have been proposed in the past to account for the removal of magnesium from seawater (*10*) should be sensitive to ambient *p*H or SiO_2 activity, or both, and independent of the oxidation-reduction state of the sediment. The reaction represented by Eq. 2, however, is controlled by the metabolic, or conceivably inorganic, reduction of sulfate, which should be independent of silica activity and should not be affected by *p*H, although the reaction itself may change the *p*H in the sediment.

There are several ways of estimating the possible quantitative significance of this reaction for the removal of magnesium from the oceans. If half of the river input of sulfate is removed as sulfide according to Eq. 2, then 26 percent of the river input of magnesium will be fixed by this reaction [data from (*11*)]. Alternatively, we can calculate a mean magnesium uptake for sediments in anoxic conditions from the data in Fig. 1. If all the clay brought down the rivers encountered anoxic conditions before final burial, then this reaction would account for approximately 50 percent of the river input of magnesium. The importance of the reaction will thus depend on the extent to which anoxic conditions occur within the top few meters of terrigenous sediments, and on the relative rates of deposition of oxidizing and anoxic sediments. Other mechanisms by which magnesium is removed from the oceans are initial ion exchange, substitution in calcium carbonate, and reactions of interstitial water at depth. Overall, it appears that there is no single dominant process responsible for the removal of magnesium from the oceans, and that the reaction described here is quantitatively significant.

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Overtones of Free Oscillations and the Structure of the Earth's Interior

Abstract. *Identification of 82 percent of all possible spheroidal overtones with periods greater than 300 seconds increases the resolving power of the set of gross earth data. Results of inversion indicate a change of composition in the deepest 500 kilometers of the mantle. The assumption that the inner core is rigid is required to satisfy simultaneously the data on free oscillations and travel times.*

It has been clear for some time that only observations of the overtones of free oscillations of the earth will permit determination of the radial distribution of density in sufficient detail to provide an independent and meaningful estimate of the composition of the deep interior of the earth. Most published inversion attempts have been based primarily on observations of the fundamental modes. The diversity of the models which satisfy the travel times and fundamental mode data represents in itself a proof of the insufficiency of the constraints provided by this limited set of data.

The purpose of the work reported here was to delineate overtones having periods greater than 250 to 300 seconds. The observational material consists of 84 digitized records of seismograms from stations belonging to the World Wide Standard Seismograph Network. These represent recordings of the Alaskan earthquake of 28 March 1964 (52 vertical and 32 horizontal components). For some of the stations the seismograms were digitized for four consecutive days.

In addition to a rough estimate of the period for a particular overtone predicted by a "reasonable" earth model, I have used the following methods in the process of identification: (i) comparison of the observed ratio of amplitudes for horizontal and vertical components with that calculated for the starting model (*1*); (ii) comparison of the observed attenuation with that predicted by the partition of the elastic energy into compressional and shear parts (*2*); (iii) comparison of the average periods of the fundamental mode data as determined by spectral analysis with the values obtained from measurements in which the traveling wave method was used [unusually large differences between the two sets of values are indicative of the presence of overtones (*3*)]; and (iv) comparison of the observed but unidentified periods with those predicted by a model which satisfies data determined by the first three methods.

As a result of this analysis, the following modes have been identified (*4*) and used in the inversion: radial modes from ${}_1S_0$ to ${}_3S_0$; first spheroidal overtone, modes from ${}_1S_2$ to ${}_1S_{11}$ and from ${}_1S_{14}$ to ${}_1S_{17}$; second spheroidal overtone, modes from ${}_2S_1$ to ${}_2S_{15}$; third spheroidal overtone, modes from ${}_3S_2$ to ${}_3S_{12}$; fourth spheroidal overtone, modes from ${}_4S_1$ to ${}_4S_{10}$; first torsional overtone, modes from ${}_1T_2$ to ${}_1T_4$, ${}_1T_6$, and ${}_1T_8$; and second torsional overtone, modes ${}_2T_4$, ${}_2T_7$, and ${}_2T_8$. In addition, determinations were made for two high *Q* modes, ${}_6S_1$ and ${}_7S_2$ (*5*). The data used for the inversion also include the following selected periods and group velocities for the fundamental modes: 17 periods for modes between ${}_0S_2$ and ${}_0S_{50}$, ten group velocity values over a range from ${}_0S_9$ to ${}_0S_{47}$, 14 periods for modes between ${}_0T_3$ and ${}_0T_{46}$, and seven group velocity values over the range from ${}_0T_{17}$ to ${}_0T_{46}$ (*6*). The inversion method used has been described by Dziewonski (*7*) and has been modified to include constraints on the travel times of seismic waves ScS at 0°, PcP at 0°, and PKIKP at 180°. The oceanic model O1 (*7*) with a rigidity added to the inner core (shear velocity $V_S = 3.5$ km/sec) was used as a starting model.

The final models UTD124A and UTD124B (hereafter referred to, respectively, as models A and B) are the result of three iterations and are shown in Fig. 1 (*8*), where they are compared with model HB1 of Haddon and Bullen (*9*), model 5.08M of Kanamori and Press (*10*), and the band of Monte Carlo solutions of Press (*11*). Both models A and B satisfy the travel time data within the limits of uncertainty of the observations. The same is true with respect to the change in the travel time with respect to the distance ($dT/d\Delta$) produced by the 2400-km discontinuity in model B. The data of Hales and Herrin (*12*) indicate the possibility of a discontinuity or a rapid change of the velocity gradient at this depth range.

The upper mantle, according to models A and B, is very simple and consistent with the set of averaging lengths proposed by Dziewonski (*7*); introduction of all the data for the higher modes did not cause any essential changes. The shear velocity solution shows a characteristic flattening between 700 and 900 km, and its trend and value (6.25 km/sec) are very similar to those of model SLUTD2 of Hales and Roberts (*13*).

The shear velocity distribution between 900 and 2889 km is practically identical with that found by Hales and Roberts. The derivative of the density gradient with respect to the bulk sound velocity gradient ($d\rho/dC = 0.43$ g cm^{-3} km^{-1} sec) is constant in the lower mantle and is very close to the empirical value of 0.424 of Wang (*14*) for rocks with a mean atomic weight of 21.0. The density distribution for model A shows systematic differences from models HB1 and 5.08M in the lower mantle. A particularly large difference is observed for model 5.08M (−4 percent) at the base of the mantle. All models are practically within the band of solutions of Press (*11*). Lower shear velocities of models A and B in a depth range from 480 to 650 km represent the only significant exception (*15*).

The outer core in models A and B is very similar to that in model HB1 if the short-wavelength velocity variation near the inner core is smoothed out in the latter model. The present set of data includes a number of overtones that are sensitive to changes in the compressional velocity V_P and in the density ρ in the core. The results presented here thus support the validity of the assumption of the chemical homogeneity in the outer core.

The essential difference between models A and B is the presence of a discontinuity at a depth of 2400 km. This depth corresponds to a rather abrupt change of $dT/d\Delta$ for both P and S waves (*12*). The resolving power of the free oscillation data is insufficient to permit one to determine the density gradient directly. It was chosen to be ⅓ of the compressional velocity gradient on the basis of the relationship of Birch (*16*). If the inversion procedure is designed such that a change of gradient rather than an offset is permitted at a depth of 2400 km, the result shows an increase in the density gradient. Since measurements of $dT/d\Delta$ show a decrease of the velocity gradients in this region, model B is preferred. It is conceivable, however, that a gradual change in chemical composition may take place in the lowermost mantle.

Introduction of a more complicated model is justified only if such a model shows a significantly better agreement with the observations than the simple models. Table 1 (*17*) shows the root-mean-square errors of relative differences (expressed in percents) between computed and observed periods for each overtone for several models of interest. In addition to the models already discussed, Table 1 includes values for the Gutenberg-Bullen A′ (G-BA′) model, which is often used as a reference model. Model B shows a 30 percent smaller overall root-mean-square error than model A, and the improvement is considerably greater for the second, third, and fourth overtones than for the fundamental and first overtones. This result should be expected, since the 2400-km discontinuity in model B is a short-wavelength feature and can easily be averaged out by overtones with a low radial order number. Similar observations can be made with respect to models HB1 and 5.08M. Model HB1 is in good agreement with the fundamental modes and the first two spheroidal overtones, but its agreement with the third and fourth spheroidal and both torsional overtones is poor. For model 5.08M a satisfactory agreement is achieved only for the fundamental modes and first spheroidal overtone. The match for model G-BA′ is uniformly poor.

Table 1. Standard deviations of relative differences between computed and observed free oscillation periods (*17*). S.D., standard deviation; D_{max}, maximum deviation.

Overtone	Number of observations	Model: A			B			HB1			5.08M			G-BA′		
		S.D. (%)	D_{max} (%)	D_{max} At	S.D. (%)	D_{max} (%)	D_{max} At	S.D. (%)	D_{max} (%)	D_{max} At	S.D. (%)	D_{max} (%)	D_{max} At	S.D. (%)	D_{max} (%)	D_{max} At
Radial modes	4	0.14	−0.24	${}_2S_0$	0.10	−0.15	${}_2S_0$	1.20	−1.60	${}_3S_0$	1.16	−1.82	${}_2S_0$	1.72	−2.38	${}_3S_0$
Fund. spher.	17	.05	−.15	${}_0S_4$	.05	−.13	${}_0S_4$	0.09	−0.19	${}_0S_2$	0.17	−0.44	${}_0S_2$	0.52	−0.73	${}_0S_2$
First spher.	13	.09	−.17	${}_1S_{16}$	.08	−.13	${}_1S_7$	.12	−.19	${}_1S_5$	.11	−.17	${}_1S_8$	1.04	−1.81	${}_1S_{14}$
Second spher.	14	.10	.24	${}_2S_3$	.06	.15	${}_2S_3$	.08	.19	${}_2S_1$	.20	.46	${}_2S_4$	0.78	−1.85	${}_2S_{15}$
Third spher.	9	.12	.25	${}_3S_7$	.09	.17	${}_3S_7$	.32	−.51	${}_3S_5$	.39	.62	${}_3S_7$	.21	−0.40	${}_3S_{12}$
Fourth spher.	9	.13	−.28	${}_4S_2$	.05	.09	${}_4S_3$	.36	−.73	${}_4S_{10}$	.33	.49	${}_4S_8$	.55	−1.61	${}_4S_1$
Fund. tors.	7	.12	−.22	${}_0T_3$	.09	−.16	${}_0T_3$	.12	−.23	${}_0T_3$	.09	−.17	${}_0T_3$	.37	−0.70	${}_0T_3$
First tors.	5	.09	−.18	${}_1T_3$	.10	.15	${}_1T_6$	.31	−.42	${}_1T_3$	.41	−.62	${}_1T_3$	.43	−.56	${}_1T_8$
Second tors.	3	.15	−.25	${}_2T_4$	.15	.19	${}_2T_8$	.78	−1.00	${}_2T_4$	.28	−.29	${}_2T_7$	.94	−1.08	${}_2T_4$
All data	81	.10	−.28	${}_4S_2$	.07	.19	${}_2T_8$	.34	−1.60	${}_3S_0$	.35	−1.82	${}_2S_0$	.78	−2.38	${}_3S_0$

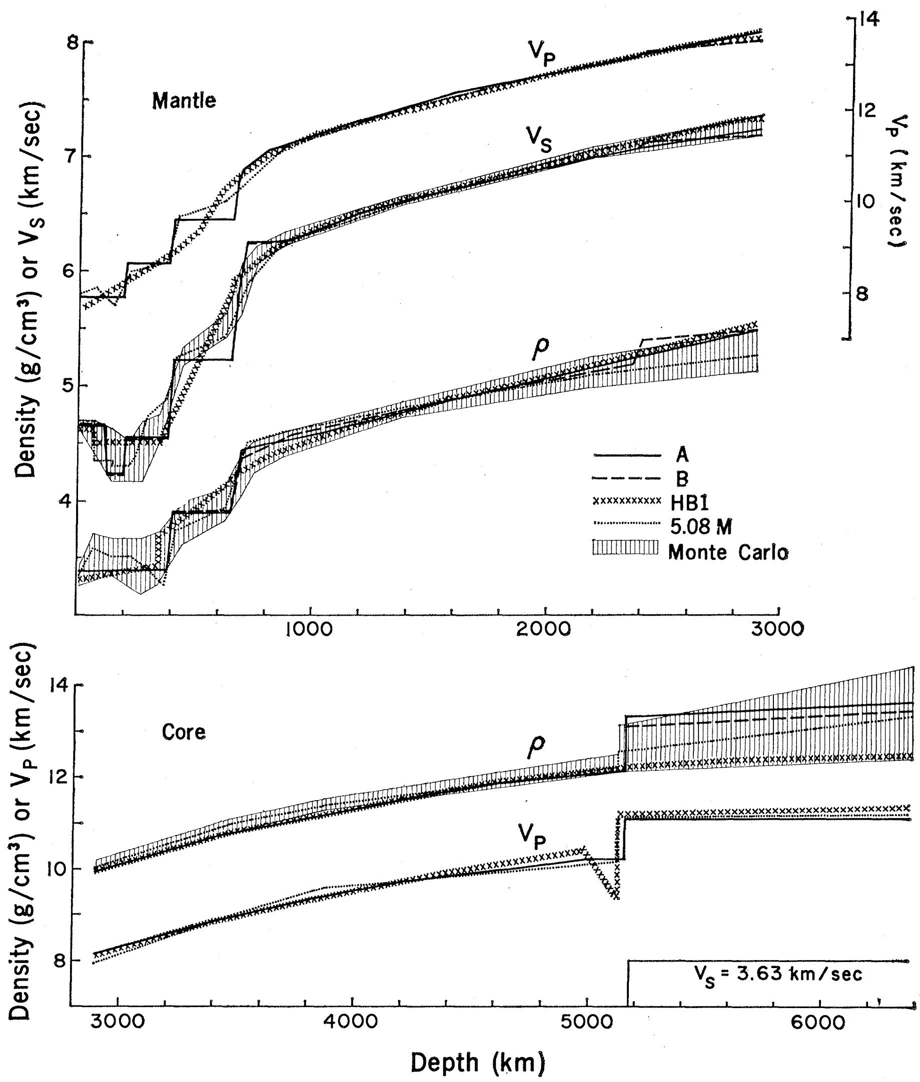

Fig. 1. Comparison of models A and B with models HB1 (*9*), 5.08M (*10*), and the band of Monte Carlo solutions for oceanic structure (*11*).

The largest differences are observed for the radial modes. This results from the fact that models G-BA′, HB1, and 5.08M have a liquid inner core. Introduction of a rigid inner core with a shear velocity of 3.5 km/sec increases the period of ${}_3S_0$ by about 1.5 percent. The difference is also significant for ${}_0S_0$ and amounts to 0.3 percent. A number of periods of higher spheroidal modes of low longitudinal order number also appreciably change with the introduction of a rigid inner core. It would be impossible to satisfy the set of data described here with a model containing a liquid inner core without violating the travel time constraints.

The results of inversion show that the new information on higher modes can be explained with an average error of 0.1 percent by a simple model (model A) which conforms to the generally accepted concepts of the structure of the earth's interior. However, some of the residuals are at this stage considerably greater than the estimated accuracy of the measurements. Model B matches the data with an average error of 0.07 percent (maximum error, 0.19 percent) and includes an additional discontinuity. It appears, however, that the precision of the data would justify a further search; it may be that some relocation or modification of the 650-km discontinuity could result in the desired improvement.

The compositional change at 2400 km indicated by model B may bear a relation to the observations of Alexander and Phinney (*18*) and Doell and Cox (*19*), who concluded that the lowermost mantle is laterally inhomogeneous.

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