presents an obvious dilemma in view of our present knowledge of the Fe-Ni-P system and the origin and later history of the pallasite meteorites.

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References and Notes

1. E. Larsson, *Arkiv Kemi* **23**, 335 (1965).
2. S. Rundqvist, *Acta Chem. Scand.* **16**, 992 (1962); ——— and F. Jellinek, *ibid.* **13**, 425 (1959).
3. S. Rundqvist and E. Larsson, *ibid.*, p. 551.
4. First described at the 29th annual meeting of the Meteoritical Society [P. R Buseck, *Meteoritics* **3**, 104 (1967)].
5. Type material will be kept in the Nininger collection of the Center for Meteorite Studies at Arizona State University.
6. The mineral and its name has been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.
7. Slightly different values result if only the lines that belong uniquely to the new phase are used. As these lines are few in number, are very weak, and result in relatively large errors, the values of the cell edges that they yield are considered less accurate than those from the entire listed pattern.
8. M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill, New York, 1958).
9. V. F. Buchwald, *Acta Polytech. Scand.* **51**, 1 (1966); A. S. Doan, Jr., and J. I. Goldstein, *Proceedings of the International Symposium on Meteorite Research* (Reidel, Dordrecht, Netherlands, in press).
10. R. Vogel and H. Baur, *Arch. Eisenhuettenw.* **5**, 269 (1931).
11. Sponge Fe and red P (United Minerals & Chemicals Corporation) (both 99.999 percent pure) were used with Ni sponge (99.977 percent pure) (obtained from Dr. E. M. Wise of the International Nickel Company through the assistance of Dr. G. Kullerud).
12. P. R. Buseck and J. I. Goldstein, *Science* **159**, 300 (1968).
13. G. Kullerud, *Annu. Rep. Dir. Geophys. Lab. Carnegie Inst. Wash. Year B.* **62**, 175 (1963). Dr. Kullerud reports that as much as 3 to 4 percent Ni can occur in troilite coexisting with taenite at 800°C (personal communication).
14. P. R. Buseck and J. I. Goldstein, *Bull. Geol. Soc. Amer.*, in press.
15. American Society for Testing and Materials X-Ray Powder Data File Card No. 2-1143 for Fe_2P and No. 3-0953 for Ni_2P.
16. I thank Drs. H. Axon, V. Buchwald, J. Goldstein, and M. Hey for useful discussions. F. Wood and G. Scott helped in the laboratory and Dr. Goldstein calculated the microprobe corrections. The Ollague specimen came from the Nininger Meteorite Collection at Arizona State University. Part of the work was done at the NASA Goddard Space Flight Center. Supported by the Research Corporation, Arizona State University Grants Committee, and NSF grant No. GA-1200. Contribution No. 35 from the Center for Meteorite Studies, Arizona State University.

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Potassium Enrichments in Interstitial Waters of Recent Marine Sediments

Abstract. *Potassium enrichments in marine sediments have been reported which would imply a rate of diffusion of potassium into the oceans much larger than any of the know rates of addition or removal by other mechanisms. Experiments with mixtures of seawater and clay suggest that spurious enrichments can be produced if sediment samples are allowed to warm up before the pore water is expressed.*

Potassium ion concentrations in interstitial waters of marine sediments are reported to be enriched relative to the overlying seawater (*1–3*). Shishkina (*1*) summarized detailed analyses of 29 representative cores from the deep oceans and found that in the first half meter of sediment K^+ is enriched relative to Cl^- by 17 percent in red clays, 12 percent in calcareous (*Globigerina*) oozes, and 11 percent in diatom oozes. These sediment types characterize 38, 48, and 14 percent, respectively, of the area of pelagic ocean floor (*4*). One may thus infer a worldwide average potassium enrichment in the first half meter of sediment of about 14 percent.

An average potassium concentration gradient of roughly 0.56 percent per centimeter (taking the average depth of the first half meter as 25 centimeters) bespeaks a very considerable upward flux of potassium ion due to simple diffusion. A similar downward diffusion flux of chloride ion has been estimated by Shishkina (*5*) on the basis of chloride depletions she has found in Black Sea sediments. We have not measured diffusion rates of K^+ ion in mixtures of sediment and seawater, but related measurements have been made by others so that a reasonable estimate is possible. The following factors must be considered.

1) Diffusion coefficients of electrolytes (except H^+) in water at 25°C fall in the range 1 to 2×10^{-5} cm²/sec (*6*). The most mobile major ions in seawater are K^+ and Cl^-, having self-diffusion coefficients and a joint diffusion coefficient in 0.5*N* electrolyte solutions of about 1.8×10^{-5} cm²/sec, half again larger than the value for Na^+.

2) The obstructive effect of nonreactive sediment particles on diffusion rates will depend on size-sorting of sediments. With a well-washed fine sand Duursma (*7*) found a self-diffusion coefficient for Cl^- of 5.5×10^{-6} cm²/sec at 20°C, corresponding (*6*) to about 6.0×10^{-6} cm²/sec at 25°C, or exactly one-third of the diffusion rate in bulk solution. In sediments of mixed sizes the obstructive effect would be greater.

3) The cation exchange capacity of clay minerals in the sediment will, generally speaking, diminish the rates of transient diffusion of cations (*7*), slightly enhance the rates of steady-state diffusion of cations, and will not affect the rates of independent anion diffusion. During transient diffusion the cation exchange capacity will slow down cation spreading rates by buffering the composition changes even though the actual solution fluxes are undiminished. In steady-state diffusion, by contrast, there are no composition changes; there are only fluxes, and these may even be slightly augmented by the surface mobility of exchangeable cations bound on clay (*8*). We are dealing here with a case of steady-state diffusion in which the cation exchange effects are probably negligible.

Duursma (*7*) measured Cl^- tracer diffusion in a Mediterranean calcareous-clay sediment mixed with seawater and found a diffusion coefficient of 3.5 to 5.5×10^{-6} cm²/sec at 20°C. These measurements involved only the interdiffusion of Cl^- isotopes. Shishkina (*5*), on the other hand, measured the rate of spreading of sea salt from a high-salinity sediment core to a low-salinity core placed in contact with it and found a diffusion coefficient for Cl^- in Atlantic Ocean cores of 2.4 to 4.3×10^{-6} cm²/sec. The diffusion of Cl^- in her experiments, although independent of cation exchange, required the joint diffusion of seawater cations that are preponderantly slower than Cl^- (*6*).

The steady-state diffusion rate of K^+ in sediments, if mainly compensated by counterdiffusion of other slower cations, should be nearly equal to the spreading rate of Cl^- as measured by Shishkina. The diffusion of K^+ can be faster, approaching the rate of Cl^- tractor diffusion, if it is compensated instead by joint diffussion of Cl^-.

4) A steady-state diffusion rate at 2°C, a typical temperature at the ocean floor, will be roughly half what it would be in the laboratory at 25°C (*6*). The hydrostatic pressure at a typical depth of 3800 m increases ionic mobilities about 5 percent (*9*).

Taking all these factors into account, we estimate that the diffusion coefficient for K^+ in the top half meter of marine sediment is not less than 10^{-6} cm^2/sec. We assume that the K^+ diffusion flux from the ocean floor is a steady-state flux since the time required to set up a steady state in the first half meter should not be more than a few centuries.

Taking the diffusion coefficient (D) to be 10^{-6} cm^2/sec and multiplying by the concentration gradient ($\partial C/\partial Z$) of 0.56 percent per centimeter, we find the upward diffusion flux to be

$$K^+ \text{ flux} = -D\,\partial C/\partial Z = 0.56 \times 10^{-8}\,C_0 \text{ unit/cm}^{-2}\,\text{sec}^{-1}$$

where C_0 is the K^+ content, per cubic centimeter, of the overlying seawater in any convenient unit.

With an average ocean depth of 3800 m (*4*) the total seawater potassium overlying each square centimeter of sediment is $3.8 \times 10^5\,C_0$ unit/cm^2. The total "refill time" or "residence time" of potassium in the oceans, relative to the diffusion flux, may then be calculated as

$$\text{Refill time} = (\text{total } K^+)/(\text{input flux}) = 6.8 \times 10^{13} \text{ seconds}$$

At $\pi \times 10^7$ seconds per year the refill time is about 2.2 million years.

This is less than a fourth the residence time of 10 million years calculated (*10*) on the basis of the net flow of dissolved potassium into the oceans from the continents, corrected for atmospheric recycling. It is about a third the residence time of 6.7 million years calculated on the basis of gross flow of river-borne dissolved potassium into the oceans (*11*), and about a fifth of the residence time of 11 million years calculated on the basis of the removal of total potassium from the ocean by sedimentation (*12*). Evidently, the potassium input to the ocean by diffusion flux is five times the estimated rate of removal by sedimentation, and the combined input of dissolved potassium is more than six times the estimated rate of removal of all potassium, leaving out of account any input of detrital potassium of fluvial or volcanic origin. If one can take such budgets seriously, this one is seriously out of balance.

If this diffusion flux is real it must be the dominant mechanism of K^+ influx into the ocean. Moreover, if it is due to weathering of K feldspars (*2*, *13*) or volcanic detrital materials, it implies a complementary rate of potassium ion removal by some other mechanism, either working against the observed gradients or localized in as yet unobserved areas where the gradients are reversed. The removal of dissolved potassium is awkward to account for, even without the complication of a large diffusional influx (*14*). The level of potassium in the ocean would have to be largely determined by the competition between the diffusion input and the unknown removal process, a situation distinctly different from the chemical equilibrium model of Sillén (see *15*).

An alternative is that the potassium enrichments are produced by some kind of biological pumping (*14*). If so, the diffusion flux we calculate is a consequence of the biological process and a measure of it rather than an independent source of K^+.

We first suspected that the accepted method of squeezing sediment samples to express interstitial water might introduce artificial enrichments, but preliminary experiments did not support this. However, we did notice that temperature changes caused pronounced effects. Since the typical pelagic sediment sample originates at the ice-cold sea floor, is brought up through the warmer waters near the surface, and is ultimately squeezed in a still warmer laboratory, large and systematic temperature changes occur. These may cause composition changes in the pore water by shifting its ion exchange equilibrium with the sediment.

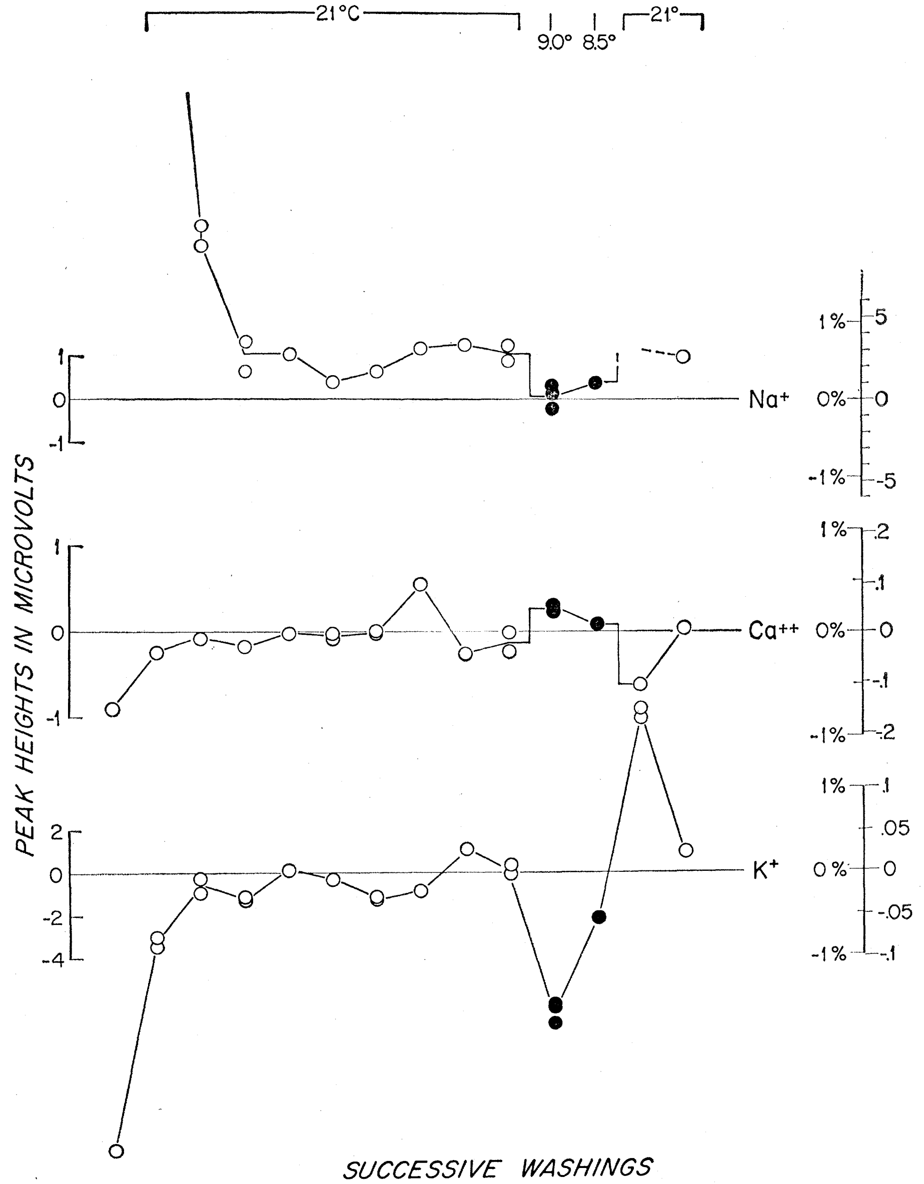

Fig. 1. Changes in Na^+, Ca^{++}, and K^+ difference peaks in seawater during successive washings of a 6.6 percent montmorillonite clay suspension. The peaks are calibrated in percentages and in milliequivalents per liter.

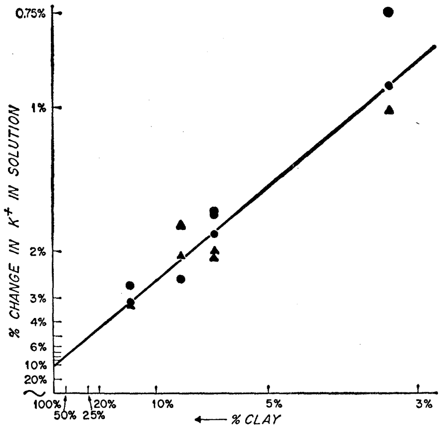

Fig. 2. Effect of 12°C temperature change on clay suspensions. The reciprocal of the percentage change in K^+ (ordinate) is plotted against the ratio of the weight of water to that of clay (abscissa). Circles represent results obtained on cooling; triangles, on warming.

In order to investigate this temperature effect we washed samples of montmorillonite clay (Wyoming bentonite, John C. Lane tract, Upton, Wyoming) repeatedly with Sargasso Sea surface water. After all the samples had been washed and centrifuged at least ten times over a period of 8 days, equilibrium between clay and seawater was deemed to have been reached at the 21°C temperature of our controlled-temperature room. We transferred the samples to a cold room at 9°C where they underwent two washings for which a refrigerated centrifuge was used. Two more washings at 21°C concluded the experiment. We analyzed the supernatant seawater from all washings for differences in cation composition by the method of difference chromatography described by Mangelsdorf (*16*) (Fig. 1).

During the preliminary washings Na^+ came off the clay into the water in successively smaller amounts, while K^+ was taken up. With successive washings the difference peaks tended to vanish as equilibrium with seawater was approached (*17*). When the washing temperature was changed from 21° to 9°C, potassium was taken up by the clay from the seawater. This depletion of K^+ in the seawater increased with the clay content of the mixture and amounted to about 3 percent in a 12.9 percent clay mixture. The percentage changes in Ca^{++} and Na^+ in the seawater were much less in all samples (*18*), with Na^+ going onto the clay slightly and Ca^{++} coming off. When the warmer washings at 21°C were resumed, all of these changes were reversed. The reversal was exact if allowance was made for the incomplete recovery of the samples from the prior cooling (*19*).

If the reciprocal of the percentage change in K^+ is plotted against the ratio of the weight of water to that of clay (Fig. 2), we obtain a plot that would give a straight line if we had an ideally simple binary system with a single exchange equilibrium constant that changed with temperature. The quality of our data here is such that a crude straight line fit is adequate even though our system is surely not that simple.

Extrapolating this line, we see that at 50 percent clay content, which might be typical of a marine sediment, we could expect an 8 percent potassium change for the same 12°C temperature change—the order of 1 percent enrichment for each 1½ degrees of temperature increase.

If marine clays behave similarly, at least part of the reported K^+ enrichments could be due to this effect. So far as we know, no investigator has measured the warming of cores before the pore water was expressed, although the importance of prompt squeezing has been emphasized (*20*). Significantly, one of the effects of delayed squeezing is reported to be additional K^+ enrichment (*20*).

Although marine clays may well behave differently from our montmorillonite samples, if the principal difference is one of total exchange capacity the actual effect should still be given by a point on the line in Fig. 2 corresponding to an equivalent montmorillonite content. There may also be differences in exchange characteristics of different clays. However, we found K^+ and Na^+ to be enriched while Ca^{++} and Mg^{++} were depleted. The percentage change was greatest for K^+, followed by Mg^{++}, Na^+, and Ca^{++} in that order. Since exactly these changes, in approximately this order (Ca^{++} depletions are sometimes large) have been reported by three sets of investigators (*1–3*), one is inclined to suspect a similar mechanism at work.

We do not mean to suggest that all cation composition changes so far observed in sediment pore waters are thermal artifacts. Some effects, including 30 percent K^+ enrichments we have found in sediment samples from Buzzards Bay (Massachusetts), are too large to be accounted for in this fashion. Nonetheless, the possible magnitude of thermal errors is such that any diffusion flux calculations, for potassium at least, are uncertain by an amount greater than all the other known fluxes into or out of the ocean. Until this uncertainty is cleared up, the K^+ budget of the ocean must remain in doubt. Apart from the question of enrichments and diffusion, our experiments also suggest that a significant minor part of the potassium uptake by clays entering the ocean occurs as they descend to depths from the warmer surface waters.

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References and Notes

1. O. V. Shishkina, *Geokhimiya* **6**, 564 (1964); English translation in *Geochem. Int.* **3**, 522 (1964).
2. R. Siever, K. C. Beck, R. A. Berner, *J. Geol.* **73**, 39 (1965).
3. R. R. Brooks, B. J. Presley, I. R. Kaplan, *Geochim. Cosmochim. Acta* **32**, 397 (1968).
4. H. U. Sverdrup, M. W. Johnson, R. H. Fleming, *The Oceans* (Prentice-Hall, Englewood Cliffs, N.J., 1942).
5. O. V. Shishkina, *Khim. Protsessy Moryakh Okeanakh Akad. Nauk SSSR* **1966**, 26 (1966); abstract in *Chem. Abstr.* **67**, 47060 (1967).
6. R. A. Robinson and R. H. Stokes, *Electrolyte Solutions* (Butterworths, London, ed. 2, 1959), Tables 11.1 and 11.7; appendices 6.1, 11.1, and 11.2.
7. E. K. Duursma, in *Disposal of Radioactive Wastes into Seas, Oceans and Surface Waters* (International Atomic Energy Agency, Vienna, 1966), pp. 355–371.
8. J. C. van Schaik, W. D. Kemper, S. R. Olsen, *Soil Sci. Soc. Amer. Proc.* **30**, 17 (1966); W. D. Kemper and J. C. van Schaik, *ibid.*, p. 534.
9. A. Bradshaw and K. E. Schleicher, *Deep-Sea Res.* **12**, 151 (1965).
10. T. F. W. Barth, *Geochim. Cosmochim. Acta* **23**, 1 (1961); *Theoretical Petrology* (Wiley, New York, ed. 2, 1962), part V.
11. F. T. Mackenzie and R. W. Garrels, *Amer. J. Sci.* **264**, 507 (1966).
12. E. D. Goldberg and G. O. S. Arrhenius, *Geochim. Cosmochim. Acta* **13**, 153 (1958); E. D. Goldberg, in *Chemical Oceanography*, J. P. Riley and G. Skirrow, Eds. (Academic Press, New York, 1965).
13. R. W. Rex and B. D. Martin, in *Clays and Clay Minerals: Proceedings of 14th Conference*, S. W. Bailey, Ed. (Pergamon Press, London, 1966), p. 235.
14. C. A. Weaver, *Geochim. Cosmochim. Acta* **31**, 2181 (1967).
15. L. G. Sillén, in *Oceanography*, M. Sears, Ed. (AAAS, Washington, D.C., 1961), p. 549; ———, in *Equilibrium Concepts in Natural Water Systems*, W. Stumm, Ed. (American Chemical Society, Washington, D.C., 1965).
16. P. C. Mangelsdorf, Jr., *Anal. Chem.* **38**, 1540 (1966). For the present work we used a column 8 cm long, 0.6 cm in diameter, of amberlite CG-120, type 3, cation exchange resin at a driving pressure of 100 lb/in². The samples and the reference seawater were diluted to a salinity of 27 per mille for the analysis. Each analysis required 4 ml of sample and took about 15 minutes.
17. The Na^+ peak maintained a significant residual value corresponding to about 1 percent enrichment. Since this effect was independent of the clay content and of the time interval

between washings (not shown), but was too large and too steady to be due to contamination, there is no immediate explanation.

18. Because of the 46 to 1 excess of Na^+ over K^+ in seawater, the barely perceptible percentage decrease in Na^+ corresponds to an actual Na^+ deficit several times larger than the K^+ deficit. This Na^+ must be made up mainly by Mg^{++}, which implies a percentage enrichment of Mg^{++} perhaps half as great as the K^+ depletion. Since the ion exchange with the clays occurs at constant total cation normality, and since our chromatographic process cancels out the effect of any evaporation, the Mg^{++} difference in milliequivalents per liter can be calculated directly as the negative sum of the Na^+, Ca^{++}, and K^+ differences.
19. To verify that the K^+ depletions and enrichments were real and not an artifact of the analysis, the seawater from the first cold washing of the 12.9 percent clay mixture and from the first warm subsequent washing were analyzed for us by Dr. Peter Brewer, using atomic absorption spectroscopy. By this technique the warm washing was found to have about 8 percent more K^+.
20. O. V. Shishkina, *Tr. Inst. Okeanol. Akad. Nauk SSSR* **17**, 148 (1956); English translation circulated by National Institute of Oceanography, Great Britain.
21. Supported by AEC contract AT(30-1)-3838. E.D.'s participation was supported by a summer studies grant from Swarthmore College. Publication No. 2248 from Woods Hole Oceanographic Institution.

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The Suboceanic Mantle

Abstract. *An independent determination of density in the suboceanic lithosphere gives 3.5 to 3.6 grams per cubic centimeter at a depth of about 100 kilometers. This high value implies the existence of an ecologitic facies. A mechanism is proposed in which eclogite fractionation from the underlying, partially molten asthenosphere plays a key role in the creation and the spreading of the rigid, lithospheric plate.*

The composition, state, and mechanical properties of the crust and mantle beneath the sea floor are highly pertinent to the mechanism of sea floor spreading and continental drift and are key to understanding the origin of basic and ultrabasic rocks. In this report I give the first independent determination of the density in a portion of the suboceanic upper mantle. Previously only relative densities could be inferred from lateral variations in gravity, or very approximate indications could be obtained by using seismic velocities and empirical or theoretical equations of state. The latter results were rough not only because of the uncertainty in the seismic velocity distribution below the very top of the mantle but also because of the dependency of the equation of state on composition and temperature.

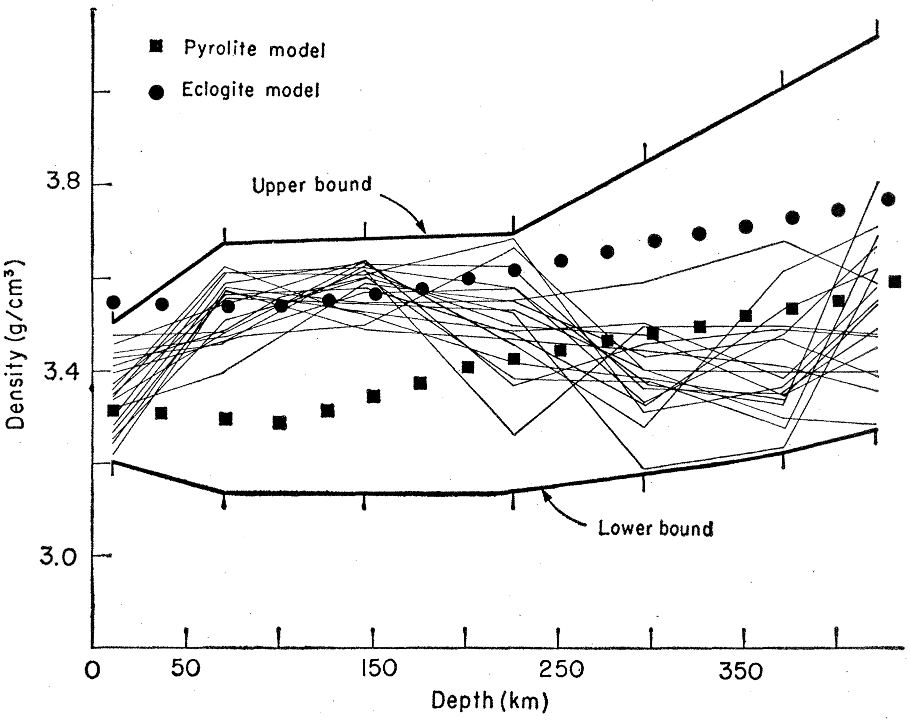

Fig. 1. Successful density models for the suboceanic upper mantle. Bounds define range permitted in Monte Carlo selection. Points show density values according to Clark and Ringwood (*10*) for pyrolite and eclogite mantles.

The following geophysical data have been inverted to obtain density and shear velocity models representative of a section from the sea surface to the center of the earth: spheroidal oscillations of the earth $_0S_0$, $_0S_2$ through $_0S_{22}$, $_1S_2$, $_1S_3$, $_1S_5$, $_1S_6$, $_1S_8$, $_1S_{12}$, $_2S_4$, $_2S_6$, $_2S_{10}$; toroidal oscillations (*1*) $_0T_3$ to $_0T_{21}$; Rayleigh wave phase velocities (*2*) for predominantly oceanic paths, in the period range 125 to 325 seconds; Love wave phase velocity for oceanic paths (*3*), period range 80 to 340 seconds; shear velocity distribution in the lower mantle restricted to a narrow range below 800 km determined from apparent shear wave velocities at the Large Aperture Seismic Array in Montana and concomitant shear wave travel times in the range 30° to 100° (*4*); a fixed compressional wave velocity distribution (*5*); mass and moment of inertia of the earth (*6*). The uncertainty in the eigenperiod and dispersion data was taken to be ± 0.4 percent, which should allow for asphericity and experimental errors (*7*); the shear wave travel times were required to fit to within ± 5 seconds, which represents the scatter in the observations.

The surface wave data derived from oceanic paths primarily provide the resolving power for the structure of the upper mantle under the oceans. These data merge smoothly into the eigenperiod data at a long period, as would be expected if gross lateral variations do not persist below the asthenosphere. The shear wave data primarily constrain the mantle below 800 km. Although the emphasis in this report is on the upper mantle, all of the data must be used to obtain self-consistent models and absolute rather than relative values of upper-mantle density. This procedure allows us to use nearly homogeneous data where most needed, that is, in deducing the structure of the suboceanic upper mantle.

A Monte Carlo procedure was used to find earth models consistent with the preceding data. In comparison with that reported previously (*8*) the program can find a larger number of successful models from among the millions of randomly generated models. The successful models fit a more extensive