he mapped, which he was at pains to define and distinguish as formations, without any thought as to their origin and subsequent history. And he was smart. There is nothing inherently wrong with Werner's major division of the rocks that make up the visible crust. On the other hand it is one of the axioms learned sooner or later by every serious beginner in geology that almost all of Werner's ideas about the origin and structure of these rocks were gorgeously wrong. I cherish more than a hunch that before 1809 Maclure realized the probable validity of this now proverbial dictum, and I have been pleased recently to see that White (*7*) has found basis in later evidence for a similar conclusion.

Why, then, did Maclure not either say so, or offer a few ideas of his own? Here we may only speculate, but let us remember that (i) geology was yet in its infancy and (ii) the power of Werner's word, propagated by men who had been virtually hypnotized by this unquestionably marvelous genius of a teacher, was something we today may find hard to understand or appreciate. At all events put me down in Maclure's corner.

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Magnesium-Iron Replacement in Clay Minerals in Anoxic Marine Sediments

Abstract. *In anoxic marine sediments iron is extracted from clay minerals to form a sulfide. Magnesium from the surrounding solution then replaces the extracted iron in the clay mineral structure. This process removes magnesium from seawater and serves as a control on the composition of interstitial waters in sediments.*

The residence time of dissolved magnesium in seawater is short as compared with the age of the oceans (*1*). Hence, over geological time, magnesium must be removed from seawater at approximately the same rate as it is supplied to the ocean by rivers. Apart from atmospheric recycling, the removal process must consist of the incorporation of magnesium into the solid phases of sediments. I propose here that a reaction of the type

$$2\,\mathrm{Fe}_{(\mathrm{clay})} + 3\,\mathrm{Mg}_{(\mathrm{soln})} + 4\,[\mathrm{S}] = 3\,\mathrm{Mg}_{(\mathrm{clay})} + 2\,\mathrm{FeS}_{2(\mathrm{pyrite})} \quad (1)$$

occurs in anoxic marine sediments. In Eq. 1 [S] represents some form of reduced sulfur or sulfide ion derived from the metabolic reduction of seawater sulfate, and $\mathrm{Fe}_{(\mathrm{clay})}$ represents ferric iron at a site at which no exchange of cations may occur in a clay mineral. Ferric iron is used in this discussion rather than ferrous iron, as the ferric form is more abundant in marine sediments; a similar equation could be written for ferrous iron. Both ferrous and ferric oxides and silicates are unstable with respect to pyrite in anaerobic marine sediments (*2*). An example of this type of reaction would be the conversion of the nontronite component in a montmorillonite to a saponite component:

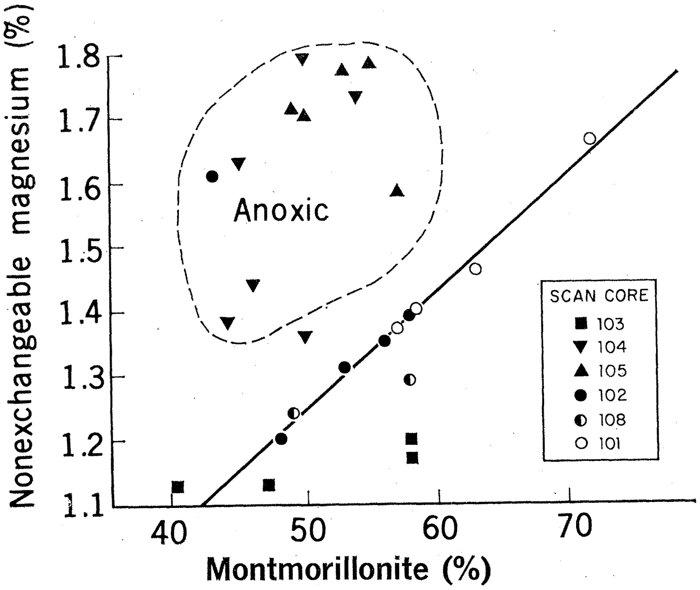
$$\begin{aligned}&(\mathrm{X})_{0.66}\mathrm{Fe}_4^{3+}\mathrm{Al}_{0.66}\mathrm{Si}_{7.34}\mathrm{O}_{20}(\mathrm{OH})_4 + \\ &\quad 6\,\mathrm{Mg}^{2+} + 8\,\mathrm{SO}_4^{2-} + 15\,[\mathrm{C}] + 13\,\mathrm{H_2O} = \\ &\qquad (\mathrm{X})_{0.66}\mathrm{Mg}_6\mathrm{Al}_{0.66}\mathrm{Si}_{7.34}\mathrm{O}_{20}(\mathrm{OH})_4 \\ &\qquad + 4\,\mathrm{FeS_2} + 15\,\mathrm{HCO_3^-} + 11\,\mathrm{H}^+ \quad (2)\end{aligned}$$

In Eq. 2 (X) represents exchangeable cations and [C] represents reduced carbon. Similar reactions could be written for iron-containing chlorites and illites. The net effect on the clay is to change its chemical composition without markedly changing its mineralogy, as determined by x-ray diffraction.

The processes of sulfate reduction and pyrite formation have been well described in the past (*3, 4*). No detailed study has been made, however, of the source of iron for pyrite formation. Berner (*5*) stated that the reduction process could be responsible for the extraction of iron from a range of silicate minerals, but he did not investigate resulting changes in the silicates.

In Recent marine sediments from Banderas Bay, Mexico (*6*), the amount of nonexchangeable magnesium (*7*) is higher in clays from sulfide-rich environments than in clays from less strongly reducing environments. The clay fraction (< 2 μm in equivalent spherical diameter) of these sediments consists of montmorillonite, kaolinite, and illite. There are no systematic differences in mineralogy between the clay fractions of the oxidizing and reducing sediments. The differences in the magnesium content cannot be explained on the basis of differences in the percentage of montmorillonite, the principal magnesium-containing phase (Fig. 1). The behavior of calcium indicates that the magnesium distribution cannot be explained on the basis of the formation of a carbonate phase. In interstitial water squeezed from the reducing sediments, magnesium was depleted relative to the overlying seawater, but the bulk of the magnesium taken up by the sediment must be provided by the diffusion of magnesium into the sediment from overlying seawater. Pyrite is present in the silt fraction (> 2 μm) of the reducing sediments. It appears that when iron is removed from the clay fraction of the sediment to form a sulfide in the silt fraction, a corresponding amount of magnesium enters the clay fraction from the surrounding solution (Fig. 2). Part of the scatter in Fig. 2 is caused by differences in the mineralogy of the sediments. The reaction shown in Eq. 2 should cause a lowering in the *p*H or a dissolution of calcium carbonate, or both. The *p*H is lowered (to 7.0 to 7.5) in both oxidizing and anoxic sediments, presumably by carbon dioxide from the oxidation of organic matter. Calcium carbonate is precipitated in the anoxic sediments, however, which suggests that Eq. 2 is an oversimplification of the process of metabolic sulfate reduction. Berner (*8*) has shown that the decomposition of organic matter in sediments can cause the pH of the sediment to increase or decrease, a particular control being the nitrogen content of the organic matter.

Analyses of the interstitial water from legs IV and V of the Deep Sea Drilling Project (*9*) show a marked covariance of magnesium and sulfate (Fig. 3). Extensive magnesium depletion occurs almost exclusively in reducing terrigenous sediments. Some of the magnesium depletion can be explained on the basis of dolomite formation, but most of the samples in which dolomite was reported appear to be departures from the trend predicted in Eq. 2. Presumably the formation of dolomite in the sediments with low interstitial sulfate is a consequence of increased carbonate alkalinity generated by sulfate reduction (*4*), causing increased dolomite supersaturation in the interstitial water. Here, as in the Banderas Bay sediments, magnesium depletion is related to sulfate reduction rather than to pH or SiO_2 concentration. Diagenetic reactions that



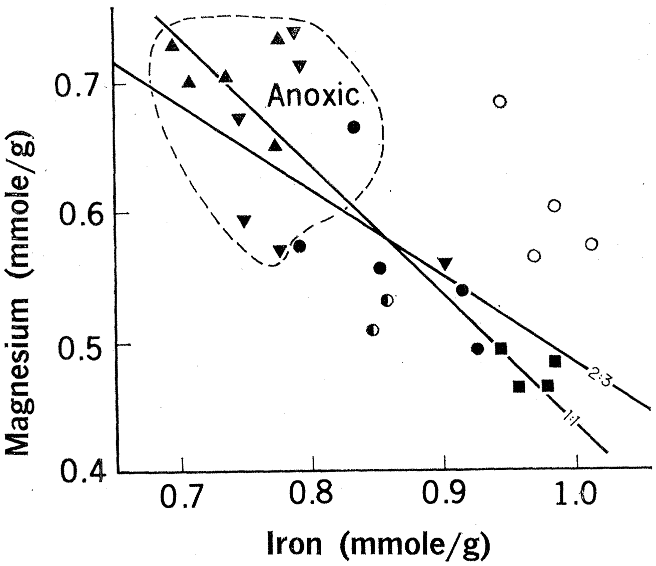


Fig. 1 (above left). Nonexchangeable magnesium content (percent by weight) of the clay fraction of Recent sediments from Banderas Bay, Mexico, plotted against montmorillonite content measured by x-ray diffraction. Each symbol represents a different core. The straight line is the predicted value on the assumption that all variation in magnesium content is due to variation in the montmorillonite content.

Fig. 2 (above right). Content of iron and nonexchangeable magnesium in the clay fraction of sediments from Banderas Bay. The symbols are the same as those used in Fig. 1.

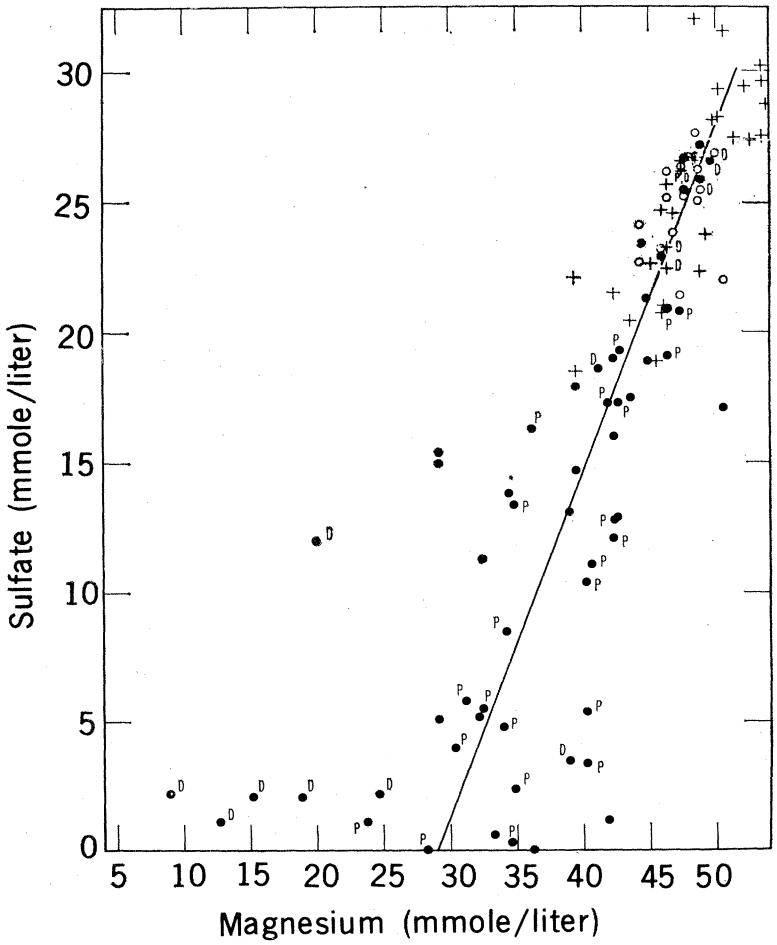


Fig. 3 (right). Magnesium and sulfate content of interstitial waters from legs IV and V of the Deep Sea Drilling Project cores; *D*, dolomite reported in the sediment; *P*, pyrite reported in the sediment. (Crosses) Biogenic ooze; (open circles) red and brown clay; (solid circles) green and gray clay and silt. The straight line is the gradient predicted on the basis of Eq. 2.

have been proposed in the past to account for the removal of magnesium from seawater (*10*) should be sensitive to ambient pH 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 pH, although the reaction itself may change the pH 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