report, burial and growth rates of nodules from a single location are required. Nevertheless, the promising first results have a number of implications for theories of nodule formation:

1) The process that keeps nodules at the sea floor (that is, that determine B) is independent of nodule size for $D > D_0$. The mechanism is not yet known, although displacement by benthic organisms (*8, 9*) and exhumation and downslope migration (*10*) on slopes or in areas of erosion are now favored.

2) The approximate residence time of nodules on the sea floor prior to burial ranges from about 300,000 years at BC-2 to 1 million years at FFG-017.

3) Claims of very rapid nodule growth (*11*) are not consistent with size and burial rate data.

4) The absence of nodules smaller than D_0 (usually 3 to 6 mm) implies that the mechanism that keeps nodules from being buried cannot distinguish these small particles from the associated sediments. Since we do not know the mechanism, however, it seems pointless to speculate about the factors that determine D_0 and its variation from sample to sample. Also, the lack of small nodules suggests that nuclei (clay lumps, rock chips, fish teeth and other skeletal remains, and fragments of older nodules) are essential for the initiation of nodule growth.

5) Locations with populations of nodules of a single size must either be effectively nondepositional (*12*) (in which case, $B = 0$), or they must lack a mechanism for continuously forming new nodules, in which case the number of nodules must decrease exponentially with time (the density of nodule coverage should be negatively correlated with nodule size). These alternatives, as well as the basic assumptions of the model, can be tested by an appropriately designed program to sample nodules and associated sediments.

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Magnesium Interaction with the Surface of Calcite in Seawater

Abstract. *Magnesian calcite overgrowth containing 4 (± 2) mole percent magnesium carbonate forms on calcite exposed to natural seawater near the ocean surface. This magnesian calcite is approximately 30 percent less soluble in seawater than pure calcite. The formation of the magnesian calcite of reduced solubility may have a major influence on calcite accumulation in deep sea sediments.*

Recently determined values for the apparent solubility of calcite in seawater (*1-3*) are approximately 30 percent less than the value for pure calcite predicted from thermodynamic considerations (*3*). A possible explanation for this discrepancy is that a layer of magnesian calcite, of greater stability than pure calcite, forms at the seawater-calcite interface. It has been predicted (*4, 5*) that a magnesian calcite containing 2 to 7 mole percent $MgCO_3$ would be more stable than pure calcite in seawater. The Mg content of magnesian calcite overgrowths on calcite from seawater, at supersaturations significantly higher than normally found in the marine environment, has been quite variable and always higher than predicted for minimum solubility [see (*6*) for summary]. These findings have led to considerable controversy over the relative influences of thermodynamic and kinetic factors in determining the composition and stability of magnesian calcites in the marine environment (*6-9*).

To help resolve these problems we have produced magnesian calcite overgrowths on Iceland spar calcite rhombs from natural seawater at a saturation state, with respect to calcite, typical of near-surface seawater. Carefully cleaved rhombs of Iceland spar calcite, approximately 0.5 cm in diameter and containing less than 1 mole percent $MgCO_3$, were soaked in double-distilled water to relieve any surface strain associated with cleaving. Individual rhombs were then soaked in Gulf Stream surface seawater that had been diluted to 35 per mil salinity and equilibrated with air. A large solution to solid ratio (10,000 to 1 by weight) was used to ensure near constancy of the solution composition. The ratio of the $CaCO_3$ total ion molal product to the apparent solubility product of calcite in seawater was 5.1 (*3*). After they were soaked in the seawater for 3 days and for 7 days the calcite rhombs were removed from the seawater and either air-dried or immersed in distilled water for approximately 5 seconds to remove any adhering seawater and then air-dried. The composition of the surface and growth layers was determined by scanning Auger spectroscopy.

The Auger analysis was conducted with a Physical Electronics Industries scanning Auger microscope, model 545. The depth profile of the relative atomic concentration ratio of Mg and Ca was obtained by sputter removal of surface layers from the sample with a 2-kV argon ion beam. A quantitative determination of the relative atomic concentrations of Mg and Ca was obtained by comparison of both the Mg and Ca peak-to-peak amplitudes to the peak-to-peak amplitude of a silver standard. Appropriate relative sensitivity and scale factors were then used to determine the Mg/Ca concentration ratio (*10*). The total error in the relative atomic concentration of Mg and Ca is estimated to be less than 25 percent.

The results of these experiments are presented in Fig. 1. The Mg/Ca ratio on the surface of the calcite sample, which was not washed in distilled water, was approximately 0.24. A lower concentra-

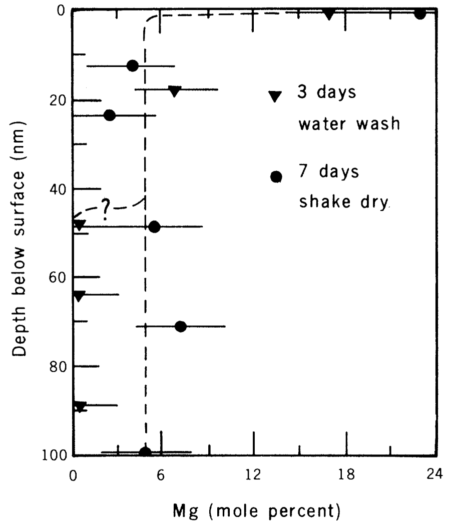

Fig. 1. Mole percentage of Mg present as $MgCO_3$ as a function of depth below the solid-solution interface based on scanning Auger spectroscopy. Error bars are based on estimated analytical precision. Note that in the sample exposed to seawater for 3 days the depth profiling reached the Iceland spar calcite. The dashed line with question mark indicates the approximate depth of the pure calcite crystal-magnesian calcite overgrowth boundary.

tion of adsorbed Mg is possible because Mg associated with sea salt left by evaporation may also contribute to the observed concentration. This Mg concentration is in good agreement with the value predicted by Cooke (*11*) who used high-pressure techniques, but is less than found in cation exchange experiments (*12, 13*). It is possible that the lower surface Mg concentrations found by Cooke as well as in these experiments are only representative of a strongly adsorbed fraction of the exchangeable Mg. Below this surface layer, the composition of the growth layer is constant to within the estimated analytical precision. The average composition of the growth layer is 4 (± 2) mole percent $MgCO_3$. In the sample that was exposed to the seawater for 3 days, the sputter removal penetrated completely through the growth layer to the Iceland spar calcite, whereas in the sample exposed for 7 days, only partial penetration through the growth layer was achieved.

The concentration of the Mg in the growth layer is in excellent agreement with that predicted for the magnesian calcite of minimum solubility in seawater (*4, 5*). These results lend support to the concept that the Mg content of calcite precipitating in seawater is kinetically controlled, and that as the rate of precipitation decreases a more stable magnesian calcite is formed (*4, 8*). The fact that no major variation in the Mg content was found within the growth layer indicates that the composition of the solution is probably more important in determining the Mg content of the growth layer than the composition of the calcite on which the deposition is occurring.

The distribution of Mg in the calcite-surface seawater interface, on the basis of results presented here and in previous studies (*11-13*), is presented in Fig. 2. If the formation of such an interface determines the apparent solubility of calcite in seawater, then serious difficulties exist in modeling the accumulation of low magnesium biogenic calcite (less than 1 mole percent $MgCO_3$) in deep-sea sediments, because the bulk solid may have a solubililty approximately 30 percent greater than that of the magnesian calcite surface phase. It is quite possible that some biogenic calcite may be transported to deep water either in fecal pellets or with organic coatings, which could prevent the formation of the more stable surface coating. These particles would be expected to start to undergo dissolution at depths where the water becomes undersaturated with respect to pure calcite but is still supersaturated based on apparent solubility constant measurements if the formation of an Mg-calcite overgrowth is slow relative to dissolution. Other biogenic calcite particles that settle through surface waters may form a less soluble coating of magnesian calcite that will not undergo dissolution until greater depths are reached where the apparent solubility is exceeded. This hypothesis is reinforced by the observation that definite dissolution of pelagic foraminifera occurs above the apparent saturation level for calcite (*3*). However, this observation does not constitute proof of our hypothesis because the oxidation of organic matter in the sediments can also contribute to dissolution.

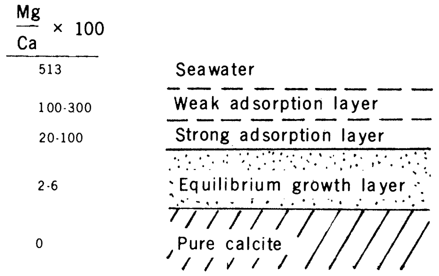

Fig. 2. Schematic representation of the calcite-surface seawater interface and estimated Mg/Ca ratios.

The rate of $CaCO_3$ precipitation determined from the thickness of the overgrowth on the calcite exposed to seawater for 3 days is 1.2 (± 0.3) mg/cm^2-year. The minimum precipitation rate on the calcite exposed to seawater for 7 days is 1.4 mg/cm^2- year. These precipitation rates are approximately 50 times slower than the $CaCO_3$ precipitation rate on synthetic calcite powder that we determined by the *p*H-stat method (*4*), using the same seawater and saturation state. A possible explanation for the major difference in precipitation rates is that the surface area of calcite per unit volume of solution was approximately 10^4 times greater in the *p*H-stat experiments than in the single rhomb experiments. Adsorption of inhibitors (organic or inorganic), which are present in the natural seawater at low concentrations, may be responsible for the lower rate of calcite precipitation observed in the single rhomb experiments. It is possible that the concentration of the inhibitors on the calcite surfaces in the *p*H-stat experiments was significantly lower than on the calcite rhomb surfaces because of the much higher calcite surface area to solution volume ratio in the *p*H-stat experiment. If the Mg concentration in calcite overgrowths is kinetically controlled (*4, 8*), then adsorption of inhibitors as well as the saturation state may influence the Mg concentration of calcite overgrowths precipitated from seawater.

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