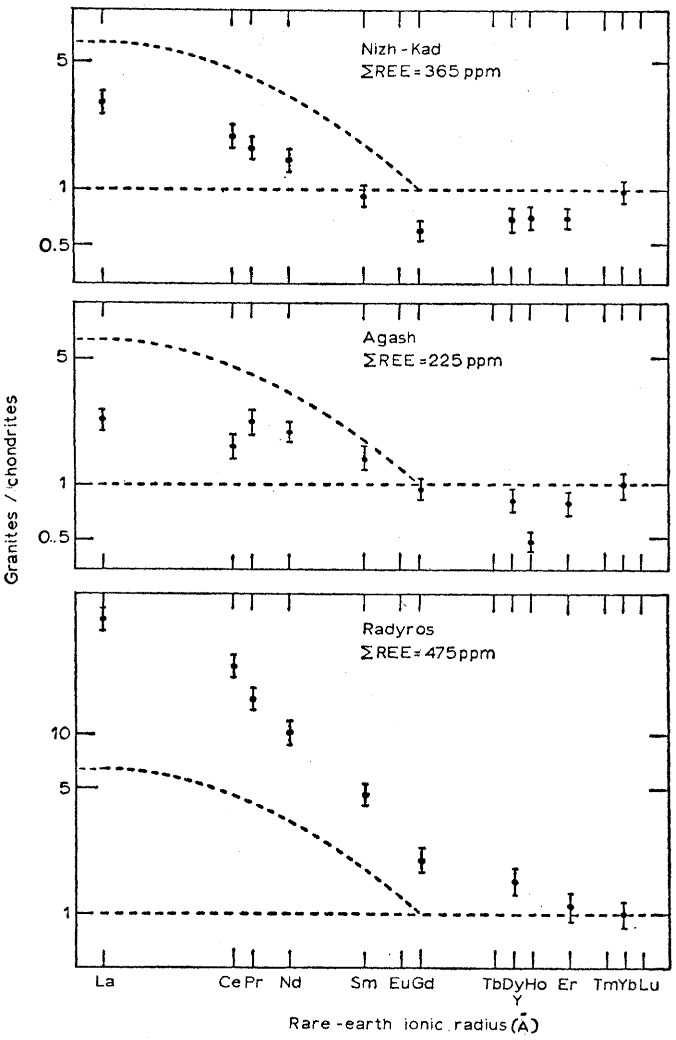


Fig. 5 (left). Comparison plot for Russian Platform sediments [data from Balashov *et al.* (*21*)]. In each graph the dashed upper curve represents North American shales. Fig. 6 (right). Comparison plot for three granites [data from Balashov (*14*)]. In each graph the curve represents North American shales.

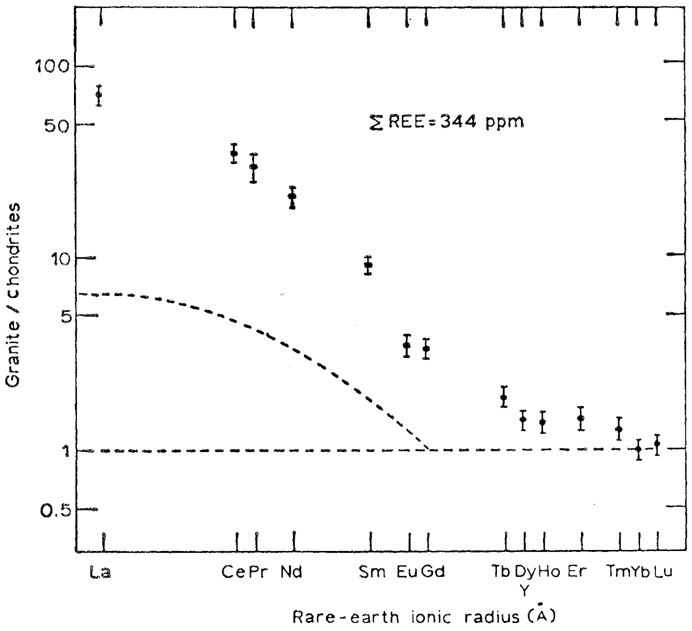
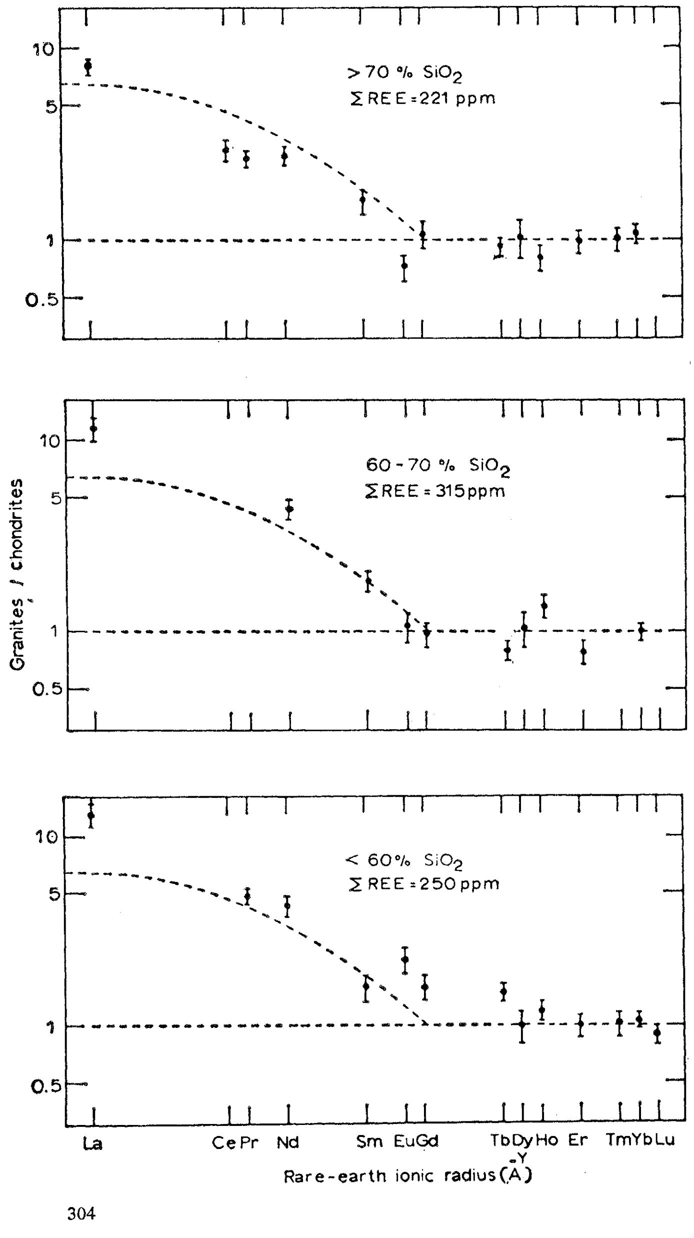
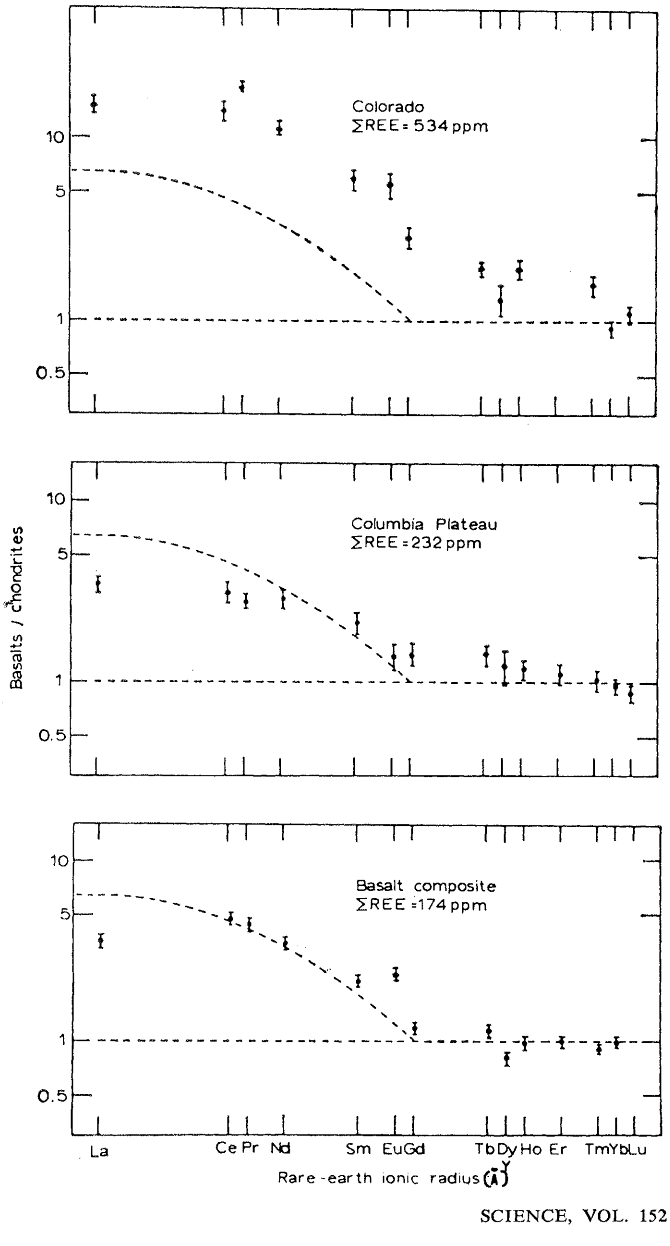


Fig. 7 (left). Comparison plot for G-1 granite.

Fig. 8 (below, left). Comparison plot for composites of intermediate and acid igneous rocks.

Fig. 9 (below, right). Comparison plot for basalts. [Data on Columbia Plateau basalt from Schmitt *et al.* (*32*)]





earth patterns of individual sediments differ by 15 percent or more from the average sediment pattern, but that only about one sediment in 20 shows a trend of deviation from the average as large as 50 percent. Deviation by more than 200 percent is very rare.

This rather remarkable constancy of rare-earth patterns in sediments might be explainable if the rare-earth elements were associated entirely with clay or detrital fractions of the various sediments, but analyses of calcite separated from limestone and of quartz from sandstone indicate that this is not the case (*24*). Most of the rare-earth elements are intimately associated with the calcite and quartz, and the rare-earth patterns of these minerals are not appreciably different from those of the heavy mineral and clay fractions.

The above results indicate only that there are no strong variations in the sedimentary rare-earth pattern which are a direct or necessary consequence of the gross composition of the sediment. Systematic variations of rare-earth pattern with sediment type were found by Balashov *et al.* (*21*) in their excellent studies of sedimentation in the Russian platform. When sedimentation occurred under arid conditions of weathering, slight differences in the relative abundances of rare earths in clay, sand, and carbonate were observed. However, the more extensive chemical processes accompanying humid conditions of sedimentation did result in fractionation of the rare-earth group in the manner shown in Fig. 5. The clay fraction, with the highest rare-earth content, was adjacent to the igneous-source rocks, and Balashov and his associates postulated that the rare-earth elements precipitated as hydroxides, along with iron, aluminum, and other hydrolyzate elements. Deeper in the basin, however, acid conditions prevailed, as evidenced by coal-bearing formations. There the sediments of lowest rare-earth content to be found in the basin occur. Finally, in the depths of the basin (at the seacoast), the rare-earth contents of the sediments are again higher. The seacoast clays are representative of the seacoast sediments (Fig. 5); they are depleted in the lighter rare-earth elements relative to the shales of the outer rim. Balashov and his associates suggested that the combination of acids and organic materials prevalent in the coal-bearing region preferentially dissolved and formed complexes with the heavier rare-earth elements and carried them in solution to the sea, where the saline, alkaline waters broke the complexes and precipitated colloids on which the hydrolyzed rare-earth elements were adsorbed. This is a very plausible hypothesis, but the mechanism suggested may be incomplete, since the rare-earth patterns of the clays adjacent to the igneous source are somewhat depleted in the heavy rare-earth elements, which probably from the earliest stages of weathering were transported toward the interior of the basin.

Table 2. Approximate concentrations (in percentages) of major elements for rock types classified according to acidity. Most of the numbers are "representative" values based on data given in Turner Verhoogen (*36*).

Element	Ultra-basic*	Basic†	Intermediate‡	Acid§
SiO_2	45	50	60	65
Al_2O_3	3	15	20	7
Fe_2O_3 + FeO	9	12	6	3
MgO	40	5	3	1
CaO	3	7	7	2
Na_2O	0.5	3	3	5
K_2O	.1	0.5	1	3

* Typical rocks: peridotite, dunite. † Typical rocks: basalt, gabbro, eclogite. ‡ Typical rocks: diorite, andesite. § Typical rocks: granite, rhyolite.

Of course, the considerable similarity among the rare-earth patterns of sedimentary rocks would not seem surprising if these patterns were merely a reflection of similar patterns for common igneous rocks. But the igneous-rock patterns are much more variable than the sediment patterns.

Crustal Igneous Rocks

For purposes of this discussion the igneous rocks are grouped according to their "acidity." This is a classification based on chemical composition as opposed to mineral assemblage or geologic occurrence. The approximate ranges of the concentrations of major-element components and some of the most common rock types associated with various degrees of acidity are listed in Table 2. From ultrabasic to acid rock there is an increase in SiO_2, K_2O, and Na_2O and a decrease in MgO, FeO, and CaO. There is a decrease in rock density with increasing acidity. In a sense, the earth's crust can be thought of as "floating" on the mantle, presumably a result of a higher proportion of acid material in the crust than beneath it.

Granite and basalt are two common igneous materials which are often taken as representative of the earth's crust for purposes of estimating crustal composition. Granitic rocks are extremely variable in composition, origin, and mineralogy. Basalts are divided into two classes, on the basis of an equilibrium mineralogy calculated from their compositions. Tholeiitic basalts have compositions which predict the appearance of the mineral quartz (SiO_2). Alkali basalts are those which contain enough potassium and sodium so that no uncombined SiO_2 remains. The first careful analyses of the rare earths of granites were made by Sahama and Vähätalo (*25*). Considerable variation among the rare-earth patterns was observed. A similar result was reported by Balashov for some Russian granites (*14*). Patterns for three of these are given in Fig. 6. A well-studied example of severe rare-earth fractionation is the G-1 granite from Westerly, Rhode Island (Fig. 7) (*26*). With so much variation in rare-earth pattern from rock to rock, it is difficult to estimate what average contribution from granites may have been made to the crustal average rare-earth pattern found in sediments. Our present best guess as to the average rare-earth pattern for granitic rocks is based on analyses of composites of intermediate and granitic rocks, as shown in Fig. 8. These composites were made up from analyzed samples, and were sorted according to rock acidity, or SiO_2 content (*27*). The sample with SiO_2 content less than 60 percent is a mixture of equal parts of 85 intermediate rocks; that with SiO_2 content greater than 60 and less than 70 percent was compounded from 191 intermediate and acid rocks; and that with SiO_2 content greater than 70 percent contains equal portions of 213 granites. In general rare-earth pattern the composites are similar to each other and to the crustal sediments. There is one significant difference between the averages for granite and for sediment. The relative content of lanthanum is higher in the granites. The values for total rare-earth contents for the composites, which range from 220 to 315 parts per million, agree well with the value of 235 parts per million for North American composite shale and with the average of

300 parts per million for the Russian Platform sediment.

Several basalts have been analyzed for their rare-earth abundances. Again, considerable variation among the patterns has been observed. All continental and ocean-island basalts examined thus far have proved to be relatively richer than the chondritic meteorites in the light rare-earth elements, and some of them even richer in these elements than the crustal sediments. The rare-earth patterns of two continental basalts, an alkali basalt from Colorado and a tholeiitic basalt from the Columbia Plateau (*28*), are shown in Fig. 9. Also shown in Fig. 9 is the pattern for a composite of 282 continental basalts, which probably represents the best available estimate of the average rare-earth content and abundance pattern for that rock type. The pattern for the composite basalt shows relative enrichment in the light lanthanides comparable to that found for the sediments. However, in the composite basalt the lanthanum content is lower, the europium content is higher, and there appears to be some fractionation among the heavier rare-earth elements.

If the igneous portions of the crust are really adequately represented by basalt and granite (sediments and metamorphic rocks probably make up less than 5 percent), then it should be possible to combine the appropriate fractions of the rare-earth patterns for basalt and granite and obtain the pattern found in the sediments, which are the weathering products of the igneous materials. The relative proportions of basalt and granite in the crust are not accurately known. Thus, the reverse procedure may be considered: determination of those proportions through calculating what relative contributions of the basalt and granite rare-earth patterns would give the sediment rare-earth pattern. This calculation was attempted by Taylor (*29*), but with data which were too few to be representative and which showed much more contrast in the rare-earth patterns of granites and of basalts than are shown by the composite granites and basalts discussed in this article.

From the data presented here it is immediately clear that the average granite pattern, which matches the sediment pattern well with respect to abundances of heavy rare-earth elements, does not complement the basalt pattern, which does not match the sediment pattern well in this respect. This may mean that the average values for basalts or granites, or both, as obtained from the composite samples, are incorrect. Nevertheless, they are the best estimates available. The trend of fractionation among the heavy rare-earth elements in the basalt pattern is slight, and the values for individual elements are very close to those of the sediment pattern, lying barely outside the limits of experimental uncertainty. If the approximation is made that these values are the same, then the granite and basalt patterns differ only in abundances of lanthanum and europium. The average value for abundance of europium in granites is somewhat low relative to abundances of samarium and gadolinium, but this relative impoverishment in europium in granites is not as great as the enrichment in europium in basalts, so it is not possible to choose a mixture of granite and basalt which will match the sediment pattern in both lanthanum and europium. If it is argued that the behavior of europium is capricious because of its reduction and separation as a 2+ ion, then the estimate of the proportions of granite and basalt is based on a single element, lanthanum. When this calculation is made, contributions of about 60 percent granite and 40 percent basalt are indicated, a result which is close to the values of 50 percent and 50 percent originally obtained by Taylor.

The sensitivity of the calculation for making the estimate is diminished, however, by the fact that the basalt and granite averages are very close to the values for the sediments for nearly all the rare-earth elements. In addition, the failure of the pattern of basalts to match the pattern of the sediments for the heavy rare earths, as indicated by the present data, introduces a large enough uncertainty in the calculation that changes as large as 20 to 30 percent may have to be made in the values of 60 to 40 percent obtained for proportions of granite and basalt needed to give the sediment pattern. Thus, the most that can be accurately said is that the rare-earth pattern in sedimentary rocks is consistent with the hypothesis that this pattern is derived from basaltic and granitic matter.

There are additional reasons why the calculation may not lead to a valid estimate of the average gross composition of the crust. In the granite-basalt hypothesis, it is necessarily assumed that basalts are, on the average, entirely equivalent compositionally to their coarse-grained relatives the gabbros. While this assumption is valid for the major elements, it appears not to be so for the rare-earth elements. Rare-earth patterns for three gabbros are shown in Fig. 10; as may be seen, they are less rich than the sediments in light rare-earth elements. So is the standard diabase, W-1, from Centerville, Virginia (*26*). More important, these rocks have much lower absolute contents of rare earths than the basalts have. The W-1 diabase contains 100 parts of rare-earth elements per million, and the gabbros of Fig. 10 contain from 28 to 123 parts of these elements per million. Gabbros from the Stillwater and Bushveldt layered intrusives (possibly chill-zone gabbros) contain, respectively, 16 and 5.5 parts of rare-earth elements per million (*30*). It is entirely possible that the bulk of the material in the inaccessible lower parts of the crust resembles gabbro rather than basalt in rare-earth content; if this is the case, estimates of crustal rare-earth content and distribution that are based on averages for granite, basalt, and sediment may be seriously in error as a result of bias in favor of surface material which is available for observation and analysis.

To summarize, the rare-earth pattern of sedimentary rocks may safely be considered to represent that portion of the earth's crust which is subject to weathering. The rare-earth content of that portion of the crust is of the order of 235 to 300 parts per million, as estimated from the North American composite shale, from the Russian Platform sediments, and from granites and basalts. These rare-earth concentrations are a maximum for the whole crust, since rare-earth concentrations at depth may be much lower. (Similarly, concentrations of other trace elements may be lower at depth than at the surface.)

Seismology indicates that, in structure, the crust under the oceans is unlike that of the continents. Wave characteristics suggest material of basaltic or gabbroic composition for the oceanic crust, but a cover of sediments has thus far prevented direct sampling of the igneous oceanic crust, so its exact nature is not known. There are islands and extended features, such as the Mid-Atlantic Ridge, which jut above the normal levels of the oceanic crust and from which samples can be obtained.

Oceanic islands are characterized by alkali basalt, plus some trachyandesite (intermediate) and trachyte (acid). The rare-earth patterns for a suite of samples from Gough Island are shown in Fig. 11. The absolute rare-earth contents are somewhat higher than the averages for basic and acid rock from the continents. The abundance patterns show richness in light rare-earth elements, like the patterns of continental materials. Similar results were obtained for an Ascension Island suite (*30*). Schmitt and his co-workers have analyzed a single sample of a Hawaiian basalt; again, a pattern showing richness in light rare-earth elements was found (*28*).

Tholeiitic basalts dredged from the Mid-Atlantic Ridge and its counterpart, the East Pacific Rise, have a very different rare-earth pattern, as illustrated in Fig. 12 (*30, 31*). These basalts are remarkably uniform in rare-earth content. Their rare-earth patterns are nearly identical to the pattern of the chondritic meteorites. The discovery that the patterns of the oceanic tholeiitic basalts are almost chondritic strengthens the suppositions that the average rare-earth pattern for the whole earth is like that of chondritic meteorites and that the crustal pattern did arise from the geochemical differentiation of the earth.

It is curious that these basalts could have a rare-earth pattern so close to that of chondrites yet be so different from chondrites in major-element composition (having basic composition as opposed to the ultrabasic composition of the chondrites) and have a rare-earth content some 17 times as high. Just how such an enrichment can occur is not known, but that it can, and without measurable disturbance of the rare-earth pattern, is evidenced by the chondritic pattern of the calcium-rich (eucritic) achondrites (*28, 32*). These meteorites, which are very similar in gross composition to terrestrial basalts, have a rare-earth-element content about 11 times that of chondrites. While no specific mechanism for enrichment in

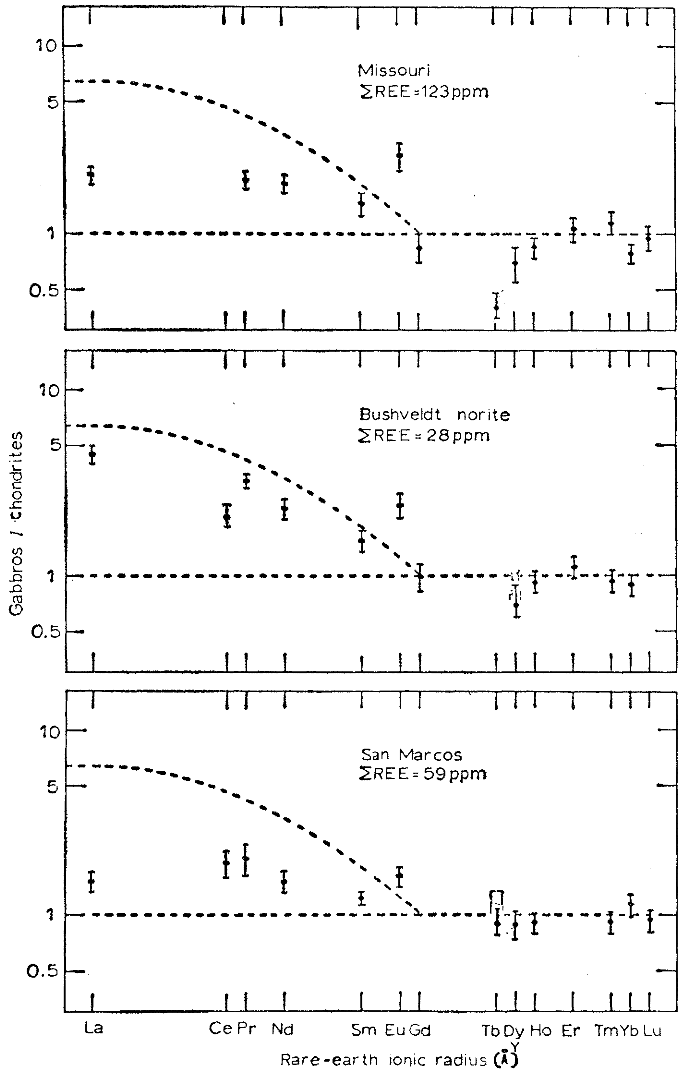


Fig. 10 (left). Comparison plot for gabbros. [Data on San Marcos gabbro from Towell *et al.* (*39*)]

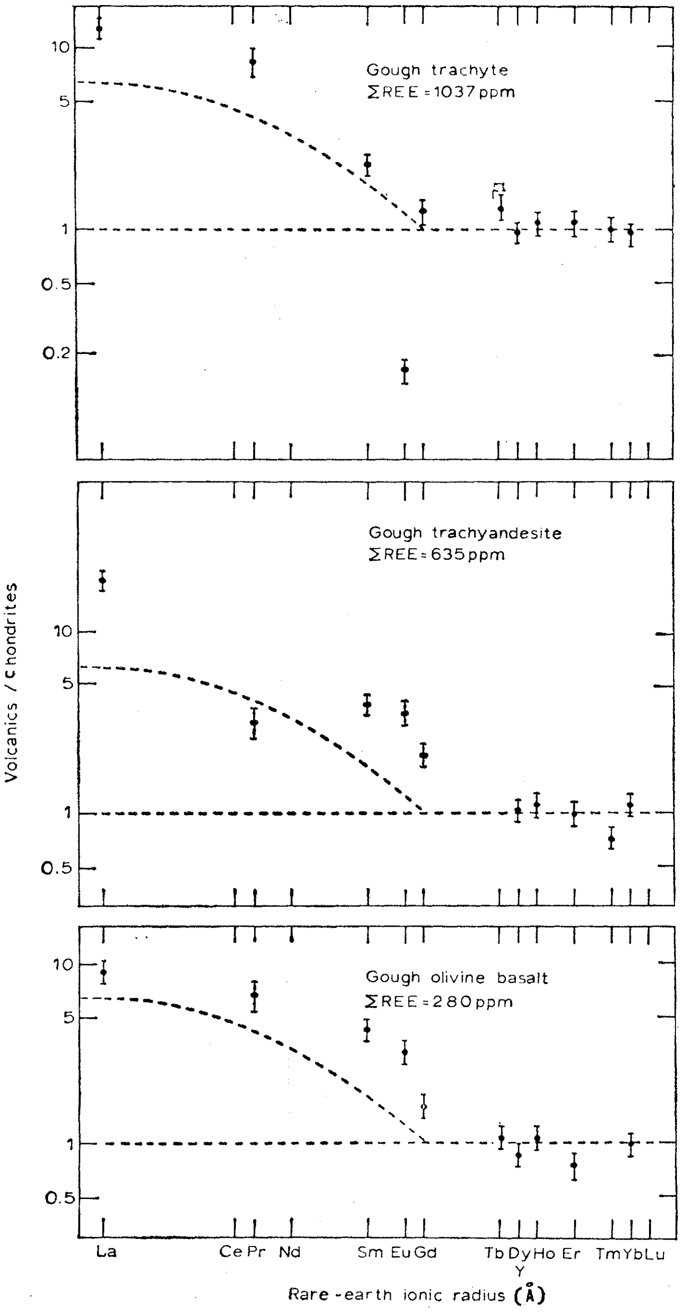


Fig. 11 (right). Comparison plot for suite of volcanic rocks from Gough Island.

rare-earth elements without internal fractionation of the group is known, some of the general features of such a mechanism can be surmised. If chondritic matter were partitioned into two phases in such a manner that the rare-earth elements were essentially drawn entirely into one phase, then, despite considerable selectivity by the rare-earth-poor phase, the total quantity of rare-earth elements entering that phase would be too low to change measurably the original pattern in the rare-earth-rich phase. The removal of olivine and iron oxide from chondritic material is needed to produce the achondritic gross composition. Analyses of dunites (olivine-rich rocks) have yielded very low rare-earth contents. This type of separation probably requires an accreted body of some size, and melting.

Another possible mechanism which might concentrate the rare-earth elements without fractionating the group is selective volatilization below the vaporization temperatures for the rare-earth compounds present. Oxides and other simple rare-earth compounds are fairly refractory. Such a process could be a cosmochemical one—that is, could have occurred before the accretion of the earth.

How important quantitatively the oceanic tholeiites are—that is, how large a fraction of the crust they constitute—is uncertain. Engel and Engel (*33*) have drawn attention to the remarkable chemical homogeneity of these rocks, whether dredged from the Atlantic, the Pacific, or the Indian Ocean, and have suggested that they are the predominant volcanic basalt of the entire oceanic regions. However, these basalts have actually been obtained only on those relatively special sites, such as the Mid-Atlantic Ridge, where igneous material extends above the sedimentary layers, so it is not certain whether these are common rocks made available to observation by the specialized features of their geologic environments or whether they are specialized materials resulting from the

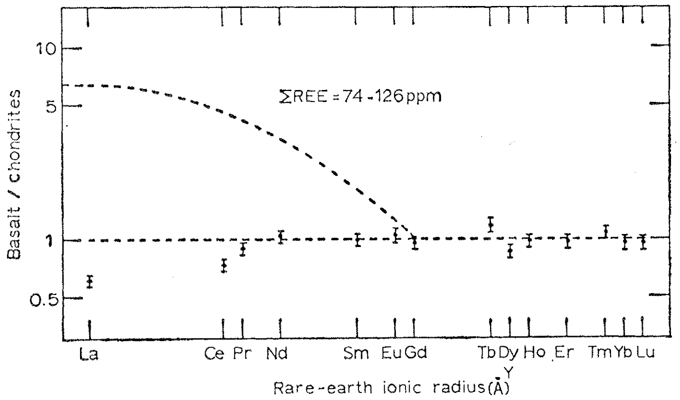
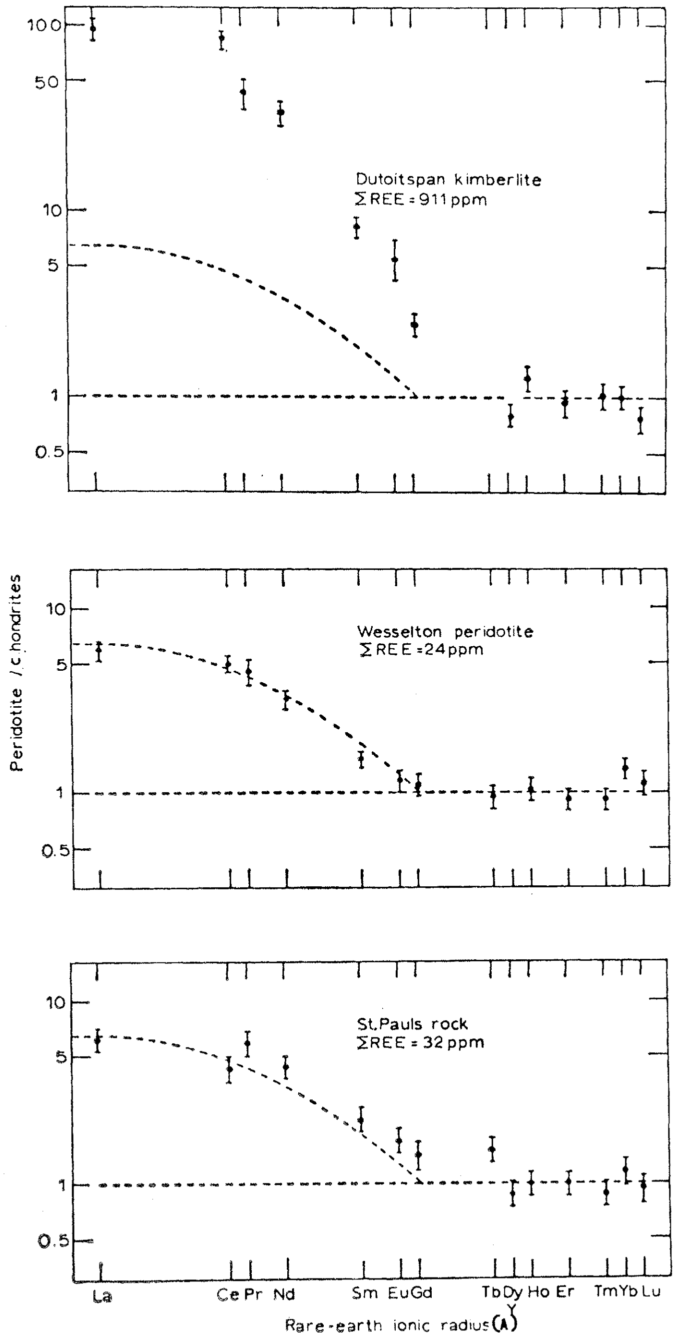
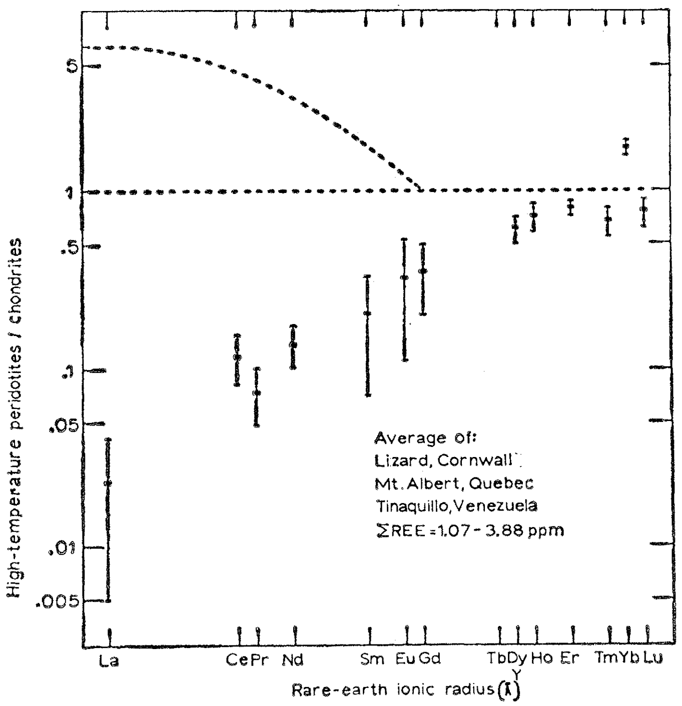


Fig. 12 (above). Comparison plot for average of rare-earth patterns of seven oceanic tholeiitic basalts from the mid-Atlantic Ridge and the East Pacific Rise. Fig. 13 (right). Comparison plot for three ultrabasic rocks. [Data for Wesselton peridotite from Schmitt *et al.* (*28*)] Fig. 14 (below). Comparison plot for average of rare-earth patterns from three high-temperature peridotites.





formation of their geologic features. Nevertheless, their uniformity of composition and their primitive rare-earth pattern may possibly indicate a close relationship with the mantle. They seem especially worthy of further investigation in this regard, since the geologic features from which these basalt samples were taken have been postulated to be due to upwelling of mantle material through the crust (*34*).

The rare-earth patterns of the oceanic tholeiitic basalts show some depletion in lanthanum, cerium, and probably praseodymium relative to the chondritic pattern. Certainly, if the earth's crustal rare-earth distribution is accurately characterized by the sediment pattern, and if the whole earth is chondritic in its average rare-earth distribution, then there must be a considerable amount of matter somewhere in the earth which has a rare-earth pattern complementary to that of sediments. The oceanic tholeiites do display such a pattern. The Engels (*33*) have pointed out that the basalts common to oceanic islands are alkali basalts, such as those of Fig. 11. The kind of oceanic tholeiite discussed here has only been dredged from underwater sites, never taken from the tops of islands. The Engels believe that the oceanic tholeiite is at least a thousand times as abundant as the alkali basalts, and they suggest that tholeiitic magma may be the parent of the alkali material. The rare-earth patterns of these two materials are consistent with this hypothesis. The oceanic tholeiites might represent the residue of an original material, of chondritic rare-earth pattern, from which island alkali basalts developed. When the relative and absolute rare-earth abundances of the two basalt types are considered, then calculation shows that a mixture of over 90 percent of oceanic tholeiite and less than 10 percent of alkali basalt is needed to give the chondritic rare-earth pattern. The major-element composition of such a magma would be classified as tholeiitic. A simple magmatic differentiation of the type required for the above hypothesis is a gross oversimplification, in view of what is known of the complexity of the origins of basalt (*35*), but the calculation does serve to illustrate the potentialities of rare-earth distributions as indicators of whether or not certain postulates are reasonable.

Igneous Rocks and the Mantle

An obvious place to seek large amounts of material with rare-earth patterns complementary to the rare-earth pattern of the crust is the mantle. The difficulty is that there are no known materials which can be safely said to be unadulterated samples of typical upper mantle material. A combination of arguments, based on seismic measurements, and on knowledge of the stability, density, and other properties of minerals under high pressure, leads to the conclusion that a prime candidate for a major component of the mantle is peridotite. Several types of occurrence of peridotite are known (*36*). There are peridotite inclusions in basalts and kimberlites. Kimberlite itself is peridotitic in composition and unquestionably of deep origin, but it has not generally been considered representative of the upper mantle. The rocks of St. Paul's Island, associated with the Mid-Atlantic Ridge, are peridotites, and it has been suggested that the island may be a piece of uplifted and exposed oceanic mantle.

Large intrusions known as alpine peridotites are known. Most of these are something of an enigma, since a peridotitic magma would have a very high temperature, and its emplacement would result in considerable contact metamorphism of the surrounding host rock. No appreciable metamorphism has been observed, so the conclusion that the intrusion occurred at low temperature is necessary. A number of mechanisms for this have been postulated; one of the more acceptable hypotheses is that crystalline material was intruded through lubrication with small amounts of nonperidotitic liquid. There are occurrences of alpine peridotites, known as high-temperature peridotites (*37*),

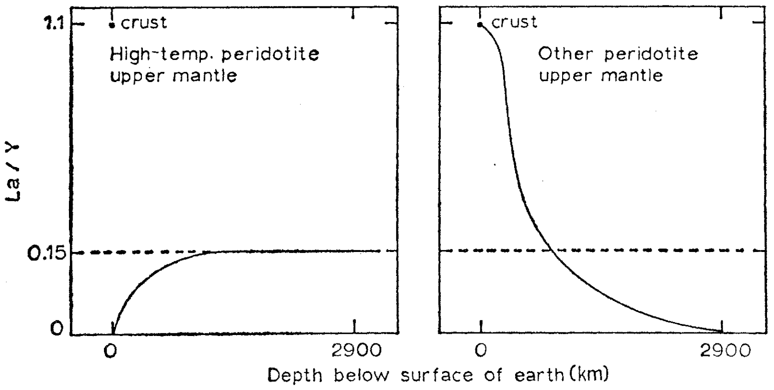
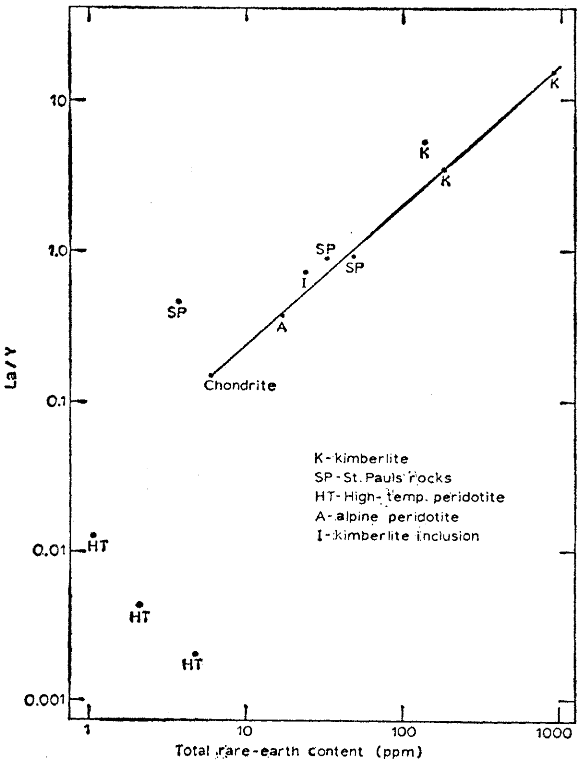


Fig. 15 (above). Diagram illustrating qualitatively two trends of rare-earth fractionation as a function of depth below the crustal surface, based on the two kinds of rare-earth patterns found in peridotites (see text).

Fig. 16 (right). The ratio of lanthanum to yttrium—an index of the extent of relative enrichment in light rare-earth elements—plotted against total rare-earth content for ultrabasic rocks. A straight line is indicated for those rocks which have a higher total rare-earth content than chondritic meteorites. A point representing the chondrites is included.



in which extensive metamorphism can be found. The various peridotites have been carefully considered by Green and Ringwood (*38*) as possible samples of matter from the upper mantle. Most or all of the available peridotitic materials may, however, be differentiated residues from magma, rather than melts or partial melts of typical mantle matter. Typical results of rare-earth analyses on three kinds of peridotites, including one inclusion in kimberlite, one kimberlite, and one rock from St. Paul's Island, are shown in Fig. 13. Nearly all the peridotites examined have been found to be relatively richer in the light rare-earth elements than chondrites are. The exceptions are one sample of peridotite from St. Paul's Island, which had a rare-earth pattern very close to that of chondrites, and three high-temperature peridotites. Considerable range in total rare-earth content, from less than 1 to more than 900 parts per million, was found for these materials. The three high-temperature peridotites were very similar to each other in rare-earth content and pattern. The average of their patterns is shown in Fig. 14; as may be seen, it is complementary to the crustal pattern. There are no indications, from the rare-earth patterns, as to which, if any, of the peridotitic materials studied are representative of the mantle.

That the entire mantle is not likely to be like high-temperature peridotite in composition can be shown as follows. The earth's crust has a mass of approximately 2.4×10^{25} grams. On the basis of an assumed average rare-earth content for the crust equal to the average for the North American shale composite, it is calculated that there are 9×10^{20} grams of lanthanum and 8×10^{19} grams of ytterbium in the crust. The mantle has a mass of 4.1×10^{27} grams. The quantity of high-temperature peridotite needed to complement the rare-earth elements in the crust to give a whole earth of chondrite-like rare-earth pattern would have a mass nearly 100 times the actual mass of the mantle. If the high-temperature peridotites are presumed to represent only the upper mantle, then the depletion in light rare-earth elements would decrease with depth in the mantle. The rare-earth elements in the crust would have been extracted preferentially from the upper mantle, and the lower mantle would be less differentiated from its primitive composition. Such a situation is qualitatively illustrated in Fig. 15, left, where the ratio of lanthanum to yttrium is plotted as a function of depth below the surface. If, on the other hand, the other peridotites better represent the upper mantle, then it, like the crust, has been preferentially enriched in the lighter rare-earth elements, so that the complementary pattern begins deeper in the mantle, as illustrated in Fig. 15, right. These diagrams are meant only to be qualitative representations based on the hypotheses (i) that the crustal rare-earth pattern is the pattern of sediments and (ii) that the whole-earth pattern is the pattern of chondrites, and on the assumption (iii) that one or the other of the peridotite types is representative of the upper mantle. These qualitative trends of rare-earth pattern distribution in the mantle are independent of absolute rare-earth content over a considerable range of values. However, more complicated diagrams can be constructed which serve equally well. Probably the upper mantle is not homogeneous and cannot be adequately represented by either trend (*38*).

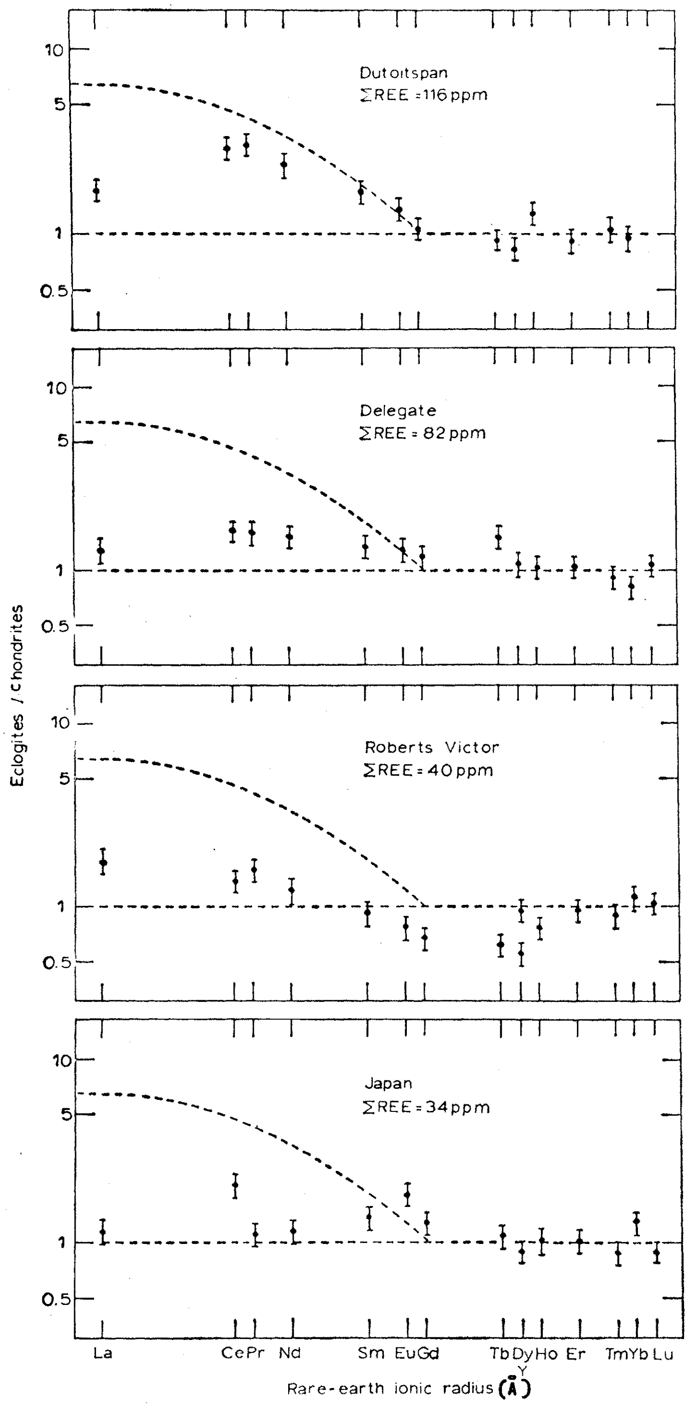
Hypotheses i and ii above have considerable foundation in measurements. But even though it appears probable that the whole-earth rare-earth pattern is chondritic, it is not certain whether the absolute rare-earth content is near that of chondrites, or of the silicate phase of chondrites, or is more like that of the eucritic achondrites. If the overall absolute content of the mantle and crust is that of chondrites, then some 75 percent of the earth's lanthanum and 10 percent of its ytterbium are found in the crust. This would require a very efficient concentrating mechanism, since the ratio for mass of crust to mass of mantle is only 1:200.

An interesting correlation between the extent of relative enrichment in light rare earths and the total rare-earth content of peridotitic materials is shown in Fig. 16. The lanthanum-yttrium ratios have been calculated for the various peridotitic materials as an index of the extent of enrichment in light rare earths. A point has been included for chondritic meteorites, which are also peridotitic in composition. The extent of enrichment in light rare earths appears to be a linear function of total rare-earth content for all the peridotitic materials which contain more total rare-earth elements than chondrites do. Those with less total rare-earth elements than chondrites scatter and show no such linear pattern. This correlation is based on relatively few points, and the next few analyses of rocks might destroy it entirely, but if it can be confirmed by further analyses, then it will provide evidence consistent with the view that some peridotites were formed by mechanisms operating on matter which had chondrite-like relative and absolute rare-earth abundances.

Another rock with properties which satisfy the physical-measurement requirements for the upper mantle is eclogite. Eclogites are compositionally equivalent to basalts, as far as major elements are concerned, but they have different assemblages of minerals, those which are stable at the higher pressures and temperatures associated with upper mantle depths. Eclogites are found as products of metamorphism, or as inclusions in basalts, kimberlites, and other substances. Four samples of eclogite inclusions have been analyzed for rare-earth elements; their patterns are shown in Fig. 17. They are reminiscent of gabbros both in absolute rare-earth contents and in rare-earth patterns. The eclogite from Shikoku, Japan, is particularly interesting since it appears to have a chondrite-like pattern. None of the eclogites has a rare-earth pattern complementary to that of the earth's crust. As was the case with the peridotites, the eclogite inclusions are possibly fragments of the mantle which were ripped loose by rising magma, but they may also be the result of crystallization from the basaltic magma.

Differentiated Intrusives

This survey of the abundances of rare-earth elements in common rock types has uncovered some qualitative trends. On the average, and only on the average, the absolute rare-earth contents appear to increase from ultrabasic rocks, through basic and intermediate rocks, to the acid granites. Again on the average, the extent of relative enrichment in the lighter rare-earth elements follows the same trend. This trend also shows clearly in the evolution of rocks of the Southern California batholith, as determined by Towell *et al.* (*39*). Four rocks were analyzed—a gabbro, a tonalite, a granodiorite, and a granite, listed in order of increasing acidity. The rare-earth patterns and the total rock contents are shown in Fig. 18, and the trends are those outlined previously as an average for crustal rocks. Towell *et al.* emphasize, however, that considerable caution must be exercised in interpreting their results as indicative of an evolutionary trend, because the exact geologic field relationships among the four rocks are uncertain, so the four may not represent successive stages of crystallization of a single magma. This point is well taken, as no such simple trend has been found by Balashov (*40*), who has summarized the rare-earth patterns in presumed successive stages of a number of differentiated Russian intrusives. An example somewhat analogous to the Southern California batholith is the Susamyr batholith (Fig. 19), in which the sequence of stages of rock crystallization is believed to be gabbro, granodiorite, granite, and aplite (*40*). The aplites of the final phase are the most acid of the rocks, but they occur as veins in the late-stage granites. Their rare-earth patterns are dominated by the heavy rare-earth elements. They were very probably emplaced from hot aqueous solutions, rather than merely crystallized from a fairly water-free silicate melt. Their richness in heavy rare-earth elements may result from their mode of origin, since solutions with relatively high contents of alkali metal ions plus fluoride, carbonate, or certain other simple anions are capable of carrying the rare-earth elements as complexed species. The heavy rare-earth elements show the greatest tendencies to form such complexes and are thus likely to be more concentrated in solutions of this type than are the light elements. When the water is released, or the



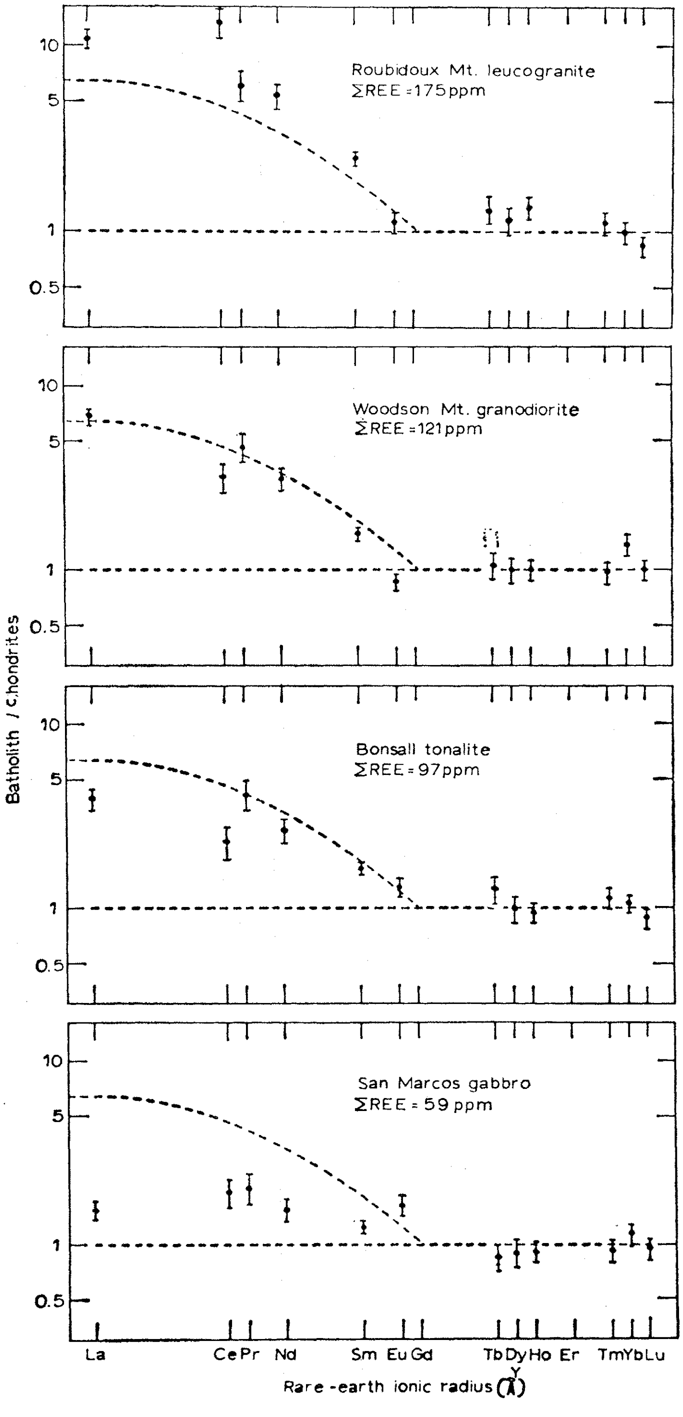


Fig. 17 (left). Comparison plot for eclogites. In each graph the dashed upper curve represents the average for North American shale. [Data for Delegate and Roberts Victor eclogites from Schmitt *et al.* (*28, 32*)] Fig. 18 (right). Comparison plot for rocks of Southern California batholith. [Data from Towell *et al.* (*39*)] complexes are broken by other means, the rare-earth elements are left behind with the crystalline residue.

The operation of this mechanism to form patterns dominated by the heavy rare-earth elements has been demonstrated by Mineyev (*41*), who studied metasomatic rocks produced by the passage of hot solutions through a body of granite. The solutions contained alkali fluorides, which dissolved the rare-earth elements and carried them to the surface of the granite body, where a series of reactions (albitization) occurred which broke the complexes, as illustrated in the following example, where yttrium (Y) is chosen as a representative heavy rare-earth element.

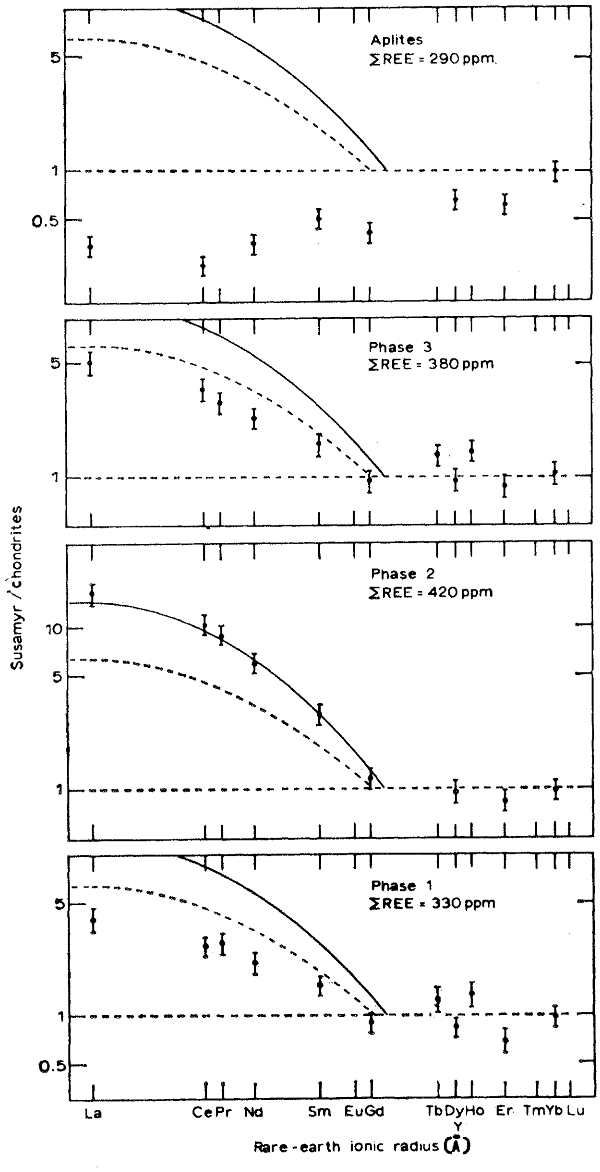
$$\text{Na, Ca plagioclase (solid)} + \text{NaYF}_4 + \text{(K, Na)F} \longrightarrow \text{Na plagioclase (solid)} + \text{NaCaYF}_6\ \text{(solid)}$$

Figure 20 shows the rare-earth patterns in an albitized sandstone at the edge of the granite pluton, and in two metasomatized portions of granite. High relative concentrations of heavy rare-earth elements accompanied deposition of large amounts of the complexing fluoride. The occurrence of the rare-earth mineral gagarinite (NaCaYF$_6$) in the calcium-rich wall rocks adjacent to the granite body is additional evidence favoring the proposed mechanism.

Thus, it may be possible to differentiate between rare-earth patterns resulting from differentiation of dry magmatic liquid and those resulting from deposition of rare-earth elements from hot aqueous solution. This possibility was also suggested by Jensen and Brunfeldt (*15*).

Mineral Rare-Earth Contents and Patterns

Mere knowledge of the rare-earth pattern and content of a rock does not define very specifically the positions of the rare-earth elements within the rock. A number of rare-earth minerals (for example, monazite and allanite) are fairly common constituents of granites, as are a number of minerals (for example, apatite) in which the rare-earth elements are not essential components but which tend to concentrate these elements. Thus, it was for some time assumed that the rare-earth elements in igneous rocks would be concentrated in the accessory minerals. The first careful examination of this question was made by Gavrilova and Turanskaya on a Russian granite (*42*). They



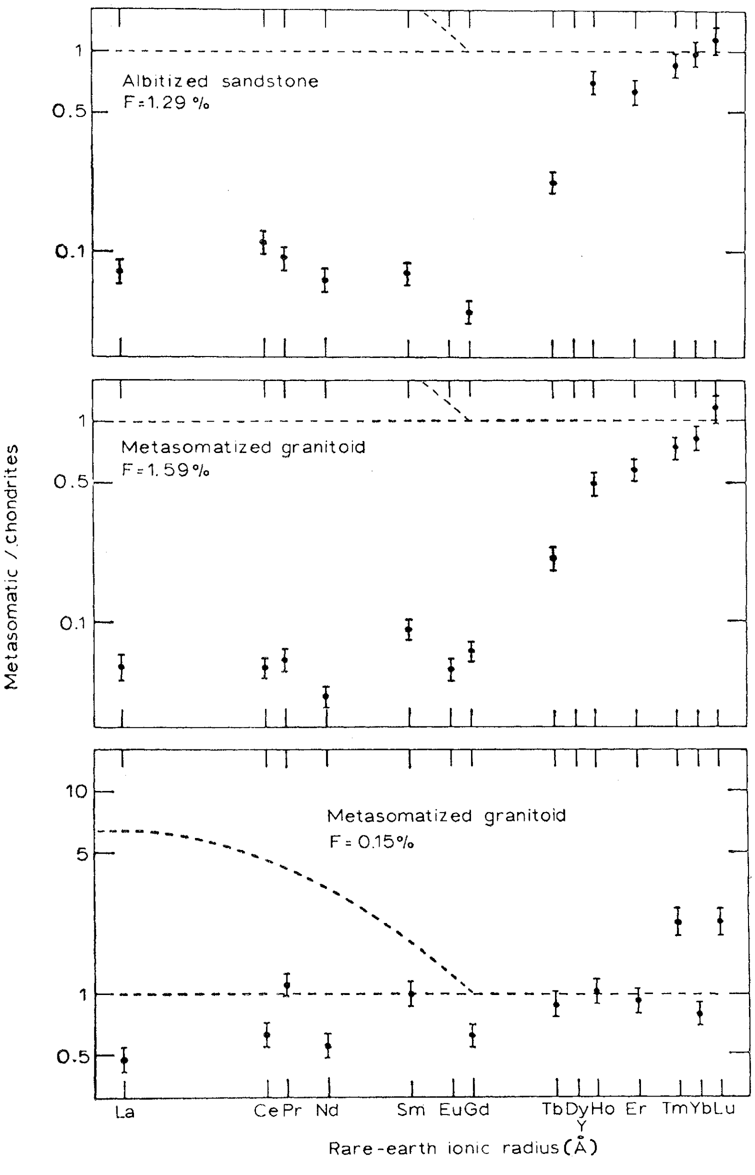


Fig. 19 (left). Comparison plot for phases of Susamyr batholith. In each graph the upper solid line represents the batholith average. [Data from Balashov (*40*)] Fig. 20 (right). Comparison plot for metasomatic rocks; *F*, concentration of fluorine. [Data from Mineyev (*41*)] showed that, while the rare-earth contents of some of the accessory minerals were quite high, a significant fraction of the rare-earth elements was contained in the major, rock-forming minerals. This result was confirmed by the work of Towell *et al.* on two of the rocks of the Southern California batholith (*39*). The rare-earth patterns of separated minerals of the San Marcos gabbro are illustrated in Fig. 21. These patterns have not been normalized relative to ytterbium, and the values have not been divided by values for the chondritic distribution, as described above; rather, the ordinate gives the fraction of the total rock content for each rare-earth element in each mineral.

In the gabbro, the accessory mineral apatite has by far the highest concentration of rare-earth elements (~2600 parts per million), but the abundance of apatite in the gabbro is so low that the bulk of these elements is contained in the major, rock-forming minerals—hornblende, augite, and plagioclase feldspar. Several features of trace element partition which have been shown to hold for other rocks (*30*) may be seen in Fig. 21:

1) The bulk of the rare-earth elements are contained in, or inseparably associated with, the major, rock-forming minerals.

2) Among the rock-forming minerals, the dark minerals (augite and hornblende, in this case) contain the bulk of the rare-earth elements.

3) Relative to the whole rock, the feldspars are enriched in the light rare-earth elements and the dark minerals in the heavy elements.

4) Europium is preferentially concentrated in the feldspars through its reduction to the 2+ state.

It is this last feature which causes the break in the otherwise smooth trends of relative rare-earth content for the minerals. It should be pointed out that, since the whole rock is "anomalously" enriched in europium, a normal amount of europium relative to samarium and gadolinium in the minerals would appear to be too low when the values for the minerals are divided by the values for whole-rock contents. In the case of the San Marcos gabbro, division of the values for rare-earth contents of individual minerals by the values for chondrites shows that the europium contents of the apatite, hornblende, and augite are indeed lower than normal relative to the samarium contents, and thus that all the minerals were competing with the feldspar for the rare-earth elements. The extent of relative depletion is noticeably less for the hornblende than for the augite and apatite. This would result if the hornblende and plagioclase competed against each other for europium in the early stages of crystallization of the magma so that, by the time augite and apatite began to form, the remaining liquid was already deficient in europium.

Just how the rare-earth ions are associated in the minerals is not known. They may be included in the lattice cation sites, adsorbed on the surfaces of mineral grains, associated with crystal defects, or even present as submicroscopic clusters of rare-earth mineral. The europium anomalies strongly suggest that europium, at least, is inside the feldspar lattice. In fact, it is quite possible that it is extra lattice energy available to the europium in feldspars as a 2+ ion, rather than a generally strong reducing potential for the liquid silicate melt, that is responsible for reduction of the europium to the 2+ state.

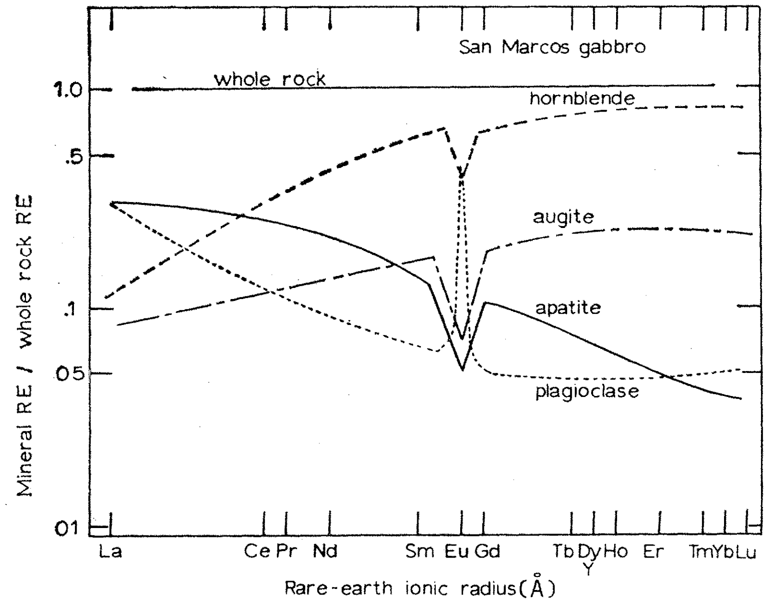


Fig. 21. Comparison plot for minerals of the San Marcos gabbro. To obtain the ratios given on the ordinate, the values for rare-earth contents of the minerals were divided by values for whole-rock rare-earth contents of the gabbro, rather than by values for chondrites as in Figs. 1–14 and 16–19. [Data from Towell *et al.* (*39*)]

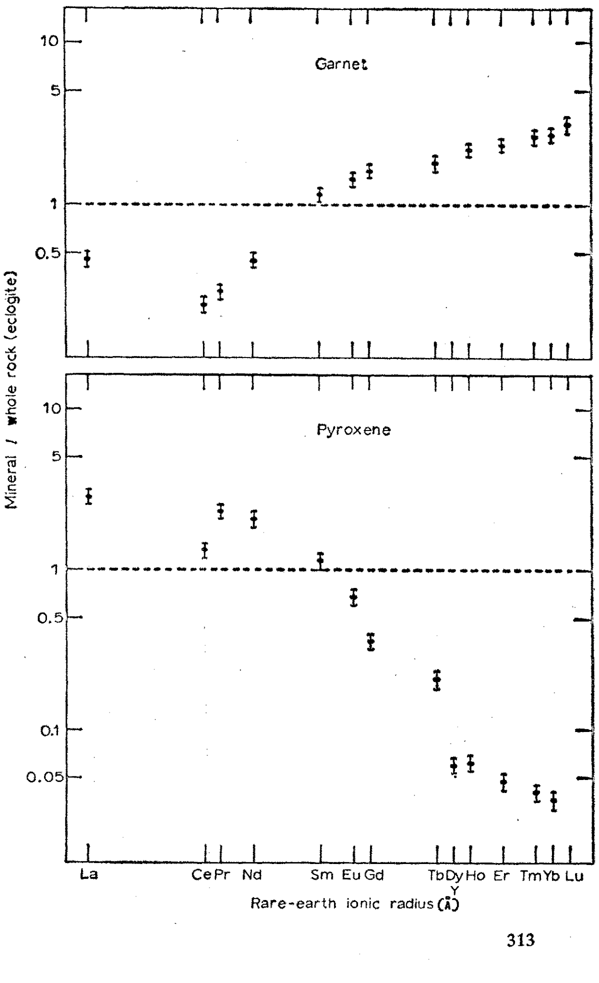


Fig. 22. Comparison plot for minerals from the Japanese eclogite. To obtain the ratios given on the ordinate, the values for rare-earth contents of the minerals were divided by values for whole-rock rare-earth contents of the eclogite.

The unequal partition of the rare-earth elements among rock-forming minerals is a plausible mechanism for the development of the various rare-earth patterns which are found in nature. A rock that exhibits extreme partition of these elements between major minerals is the Japanese eclogite (*30*). The principal minerals are garnet and pyroxene. The rare-earth concentrations of these minerals, divided by the rare-earth concentration of the whole rock, are shown in Fig. 22. The major portion of the heavy rare-earth elements is found in the garnet fraction, while the light elements are mostly in the pyroxene. Thus, partial solidification of an eclogitic liquid could leave a rare-earth pattern in the residual liquid very different from that in the original melt.

Summary

Somewhat contrary to the initial expectations of geochemists, partial separations of the rare-earth elements occur commonly in nature. While this process leads to a wide variety of rare-earth patterns, there are at least two of widespread significance. One of these is found in all chondritic and in certain achondritic meteorites, and presumably is that of the primordial matter from which the solar system developed. The other is the average pattern for sedimentary rocks, and is characteristic of the weathered portions of the earth's crust. These two patterns are identical for the elements gadolinium and lutetium, indicating that the earth and chondrites had a common source of matter. Oceanic tholeiitic basalts have rare-earth patterns which are identical with the chondrite pattern for all the rare-earth elements except lanthanum, cerium, and praseodymium. This suggests that the average rare-earth pattern for the whole earth matches the chondritic pattern, and that the distribution characteristic of the upper crust is a result of geochemical differentiation.

It is not possible from the available data to estimate with any confidence the average absolute rare-earth content of the earth. A chondritic absolute rare-earth abundance for the whole earth cannot be ruled out, but this hypothesis requires very efficient concentration of the rare-earth elements into the crust.

The rare-earth patterns in individual sedimentary rocks are all close to the average pattern for sediments, but significant differences do occur. There are apparently no systematic differences, on the average, which are related to gross composition of sediments. Under humid conditions of weathering, however, systematic differences of pattern with rock type have been revealed for sediments within a single basin.

The rare-earth patterns of individual igneous rocks show considerably more variation from the crustal average than patterns for sediments do. The rare-earth contents and patterns of basalts and granites are consistent with the view that sediments derive from such material.

The rare-earth patterns for most potential mantle materials (peridotites and eclogites) show varying degrees of enrichment of the light elements relative to the chondritic pattern. Striking exceptions are the high-temperature peridotites, which, relative to chondrites, are severely depleted in the light elements. There is no evidence from the rare-earth patterns which bears on the question of mantle origin for these rocks. Other patterns dominated by the heavy rare-earth elements have been found in acid rocks and seem to be due to the action of hot solutions which preferentially carry the heavy elements, as they form the most stable complexes.

The rare-earth elements are trace constituents of all common crustal rocks and are situated in both their accessory and their major, rock-forming minerals. Partition of the rare-earth elements among these minerals is unequal and results in fractionation within the rare-earth group. This unequal partition provides a plausible explanation of their separation in nature. Europium does not always follow the fractionation trends of the other elements but commonly separates as a 2+ ion.

Evaluation of the extent to which rare-earth patterns may serve as useful indicators of specific geochemical processes must await further investigation.

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