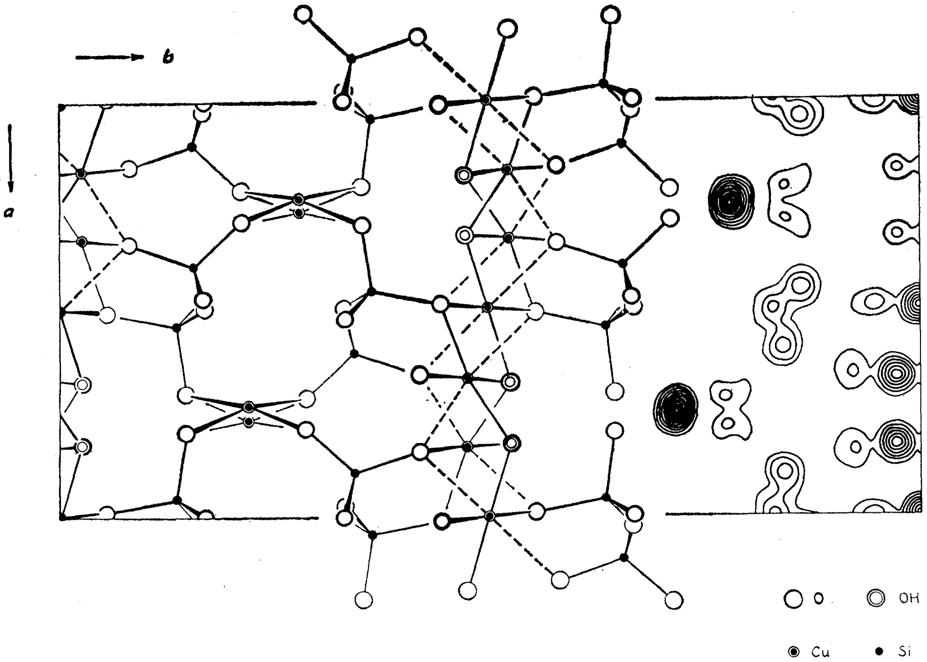

Fig. 1. The structure of shattuckite projected along the *c*-axis, showing the silicon-oxygen bonds as solid lines and the copper-oxygen bonds as dashed lines. One unit cell is contained within the rectangle. A representation of the electron density projection is shown at the right of the unit cell.

known zigzag chains in pyroxene. Those unshared oxygen atoms not involved in the copper-oxygen sheet are joined to those of opposite layers by additional Cu atoms forming ladder-like $(CuO_2)_n$ chains parallel to the *c*-axis. These features are shown in a projection of the structure along the *c*-axis in Fig. 1. Of the three types of Cu atoms present, two are located in the layer network in octahedral coordination showing the strong tetragonal distortion commonly exhibited by Cu(II). The third type is located in the latter chains in approximately square coordination.

The structure of planchéite has now also been solved in a similar manner. It is found to be a simple extension of the shattuckite structure in which the silicate chain is doubled along the *a*-axis to form a chain closely similar to that in amphibole. A molecule of water is inserted on the twofold axes in the structure to fill the void formed by the hexagonal rings in the amphibole-like chain. The structure analysis establishes the formula conclusively as $Cu_8(Si_4O_{11})_2(OH)_4 \cdot H_2O$. In view of the prevailing difficulties of obtaining homogeneous samples, this result is consistent with the best chemical analyses, with the exception of a small excess of water in the latter. Also, infrared measurements, while showing the presence of OH groups but not H_2O in shattuckite, indicate the presence of both in planchéite.

Table 1. Crystallographic data for shattuckite from Ajo, Arizona, and planchéite from La Rioja, Argentina.

Property	Shattuckite	Planchéite
$n\alpha$	1.753 ($\|\|b$*)	1.697 ($\|\|c$*)
$n\beta$	1.782 ($\|\|a$†)	1.718 ($\|\|b$‡)
$n\gamma$	1.815 ($\|\|c$§)	1.741 ($\|\|a$‡)
$2V$ (calc.)	88°	88½°
Space groups	*Pcab*	*Pcnb*
a	9.876 Å	19.04 Å
b	19.812 Å	20.01 Å
c	5.381 Å	5.27 Å
Z	4	4
D (x-ray)	4.138 g/cm³	3.85 g/cm³
D (meas.)	4.11 g/cm³	3.65-3.80 g/cm³

* Very pale blue; † pale blue, ‡ blue, § deep blue.

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4 August 1966

Rare Earths in European Shales: A Redetermination

Abstract. *The rare-earth elements in a composite of European shales originally analyzed by Minami in 1935 have been analyzed by neutron activation. The apparent europium deficiency and the differences in relative elemental abundances for the rare earths from American and Russian sediments, as inferred from the older values, are obviated.*

In 1935 Minami (*1*) measured the rare-earth element contents (lanthanides plus yttrium) of three composites of European and Japanese shales by an x-ray spectrographic technique. The resulting values, and those obtained by Noddack (*2*) for rare earths in meteorites, furnish the most striking example known of the Oddo-Harkins rule that, in nature, the relative elemental abundance of an element of even atomic number tends to exceed that of either of the elements of adjacent, odd atomic numbers. Goldschmidt (*3*) inferred from the data that after partial separations of the members of the rare-earth group had been effected by certain (unspecified) processes of igneous rock formation, processes of weathering and sediment formation mixed the rare earths back into their average crustal relative abundances. This and other conclusions based on Minami's data appear to have greatly influenced Goldschmidt's general views of geochemical processes and thus, to some extent, the development of the field of geochemistry. Minami's values have been used in nearly all compilations of terrestrial elemental abundances; general features of the rare-earth abundance distribution he observed were corroborated by Sahama (*4*).

Modern techniques of analysis have made possible such accurate determinations of rare earths that small differences (0 to 10 percent) in elemental abundances can be observed; thus, further consideration must be given to the accuracy of the specific values reported by Minami. Using neutron activation analysis, Haskin and Gehl (*5*) found relatively little variation in the abundance distributions of the rare earths among ten specimens of limestone, sandstones, and shales. By averaging the relative abundances for seven of the samples, they obtained a distribution similar to that found by Minami;

this they considered to be a refinement of measurements made by Minami, with more accurate values resulting from a superior analytical method. Apart from considerable random scatter among adjacent elements, Minami's results differ from the neutron activation data by having a significantly lower proportion of light lanthanides, relative to the heavy rare earths.

It has been pointed out that there is no a priori reason to expect a single, average rare-earth distribution for sediments from large but separate geographic areas (*6*). Since the two sets of data were taken from sediments of three different continents, perhaps the observed difference was real. The relatively low europium content of the European and Japanese shales might reflect retention of that element in the material from which the Eurasian landmass derived, as compared with the absence of such an effect in the North American shale (*7*). Finally, Masuda (*8*) preferred to use the distribution obtained by Minami because it fits his theory of the development of the crustal rare-earth abundances from chondritic matter better than do the results of the neutron activation studies. The analytical results of the ten North American sediments cannot be construed to fix so well an accurate average rare-earth abundance distribution for all crustal sediments that the subject is unworthy of further investigation. Sediments from other continental areas should be examined.

A composite of 40 North American shales was analyzed by Frey (*9*) and found to have the same relative rare-earth abundances (to within ± 10 percent) as the previous average of Haskin and Gehl, and the same average recently reported by Balashov and co-workers for the Russian Platform (*10*). Thus, the possibility that there is little actual difference in rare-earth relative distributions from different continents seemed strong, despite the apparent disagreement with Minami's results.

Fortunately, portions of the original shale composites analyzed by Minami still exist. Several grams of one of these (European paleozoic shales) were furnished by Wedepohl and Herrmann of the University of Göttingen (*11*). The rare-earth content of the composite was recently determined by them, using an x-ray spectrographic method (see Table 1). The agreement between our measurements and those of Wedepohl and Herrmann is, on the whole, quite good, although the differences for Eu, Gd, Ho, Yb, and Lu are outside the range of experimental precision. The values obtained by Minami agree remarkably well with the other two sets for the elements Sm to Yb, and Y. However, the elements lighter than Sm are increasingly depleted in Minami's values as compared with the other analyses. Probably, significant portions of the light lanthanides were lost during the pre-analytical chemical separations.

Because the absolute, as well as the relative, rare-earth abundances in the European shales and the North American shales appeared to be nearly the same, a second determination of each of those samples was made (Table 1). A systematic error was somehow made in the original determination of this composite so that the old values (*9*) are 22.5 percent too high. When reduced by a factor of 1.225, the old values (with the exception of Eu and Tb) agree within ± 10 percent with the new measurement. The newer values are superior, due to higher reactor neutron flux and improved flux monitoring. Their accuracy has been confirmed by a further partial analysis of the sample by K. A. Collins. The reason for the 22.5 percent error in the earlier analysis is unexplained, as no such difference was found when three other materials analyzed at about the same time were checked.

Table 1. Rare-earth contents of sediments in parts per million.

Element	European shales			North American shales (this work)	Russian Platform (*10*)
	(*1*)	(*11*)	(This work)*		
Y	30	45	31.8 ± 0.6	27	49
La	16	48.8	41.1 ± 0.7	32	50
Ce	33	96	81.3 ± 2.2	70	98
Pr	4.9	10.9	10.4 ± 0.4	7.9	12
Nd	28	41	40.1 ± 2.7	31	44
Sm	7.6	7.0	7.3 ± 0.15	5.7	9.5
Eu	1.2	1.2	1.52 ± 0.08	1.24	
Gd	8.5	6.0	6.03 ± 0.03	5.21	7.8
Tb	1.0	1.0	1.05 ± 0.03	0.85	1.8
Dy	6.2	5.8			6.2
Ho	1.9	1.8	1.20 ± 0.02	1.04	1.8
Er	3.3	4.0	3.55 ± 0.33	3.4	4.3
Tm	0.26	0.6	0.56 ± 0.00	0.50	
Yb	3.9	3.9	3.29 ± 0.05	3.1	4.2
Lu	1.1	0.8	0.58 ± 0.01	0.48	
Total†	147	274	230	193	282

* Errors are mean deviations for two separate determinations. † Missing analytical values were estimated.

Table 2. Normalized ratios for comparison of rare-earth distributions.

Element	Eur./ Amer.	Russ./ Amer.	Russ./ Eur.
Y	0.97	1.24	1.20
La	1.05	1.07	0.95
Ce	0.95	0.96	0.95
Pr	1.08	1.03	0.90
Nd	1.06	0.97	0.86
Sm	1.07	0.86	1.02
Eu	1.01		
Gd	0.94	1.03	1.01
Tb	1.00	1.45	1.34
Ho	0.94	1.18	1.17
Er	1.16	0.86	0.95
Tm	0.92		
Yb	0.86	0.93	1.00
Lu	0.99		
Normalizing factor	1.22	1.46	1.28

Two rare-earth abundance distributions can be readily compared to determine whether they are alike by dividing the concentration in parts per million of each element in one by the concentration of the corresponding element in the other. If all the resulting ratios for the elements between the two distributions are the same, so are the distributions. In practice, precisely identical ratios for all the elements in probably identical distributions are never observed because of random analytical errors (usually about ± 10 percent) for each element. This leads to a standard deviation for each ratio of approximately ± 15 percent, with occasional wider variations which often result from systematic errors between different analysts. Observation of the extent of similarity (or difference) between two distributions is enhanced if the effects of different absolute concentrations are removed by dividing all of the individual element ratios for the two distributions by a single, appropriate factor which makes the largest number of those ratios equal to or approximately 1. The results of such a treatment of the European and North American shales and the Russian Platform average are shown in Table 2. The European and North American shale distributions are identical to within ± 10 percent standard deviation, since more than two-thirds of the normalized ratios are between 0.90 and 1.10. (Only our results were used in this comparison, to eliminate any systematic discrepancies between analysts.)

The Russian Platform average agrees with the European and American shale distributions to within ± 15 percent standard deviation. The magnitudes of the differences are about what is expected from analytical and sampling errors. We conclude, therefore, that the relative elemental abundances of the rare earths are the same (at least to within 15 percent) for separate, large areas of the continental crust. The absolute rare-earth contents of shales are somewhat less well known, since the American, European, and Russian samples vary from 190 to 280 parts per million.

Comparison of the data for the American and European shales with rare-earth abundances in 20 chondritic meteorites (*12*) gives no indication that Eu was selectively retained by any residual material out of which the crust might have been derived.

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13. We thank Drs. Herrmann and Wedepohl for supplying the sample of European shales. Supported by ONR contract NR-083-180.

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Sex Attractants in Frass Produced by Male Ips confusus in Ponderosa Pine

Abstract. *The attractant response of* Ips confusus *to frass produced by male beetles boring in ponderosa pine can be reproduced, in a laboratory bioassay, by a combination of compound I with either compound II or compound III, all isolated from frass. The same response by both sexes was elicited by mixtures of synthesized compounds. Compound I is (−)-2-methyl-6-methylene-7-octen-4-ol; compound II, (+)-*cis*-verbenol; and compound III, (+)-2-methyl-6-methylene-2,7-octadien-4-ol.*

We have isolated and identified three terpene alcohols from the frass produced by male *Ips confusus* (LeC.) boring in ponderosa pine, which we believe are the principal components of the sex attractant that is responsible for the mass attack following initial boring activity. The compounds, each of which has been synthesized, are shown in Fig. 1.

In the laboratory bioassay, a typical attractant response (*1*) was elicited by each of two mixtures: 1 μg of compound I with 0.01 μg of compound II, and 1 μg of compound I with 1 μg of compound III. Neither optimum combinations nor minimum levels have been determined. The compounds were inactive singly at these levels: compound I at 100 μg, compound II at 20 μg, and compound III at 100 μg; they were not tested at higher levels.

We have not accounted for all the activity of the total frass extract. Apparently there are a number of other components whose total activity is greater than the sum of their individual activities, but the compounds described in this report appear to be the principal active components. In the laboratory bioassay, insects responded to combinations of these components in the same way that they did to the frass or frass extract. Also, the response to mixtures of synthesized compounds mimicked that obtained from the corresponding mixtures of compounds isolated from frass.

These synergistic effects are striking, and they emphasize the difficulties involved in monitoring fractions and obtaining quantitative estimates of potency by bioassay. An apparently inactive fraction cannot be discarded until it has been tested in combination with other fractions. No masking effects have as yet been encountered in this study.

The compounds were isolated from 4.5 kg of frass produced by male beetles (*1*). Isolation of compound I and procedural details through the second gas-liquid chromatography fractionation (carbowax column) for the isolation of compounds II and III have been reported (*2*). The material that was eluted from the carbowax column from 29 to 35 minutes (100 mg) contained compounds II and III; this was chromatographed again under the following conditions: 15 percent TCEP on Chromosorb W; aluminum tubing, 10 feet by ¼ inch (3 m by 0.6 cm); column temperature, 105°C; detector temperature, 120°C; 54 cm³ of He per minute; on-column injection; retention time 37 to 52 minutes; 19 mg collected.

This fraction contained compound II together with a larger component that was eluted immediately afterward. Compound III was collected from 58 to 73 minutes (56 mg). The 19-mg fraction containing compound II was chromatographed again under these conditions: 10 percent TCEP on Chromosorb W; aluminum tubing, 6 m by 0.6 cm; column temperature, 100°C; detector temperature, 120°C; 40 cm³ of He per minute; retention time 75 to 80 minutes; 11 mg was collected. This step was repeated and 3.5 mg was collected. None of the other columns available separated compound II from the larger component. A final gas-liquid chromatography fractionation was carried out to remove TCEP contamination (column bleed): 8 percent carbowax 20 M on Chromosorb G; glass tubing, 0.9 m by 4 mm (inside diameter); column temperature, 120°C; detector temperature, 135°C; 40 cm³ of He per minute;

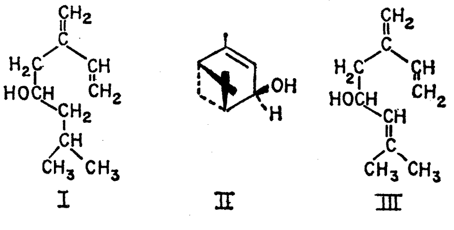

Fig. 1. Compounds I, (−)-2-methyl-6-methylene-7-octen-4-ol; II, (+)-*cis*-verbenol; and III, (+)-2-methyl-6-methylene-2,7-octadien-4-ol.