THE VARIATION OF MAGNESIUM CONCENTRATIONS IN THE TESTS OF RECENT AND FOSSIL BENTHIC FORAMINIFERA

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ABSTRACT

Microanalysis of the chemical compositions Recent benthic foraminifera supports the concept that magnesium content of the tests of foraminifera is affected by water temperature, and suggests that magnesium content in fossil foraminifera may be used as an indicator of paleotemperature. Analysis of the compositions of perforate and imperforate foraminiferal tests show that the magnesium data of some species may be combined to construct a magnesium depth curve that also parallels the oceanic temperature-depth curve. The large difference in magnesium composition between high-and low-magnesium species, however, does not allow these two groups to be combined. Two different equations, one for high-magnesium foraminifera and one for low-magnesium foraminifera, are required to describe the foraminiferal magnesium-temperature relationship. Regression analysis of relationships between temperature and partition coefficients show that the analysis of high-magnesium foraminifera is less suceptible to analytical error and therefore preferred over analysis of low-magnesium foraminifera for paleotemperature determinations.

Concentrations of magnesium in the tests of fossil benthic foraminifera from the Peruvian continental margin show variations resulting from diagenesis, mixing, and time-averaging, but down-hole foraminiferal magnesium variations still record changes in water temperature. Sites that have remained below the thermoclne show little intrasample variation, sites that have remained above the thermoclne show greater variation, and sites that have passed into and out of the thermocline show alternations of intervals with high and low intrasample variation. Concentrations of iron in fossil foraminifera are generally low as in Recent foraminifera, but some occurrences of higher iron concentrations suggest that iron may be incorporated in foraminiferal calcite in amounts greater than previously thought.

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LIST OF ABBREVIATIONS

MBSF .... Meters below sea floor

NODC .... National Oceanographic Data Center

ODP .... Ocean Drilling Program

CHAPTER I

GENERAL INTRODUCTION

A link between chemical variations in foraminiferal test material and variations in the physical environment has been sought by micropaleontologists because such a relationship may lead eventually to a method of environmental analysis applicable to the fossil record. Variation of minor and trace amounts of some elements, particularly magnesium, in the tests of foraminifera was recognized by early workers (Clarke and Wheeler, 1922; Said, 1951; Vinogradov, 1953; Emiliani 1955). Results such as those of Krinsley (1960) showed that geographic variation in chemistries may be due to environmental controls. Direct relationships between the magnesium content of foraminifera and water temperature were recognized by Chave (1954), Savin and Douglas (1973), and Bender and others (1975). Duckworth (1977) showed that magnesium content in a planktonic foraminifer reflected temperature changes during its life. Delaney and others (1985), on the other hand, believe that minor-element composition is not related directly to temperature, but to some temperature-related environmental factor. Chemical variations in foraminiferal tests have also been linked to seawater composition (Boyle, 1981, 1986; Hester and Boyle, 1982; Delaney and others, 1985).

Skeptical of empirically derived chemical environmental relationships, scientists in the past have argued that factors other than environment affect foraminiferal test chemistry (Blackmon and Todd, 1959; Ponder and Glendinning, 1974, Bender and others, 1975). Recently, however, a number of workers have applied the relationships between environment and foraminiferal test chemistry to paleoceanographic problems (e.g., Dasch and Biscaye, 1971; Cronblad and Malmgren, 1981; Graham and others, 1982; Boyle and Keigwin, 1982; Delaney, 1983, Boyle, 1986, Renard, 1986).

X-ray diffraction analyses of planktonic and benthic foraminifera (including Cassidulina subglobosa) by Blackmon and Todd (1959) showed that magnesium content varied among groups of foraminifera but was uniform within families. Other workers have found magnesium content to be similar within related taxa of planktonic foraminifera and that phylogenetic relationships influence foraminiferal test chemistry (e.g. Savin and Douglas, 1973; Lipps and Ribbe, 1967). When effects of phylogeny and environment are combined, however, confusion results. Blackmon and Todd (1959) attributed magnesium contents which deviated from those expected from phylogenetic relationships to either temperature variation or to incorrect taxonomic classification. In some instances, they were uncertain which factor was responsible. Effects of diagenesis have been of concern to those studying deep sea carbonates consisting of foraminiferal skeletal material (e.g., Krinsley, 1960, Lorens and others, 1977), but Renard (1986) considered the effects of diagenesis on strontium concentrations to be "considerably less than was previously thought". Although he recognized that diagenesis affects magnesium to a greater degree than strontium, he considered the effects small in his study of temporal variations in pelagic carbonate chemistry.

Various methods of chemical analysis have been employed in previous studies of the chemistries of tests of foraminifera. These methods include atomic absorption (Savin and Douglas, 1973; Boyle, 1981; Cronblad and Malmgren, 1981; Delaney, 1983; Delaney and others, 1985), neutron activation (Bender and others, 1975; Graham and others, 1982), X-ray fluorescence (Dasch and Biscaye, 1971) and X-ray diffraction (Blackmon and Todd, 1959). Each method was found to be suitable for the investigation involved, but required assumptions that the chemical compositions among specimens of the same species from the same location are uniform and that careful cleaning procedures could remove physiochemical contaminants from the surfaces of the tests. Following Hooper's (1964) early use of the microprobe on foraminifera, the advantage of using this instrument to analyze selected spots on single specimens of foraminifera was demonstrated by Lipps and Ribbe (1967) and Duckworth (1977). These studies have shown that the chemical composition of foraminiferal skeletal material is the result of an interplay of environmental and phylogenetic factors.

This dissertation explores, by means of an electron microprobe, the variation of some minor elements, particularly magnesium, in the calcite of the tests of modern and fossil benthic foraminifera. Special emphasis is placed on the relationship of foraminiferal magnesium content and water temperature, the preservability of that relationship in the fossil record, and the feasablilty of using the magnesium content in the tests of foraminifera as paleotemperature indicators. The study begins by addressing the fundamental question of whether phylogenetic effects can be separated from the analysis so that temperature effects may be studied. The dissertation continues with an investigation into the possibility of expanding the range of water depth that can be studied by combining several species with similiar magnesium contents, and defining groups within which phylogenetic effects are minimal. These first two studies (Chapters 2 and 3) use modern benthic foraminiferal remains whose chemical compositions are less altered by diagenetic processes. The final part of the dissertation (Chapter 4) uses the magnesium contents of fossil foraminifera to identify trends in paleotemperatures for selected sites on the Peruvian continental margin, and discusses some of the problems encountered (e.g. diagenesis, mixing, and time averaging) when working with fossil material.

Chemical analyses were carried out with an electron microprobe, which allows the analysis of areas approximately 1 micrometers in diameter. This feature provides the microprobe with two distinct analytical advantages: 1) small areas within single specimens can be analyzed, thereby eliminating the need for assuming homogeneity among specimens from the same locality, and 2) edges and pores, where postmortem physiochemical alteration may have occurred, can be avoided. The second advantage is particularly important when working with fossil material that cannot be adequately cleaned or freed from matrix.

CHAPTER 2

RELATIONSHIP OF MAGNESIUM AND OTHER MINOR ELEMENTS IN THE TESTS OF CASSIDULINA SUBGLOBOSA AND C. ORIANGULATA TO PHYSICAL OCEANIC PROPERTIES

SYNOPSIS

Microanalyses of the chemical compositions of tests of the benthic foraminifera *Cassidulina subglobosa* Brady and *C. oriangulata* Belford show that magnesium varies between specimens collected from different physical environments; variations in iron, manganese, and strontium were too small to be analyzed by microprobe. The distribution of magnesium with depth parallels temperature distribution, which suggests that temperature is the primary property controlling variation in magnesium concentration in the tests of these species. The concentration of magnesium is lower in the calcite of these foraminifera than in physiochemically precipitated calcite from comparable depths; the foraminifera precipitate calcite that is in disequilibrium with the surrounding water. Magnesium appears to vary in *C. oriangulata* in the same way it varies in *C. subglobosa*, which implies that the chemistries of some members of the same genus behave similarly under similar conditions. The

parallel between magnesium variability in benthic foraminifera and in ocean thermal structure suggests that magnesium content in foraminifera is of potential value not only for single paleotemperature determinations, but also for paleoceanographic thermal reconstruction over a broad range of water depths.

INTRODUCTION

Many of the earliest attempts at finding a relationship between foraminiferal test chemistry and variations in the physical environment were inconclusive because the overprint of phylogenetic and other effects has obscurred the relationships. Some promising results from the investigation described here and from other recent work , however, indicate that minor-element chemistry may be useful in paleoceanography, provided studies are designed so that proper constraints are placed on the variables.

Results from previous studies have shown that both phylogenetic relationships and environment affect the chemistry of foraminiferal tests (e.g. Chave, 1954; Blackmon and Todd, 1959, Krinsley, 1960; Savin and Douglas, 1973; Bender and others, 1975; Duckworth, 1979; Boyle, 1981, 1986; Delaney et al., 1985). In combination, the overprint of one factor on the other may cause confusing results. Only by separation of one effect from the other (i.e., holding one factor constant while varying the other) can phylogenetic-chemical and environmental-chemical relationships be effectively studied. The objective of this research is to isolate and study the effects of the physical environment on the minor-element chemistry of benthic foraminifera in order to test the premise that variations in their chemistries reflect variations in environmental conditions. Phylogenetically induced chemical variations have been eliminated from this investigation by limiting the study to two species, Cassidulina subglobosa Brady and C. oriangulata Belford. The results of Blackmon and Todd (1959) indicate that chemistries (at least of magnesium) are uniform within families of foraminifera. An examination of the hypothesis that chemistries of two species from the same genus will behave similarly under similar physical conditions was also part of this investigation.

The study was further constrained by analyzing specimens from one area only, namely, the Solomon Islands/Ontong-Java Plateau area (tropical western Pacific), thereby eliminating regional differences in water chemistry. Cassidulina subglobosa occurs over a wide range of depths in the study area and thus inhabits several water masses of various physical properties. The range of C. oriangulata overlaps that of C. subglobosa and continues into shallower water. These constraints were designed to minimize lateral variations while maximizing vertical variations. Analyses were confined to the elements Mg, Mn, Fe, and Sr, which have been reported in the calcite of foraminifera, and Ca, the principal cation in calcite.

METHODS

Specimens and Mounts

Specimens of foraminifera were picked from 16 washed (in a sieve with 63 micrometer openings) and dried core-top samples from the area of the Solomon Islands and Ontong-Java Plateau (Fig. 1). The samples were taken from the free-fall and gravity cores in the collections of the Hawaii Institute of Geophysics (S67, S68 and KK82 series), and from the tops of USGS (L6-84-SP series) dart cores and United Nations (UN79 and UN81 series) cores. Specimens of Cassidulina subglobosa were picked from samples collected from 260 to 4,332 m depth; specimens of C. oriangulata were picked from samples collected from 102 to 399 m depth.

Of several mounting methods attempted, the most successful involved pressing the specimens into drops of epoxy on a glass microscope slide. This procedure insured

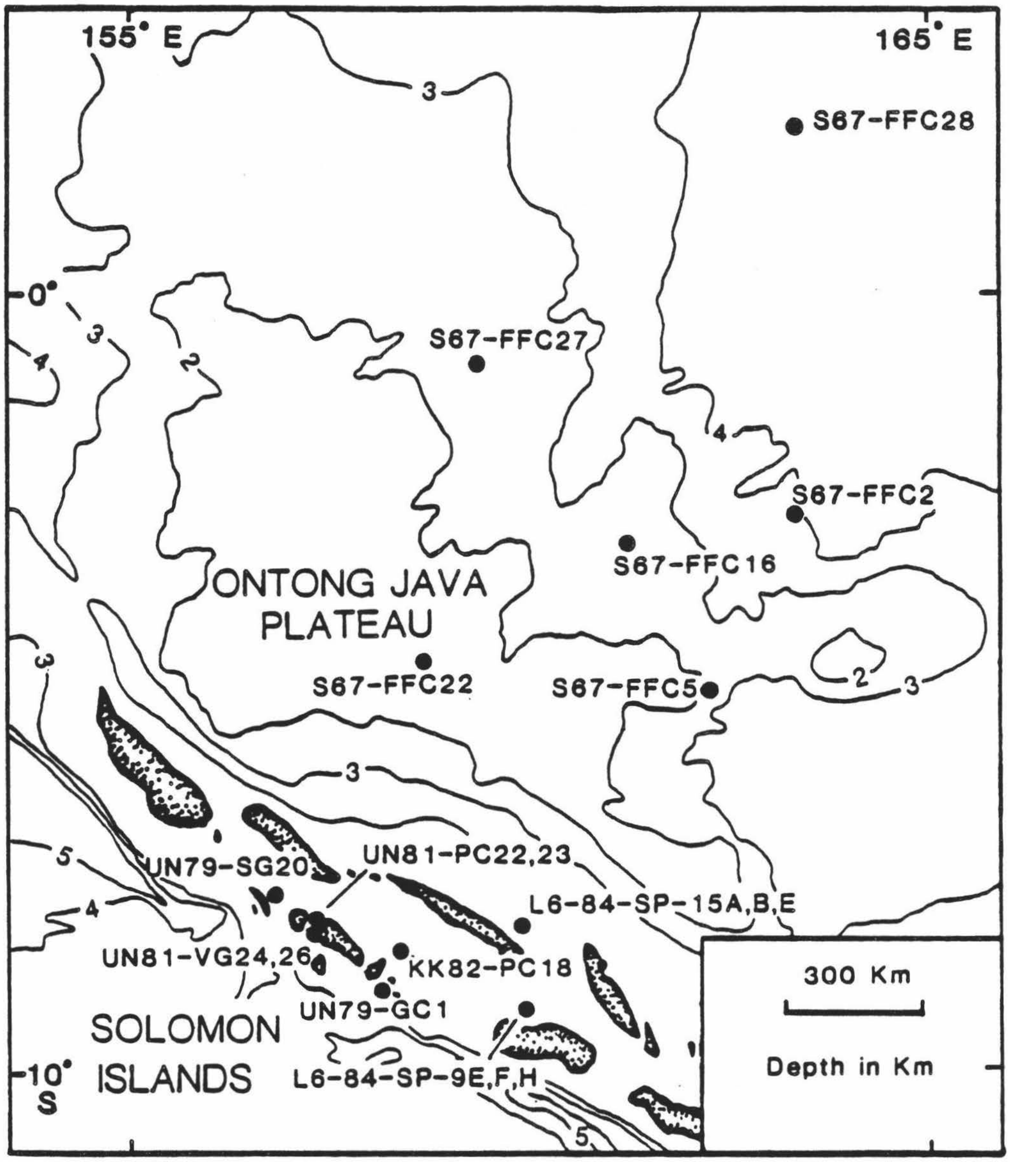


Figure 1. Map of core locations. Cores with prefixes S67 and KK82 are from the Hawaii institute of Geophysics, UN79 and UN81 from the United Nations-SOPAC, and L6-84-SP from the United States Geological Survey.

that the specimens remained at approximately the same level on the slide and permitted sectioning of several specimens at once. Specimens were sectioned to expose the interior of the chambers by wet-grinding on a lap plate with 1000-grit silicon-carbide abrasive powder. A second drop of epoxy was added to the sectioned specimens to fill the chambers and strengthen the test. The specimens were then resectioned on the lap plate and polished on a motorized lap wheel with 0.3 micrometer alumina polishing paste. Immediately prior to microanalysis, specimens and standards were coated with carbon to make them electrically conductive.

Microanalysis

Minor and major elements were analyzed on a wavelength-dispersive, three-spectrometer (with diffracting crystals PET, TAP, and LiF), automated Cameca electron microprobe, using an accelerating voltage of 15 kV. Crystals of dolomite, calcite, siderite, rhodochrosite, and strontianite were used as standards for Mg, Ca, Fe, Mn, and Sr, respectively. Peak intensity (K-alpha for Mg, Ca, Mn, and Fe; L-alpha for Sr) for each element was measured by 9 repeat analyses on each standard, until the sigma values were less than 1.0.

A beam current of 10 nA and a counting time of 20 sec (10 sec for each peak count, 5 sec for background on either side of the peak) were found to be optimum for analysis of the carbonate tests. The beam was focused to a spot approximately 4 micrometers in diameter. Under these operating conditions, minimal damage was sustained by the wall of the specimens under the electron beam.

Care was taken to avoid edges and pores of specimens where postmortem physiochemical precipitates are likely to occur and where surface irregularities may misdirect X-rays or the beam spot may extend off the specimens and onto epoxy. In a few instances, the beam was inadvertently placed on an irregular surface, resulting in computed total carbonate weight percents that were considerably greater or less than the expected value of 100 percent. Computed analyses totalling more than 105 weight percent or less than 95 weight percent were omitted from the data file.

The number of spot analyses made on each specimen ranged from 7 to 12, depending on the availability of optimum surfaces for probing. Generally, larger specimens, such as adult *Cassidulina subglobosa*, provided a greater area for probing than smaller specimens such as adult *C. oriangulata* and juveniles of both species.

Data Analysis

The microprobe computer calculates concentrations of each cation by comparing the X-ray intensity of the specimen to the ratio of X-ray intensity to concentration for the standard (with ZAF corrections). Concentrations are are reported as cation weight percents. The carbonate radical was stoichiometrically added to the cation weight percents and the cation-carbonate weight percents were computed. Carbonate weight percents reported here are averages of the 7 to 12 spots analyzed on each specimen. The standard deviation of the analyses of each cation for each specimen was also computed.

A measure of the precision of the magnesium analyses can be obtained from the variability of the value of $MgCO_3$ in periodic analyses of the standard. The mean value of analyzed $MgCO_3$ in the dolomite standard was 45.64 weight percent; the standard deviation of the analyses was 0.89 weight percent (or 2 percent of the mean). An indication of the accuracy of the microprobe measurements may be obtained from the differences between the analyzed and given compositions in the standards. The given value of $MgCO_3$ in the dolomite standard is 45.55, which differs from the average analyzed value by 0.09 weight percent (or 0.20 percent of the given value).

RESULTS

Values of $MgCO_3$ in tests of *Cassidulina subglobosa* and *C. oriangulata* range from 0.03 to 1.15 weight percent (Tables 1 and 2). Highest concentrations of $MgCO_3$ occur in specimens of *C. subglobosa* and *C. oriangulata* from 600 m depth and shallower, whereas lowest concentrations of $MgCO_3$ occur in specimens of *C. subglobosa* from below 600 m. As previously known, $CaCO_3$ constitutes the major portion of the foraminiferal tests analyzed. Values range from 95.97 to slightly over 100.00 weight percent $CaCO_3$ Values greater than 100 weight percent $CaCO_3$ may be the result of either experimental error, such as slight imperfections in the polish of the specimens, or the inaccuracy of the assumption that all cations are stoichiometrically linked with the carbonate radical (Dodd, 1967).

Manganese was detected in nearly all the specimens, but values are generally low (less than 0.10 weight percent). Iron also appears to be present in most of the foraminifera, but, as with manganese, the percentages are low (all but one less than 0.10 weight percent). Strontium was not detected in any of the spot analyses.

TABLE 1. -- Depths, water masses, and average weight percents (with standard deviations) of carbonates of specimens of Cassidulina subglobosa. T = thermocline, O = oxygen minimum, I = intermediate water, D = deep water, B = bottom water.

Core Number	Depth (m)	Water Mass	N	$MgCO_3$	Std. dev.	$CaCO_3$	Std. dev.	$MnCO_3$	Std. dev.	$FeCO_3$	Std. dev.
UN81-VG24	260	T	10	1.05	0.56	99.42	0.77	0.04	0.05	0.13	0.12
UN81-PC23	360	T/O	9	0.35	0.08	99.55	1.02	0.01	0.01	0.07	0.06
UN81-PC22	500	T/O	11	0.24	0.09	100.70	1.06	0.05	0.05	0.06	0.07
L6-84-SP-9F	525	I	7	0.51	0.21	98.89	2.05	0.04	0.05	0.06	0.06
L6-84-SP-15B	614	O	11	0.12	0.07	98.88	1.10	0.02	0.02	0.06	0.07
L6-84-SP-9C	685	O	11	0.11	0.09	100.21	1.16	0.05	0.05	0.05	0.07
L6-84-sp-15A	778	O	11	0.06	0.06	99.49	1.43	0.03	0.05	0.04	0.05
UN79-GC1	865	O	11	0.09	0.04	100.25	1.11	0.04	0.06	0.02	0.02
L6-84-SP-15E	895	O	11	0.16	0.06	99.65	1.33	0.04	0.05	0.04	0.04
KK82-PC18	1320	O	11	0.13	0.04	100.78	1.16	0.03	0.07	0.06	0.07
S67-FFC22	1718	O	10	0.12	0.07	100.92	1.06	0.03	0.06	0.04	0.06
S67-FFC5	2222	O	11	0.09	0.06	99.22	0.98	0.03	0.04	0.05	0.06
S67-FFC27	2264	O	8	0.07	0.07	96.35	0.94	0.02	0.03	0.03	0.05
S67-FFC16	2712	D	10	0.11	0.06	95.97	0.52	0.02	0.03	0.04	0.06
S67-FFC2	3451	D	12	0.07	0.05	99.98	1.26	0.03	0.05	0.03	0.04
S67-FFC28	4332	B	10	0.03	0.04	99.44	1.58	0.04	0.05	0.04	0.04

TABLE 2. -- Depths, water masses, and average weight percents (with standard deviations) of carbonates of specimens of *Cassidulina oriangulata*. T = thermocline, O = oxygen minimum.

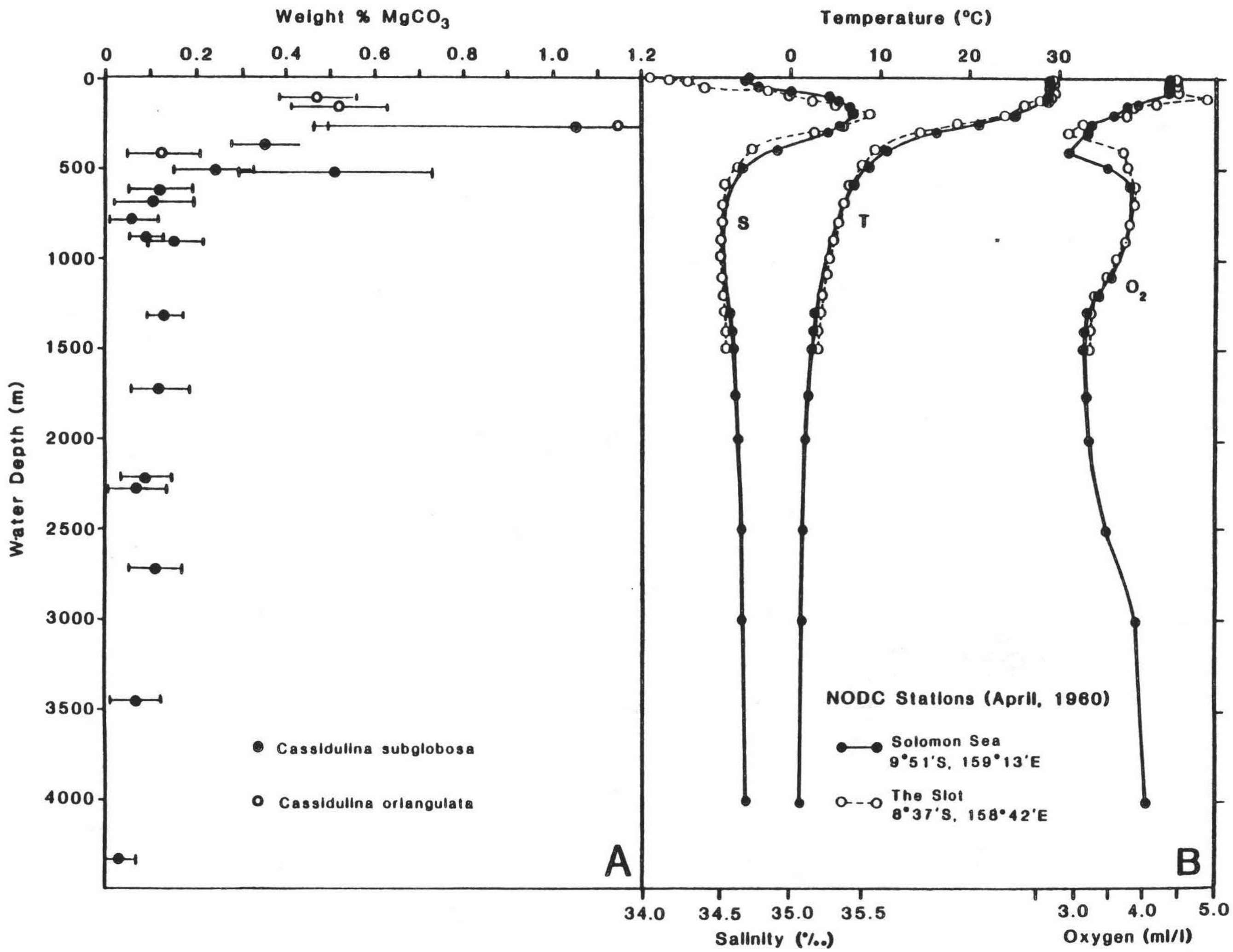
Core Number	Depth (m)	Mass	N	$MgCO_3$	Std. dev.	$CaCO_3$	Std. Dev.	$MnCO_3$	Std. dev.	$FeCO_3$	Std. dev.
UN79-SG20	102	T	9	0.47	0.09	99.23	1.99	0.02	0.03	0.02	0.03
UN81-VG26	150	T	11	0.52	0.11	98.75	2.64	0.05	0.07	0.07	0.05
UN81-VG24	260	T	10	1.15	0.68	98.58	1.45	0.06	0.07	0.07	0.05
L6-84-SP-9H	399	T/O	11	0.13	0.08	100.28	1.81	0.03	0.04	0.07	0.08

DISCUSSION OF RESULTS

Magnesium

The concentration of magnesium in the tests of the foraminifera studied appears to have an inverse relationship to depth of the water from which the specimens were collected. This relationship is most apparent in the species *Cassidulina subglobosa*, which has a wider depth range than *C. oriangulata*. A plot of the depth of occurrence of the foraminifera versus magnesium content (Fig. 2A) shows that although the relationship between depth and magnesium content is generally inverse, it is not linear. Magnesium concentration decreases rapidly with depth from the surface to about 600 m water depth. Magnesium concentrations are highest at 260 m. Below 600 m, magnesium decreases gradually with increasing depth to the greatest depth (4,332 m) from which a specimen was collected. The variation of magnesium with depth closely parallels the distribution of temperature (Figure 2). In tropical regions such as the Solomon Islands/Ontong-Java Plateau area, water at the surface is warm. Through the thermocline below the warm surface layer, temperature drops rapidly with depth to about 600 m. Below the thermocline, ocean temperature decreases gradually with depth.

Figure 2. Comparison of the depth distribution of magnesium in the tests of *Cassidulina subglobosa* and *C. oriangulata* with the depth distribution of physical oceanic properties. A) Weight percent $MgCO_3$ determined by microprobe for *C. subglobosa* (closed circles) and *C. oriangulata* (open circles). B) Salinity (S), temperature (T), and oxygen (O) profiles in the Solomon Islands-Ontong-Java Plateau area (data from the National Oceanographic Data Center).



Weight % $MgCO_3$
0
0.2
0.4
0.6
0.8
1.0
1.2
Water Depth (m)
0
500
1000
1500
2000
2500
3000
3500
4000
Cassidulina subglobosa
Cassidulina oriangulata
A
Temperature (°C)
0
10
20
30
S
T
O_2
NODC Stations (April, 1960)
Solomon Sea
9°51'S, 159°13'E
The Slot
8°37'S, 158°42'E
B
34.0
34.5
35.0
35.5
Salinity (‰)
3.0
4.0
5.0
Oxygen (ml/l)

A maximum of magnesium concentration at 260 m resembles the salinity maximum at that depth (Figure 2), but the accuracy of the analyses at the maximum is questionable because of the large error associated with those two measurements (Table 1 and 2; Figure 2). Aspects of the sediment sample from which the anomalous specimens were picked, including rounded grains and poorly preserved specimens, suggest that transportation may be responsible for this magnesium inflection at this depth.

Below 600 m, both magnesium concentration and temperature gradually decrease with depth, whereas salinity increases. Thus, except for the odd inflection in the magnesium data at 260 m, most of the magnesium distribution closely parallels the temperature profile and supports the conclusion that the variation is primarily controlled by temperature, not salinity. The magnesium-depth trend does not appear to parallel oceanic oxygen content (Fig. 2B). The similarity between the plot of magnesium content of the two species of Cassidulina, particularly that of C. subglobosa, and the oceanic temperature profile suggests that concentration of magnesium in the tests of foraminifera is related to ocean temperature and may be useful in reconstructing marine paleotemperature profiles.

These results are consistent with those for calcites precipitated under controlled conditions in the laboratory, as well as those physiochemically precipitated calcites occurring in nature. A magnesium-depth trend similar to the one observed in the foraminifera in this study has also been reported for physiochemically precipitated magnesian calcite from comparable depths in the ocean (Mackenzie and others, 1983), but the actual compositions of the foraminifera are clearly lower in Mg than the inorganic precipitates. Schlager and James (1978) found calcites with 3.5 - 5 mol percent (3.0-4.2 weight percent) $MgCO_3$ in cements forming in water between about 700 to 1,200 m in the Tongue of the Ocean (a deep trough between the Bahama Banks) and attributed the observed magnesium-depth trend to ocean temperature. Land and Moore (1980) found that cements and recrystallized calcite from 98 to 278 m depth on the Jamaican slope contain about 16 mol percent (13.8 weight percent) $MgCO_3$. Burton and Walter (1987) found that temperature was the primary control on the magnesium concentration of calcite precipitated artificially from seawater. Their analyses ranged from 5 mol percent (4.2 weight percent) precipitated at 5° C to 14 mol percent (11.7 weight percent) at 37° C. These physiochemically precipitated calcites have magnesium compositions that are higher than the highest magnesium content found in species of Cassidulina in this study (Tables 1, 2). If physiochemically precipitated calcites (such as cements) represent the stable carbonate phase at the sea floor, then the lower-magnesium calcites in the foraminifera are not in chemical equilibrium with the surrounding water. Inasmuch as the environment for precipitation of skeletal calcite is provided by the protoplasm of the foraminifera, it is not expected that foraminiferal calcite will be of the same composition as calcite precipitated inorganically (Kitano and Kanamori, 1966; Bender and others, 1975). Thus, whereas temperature affects foraminiferal calcite in the same way it affects physiochemical calcite, the foraminifera are able to precipitate calcites that are not in equilibrium with the surrounding seawater.

In detail, the magnesium contents in some of the foraminifera in this study deviate from the general inverse depth trend (Tables 1, 2). Scatter appears to be greater in the upper 500 m of the magnesium-depth curve than in the deeper part of the curve (Fig. 2A). One source for the deviation may be physiochemical alteration. Although steps were taken to ensure that only modern, whole, nonrecrystallized specimens were analyzed, some degree of alteration, even in skeletal material free of visible signs of recrystallization, has been reported or suspected by other workers (Krinsley, 1960; Towe and Hemleben, 1976; Lorens and others, 1977). Lorens and others (1977) found that the ratio of magnesium to calcium in planktonic foraminifera is related to the susceptibility of the foraminiferal test to solution as described by Berger (1970). Lorens and others (1977) suspect that some sort of cation exchange mechanism or selective crystal solution acts at the surface of the tests to cause alteration. In shallow water, magnesian-calcite overgrowths may form on low-magnesian calcites (Morse and others, 1979). These surface effects were avoided by the microprobe.

Because they live at the sea floor, benthic foraminifera are probably more resistant to solution in deep water than are planktonic foraminifera which live shallower in the water column, but the solution susceptibility of benthic foraminifera has not been studied. Dissolution effects are relatively small at depths less than 4,000 m (Peterson, 1966; Berger, 1970, Duckworth, 1977). It is unlikely that dissolution has significantly changed the magnesium concentration in the tests analyzed because all but one of the specimens of <u>Cassidulina</u> in this study were collected from above 4,000 m depth. The effects of postmortem physiochemical alteration may be evaluated in future work by comparing the chemistries of living and dead specimens.

A second source for deviation of some specimens from the general magnesium-depth curve is postmortem down-slope transportation of the tests. Transportation results in higher magnesium concentrations measured in specimens from deeper water, and the effect is more pronounced in shallow water than in deep water. In the upper 500 m of the curve, down-slope transport of only 200 m meters could result in mixing of specimens having about 1.0 weight percent $MgCO_3$ with indigenous specimens having less than 0.5 weight percent $MgCO_3$. Below 500 m, down-slope transport by more than 1,000 m may result in mixing of individuals that differ by only 0.1 - 0.2 weight percent $MgCO_3$. One sample from 260 m showed evidence of possible transportation such as abraded grains, exotic remains of shallow-water organisms and minor sorting. Although the best specimens were generally selected for analysis, most of the specimens of foraminifera in this sample were broken and poorly preserved. Postmortem transportation and alteration could be responsible for the magnesium anomaly in the sample from 260 m.

Blackmon and Todd (1959) reported that tests of _Cassidulina subglobosa_ from 750 m (410 fm) off Bikini had 3 mol percent (about 2.5 weight percent) $MgCO_3$, which is considerably more than the 0.06 weight percent $MgCO_3$ measured in a specimen from comparable depth (778 m) in the Solomon Islands-Ontong-Java Plateau area. Indeed, the highest value of $MgCO_3$ in this study is only half the value reported by Blackmon and Todd (1959). Sources for the discrepancy may lie in experimental errors in either the X-ray diffraction method of Blackmon and Todd (1959) or in the microprobe analyses of this study, but the accuracy at which the microprobe analyzed the composition of known standards (see discussion in preceding section) attests to the reliability of the microprobe values. Other sources of discrepancy include postmortem down-slope transportation or physiochemical alteration as discussed previously.

The $MgCO_3$ content of Cassidulina oriangulata appears to vary with depth in the same way as $MgCO_3$ in C. subglobosa (Tables 1, 2). The slightly lower magnesium concentrations in C. oriangulata suggest the possibility of a small phylogentic effect, but because only few samples contained both species, indentification of the effect is uncertain. The separation of the C. oriangulata chemistries from the C. subglobosa chemistries is small, however, when compared to the effect of temperature on the magnesium concentrations (Figure 2). Thus, no strong phylogenetic effects separate the magnesium contents of

C. oriangulata and *C. subglobosa* (Fig. 2A). A sample from 260 m contained specimens of both species, which yielded similar $MgCO_3$ compositions (1.15 weight percent in *C. oriangulata* and 1.05 weight percent in *C. subglobosa*). This result is in agreement with the conclusion of Blackmon and Todd (1959) that magnesium content is generally uniform within families of foraminifera.

Iron, Manganese and Strontium

Strontium was not detected by the microprobe in this study, but other investigators have reported its presence in minor amounts (up to 0.21 weight percent) in the shells of planktonic foraminifera (Lipps and Ribbe, 1967) and in benthic foraminifera (E. Barrera, unpublished data). Small concentrations (mostly less than 0.10 weight percent) of iron and manganese were detected by the microprobe in both species in this study, but because variations in concentrations of these elements were small and approached the detectability limit of the microprobe, no relationships between concentration and environmental conditions were apparent.

CONCLUSIONS

The data presented here suggest that magnesium concentration in foraminiferal calcite may be of value in paleoceanography. The element occurs in the tests of the foraminifera Cassidulina subglobosa and C. oriangulata in such quantities that trends in its abundance can be easily studied by the microprobe. Similarities between the depth distribution of magnesium in these species and modern oceanographic temperature-depth profiles suggests that temperature is the primary physical property of seawater controlling magnesium concentration in foraminiferal tests. High magnesium concentrations are apparently linked to warm temperature. Aspects of the thermal structure of the ocean including its uniformly cold, deep temperatures and rapid rise in temperature through the thermocline toward the surface are reflected in magnesium content of foraminiferal tests.

Quantitative differences between foraminiferal calcites and physiochemically precipitated calcites from comparable depths suggest that the foraminifera in this study do not precipitate calcites in chemical equilibrium with the surrounding water. Further studies, perhaps in the form of direct comparisons between physiochemical and foraminiferal calcite from the same seawater, may cast light on this possibility.

The magnesium compositions of *Cassidulina subglobosa* and *C. oriangulata* collected from the same depth in one region are similar. This observation is in agreement with the conclusion of Blackmon and Todd (1959) that magnesium content tends to be uniform within families of foraminifera. The parallel between the depth distributions of the two species indicates further that their magnesium concentrations behave similarly under similar physical conditions.

Deviations of individual specimens from the general magnesium-depth trend may be the result of down-slope transportation of foraminiferal skeletons. Postmortem physiochemical alteration, although not likely a factor in this study, remains a possible cause of inconclusive results in paleoecologic studies using fossil remains. Future studies of the effects of physiochemical alteration are needed to identify constraints and limitations of using magnesium as a measure of temperature.

Whereas some other studies have suggested that a positive link between temperature and the magnesium content of skeletal calcite can be useful in paleotemperature determinations, the results of this research point to an even greater potential interpretive value of magnesium content of foraminiferal tests. The similarity in behavior of magnesium concentrations in species of the same genus suggest that magnesium content and paleotemperature may be studied over the combined depth ranges of more than one species, without consideration of phylogenetic effects. Thus study of thermal structure over a broad range of depths and determination of the position of the thermocline in ancient oceans may be possible.

CHAPTER 3

A COMPARISON OF MAGNESIUM IN THE TESTS OF SEVERAL SPECIES OF BENTHIC FORAMINIFERA TO WATER COLUMN TEMPERATURE

SYNOPSIS

Analysis of the composition of perforate and imperforate foraminiferal tests show that the magnesium concentrations of some species may be combined to construct a magnesium-depth curve that parallels the oceanic temperature-depth curve. The similarity in the variation of magnesium with temperature among the three perforate species studied suggests that their magnesium compositions may be treated as the same when used as paleotemperature indicators. The similarity in magnesium-temperature variation among imperforate species also suggests that analyses of these species may be combined in paleotemperature determinations. The large difference in magnesium composition between high-and low-magnesium species, however, does not allow these groups to be combined. Regression analysis of relationships between temperature and partition coefficients show that analysis of high-magnesium foraminifera is less susceptible to error and is thus preferred over analysis of low-magnesium foraminifera for paleotemperature determination.

INTRODUCTION

Foraminifera exhibit a wide range of magnesium concentrations that are roughly related to temperature (Chave, 1954; Krinsley, 1960; Savin and Douglas, 1973; Bender and others, 1975; Duckworth, 1979; Chapter 2). Differences in magnesium contents between species, even when collected from the same environment, have led some workers to conclude that other factors such as those related to the phylogeny of the organism (the so-called "vital effects") control foraminiferal test chemistry (Blackmon and Todd, 1959; Bender and others, 1975). The overprint of these other factors obscures the effects of temperature on the incorporation of magnesium in foraminiferal calcite, thereby confounding attempts at finding a magnesium-temperature relationship useful for paleotemperature determinations.

The concentration of magnesium may be a useful measure of paleotemperature if phylogenetic effects are eliminated by analyzing only one species (Duckworth, 1979) or closely related species (Chapter 2). However, because most benthic foraminifera are restricted to narrow depth ranges, study of the magnesium-temperature relationship over a broad depth range, particularly through the thermocline, is difficult without employing several species.

This study investigates the limitations of combining data from several species of foraminifera in single paleotemperature studies. If the magnesium content in some species of foraminifera can be combined without phylogenetic overprints, the effective depth range over which magnesium-temperature relationships could be studied would then be extended to the combined ranges of the species analyzed. The occurrence of benthic foraminifera at a wide range of depths provides a natural laboratory where the effects of temperature on magnesium concentration in foraminiferal calcite may be studied. Temperatures in the western, tropical Pacific, for example, range from about 30° C at the surface to less than 5° C below 500 m. A suite of samples taken from various depths through the thermocline provides specimens of foraminifera grown naturally in a wide range of water temperatures.

The results of Blackmon and Todd (1959) show that there exists at least one strong effect, unrelated to temperature, that divides species of foraminifera into those with tests composed of low-magnesian calcite (between 0-5 mol percent $MgCO_3$) and high-magnesian calcite (between 10-15 mol percent $MgCO_3$). The effect appears, with some exceptions, to be phylogenetic; most of the Rotaliina (calcareous perforate) have low-magnesian calcite tests, whereas all of the Miliolina (calcareous imperforate) have high-magnesian calcite tests. For the present investigation, both high- and low-magnesian calcite foraminifera were studied, but the two groups were treated separately. Specimens of benthic foraminifera with low-magnesian calcite tests were analyzed to determine whether the chemistry of one species varies with temperature in the same way as others in the group; specimens with high-magnesian calcite tests were analyzed to determine if all species of this group respond to temperature in the same manner.

METHODS

Data Acquisition -- To eliminate regional variations in vertical ocean thermal structure, all specimens analyzed were collected from the Solomon Islands/Ontong-Java Plateau area (tropical western Pacific, Figure 3). Specimens of perforate (*Pullenia bulloides*, *Cibicidoides pseudoungerianus*, and *Cassidulina subglobosa*) and imperforate foraminifera (*Pyrgoella sphaera*, *Quinqueloculina lamarckiana*, and *Sigmoilina* sp.) foraminifera were picked from washed, sieved core-top sediment samples from depths between 102 m and 4,245 m.

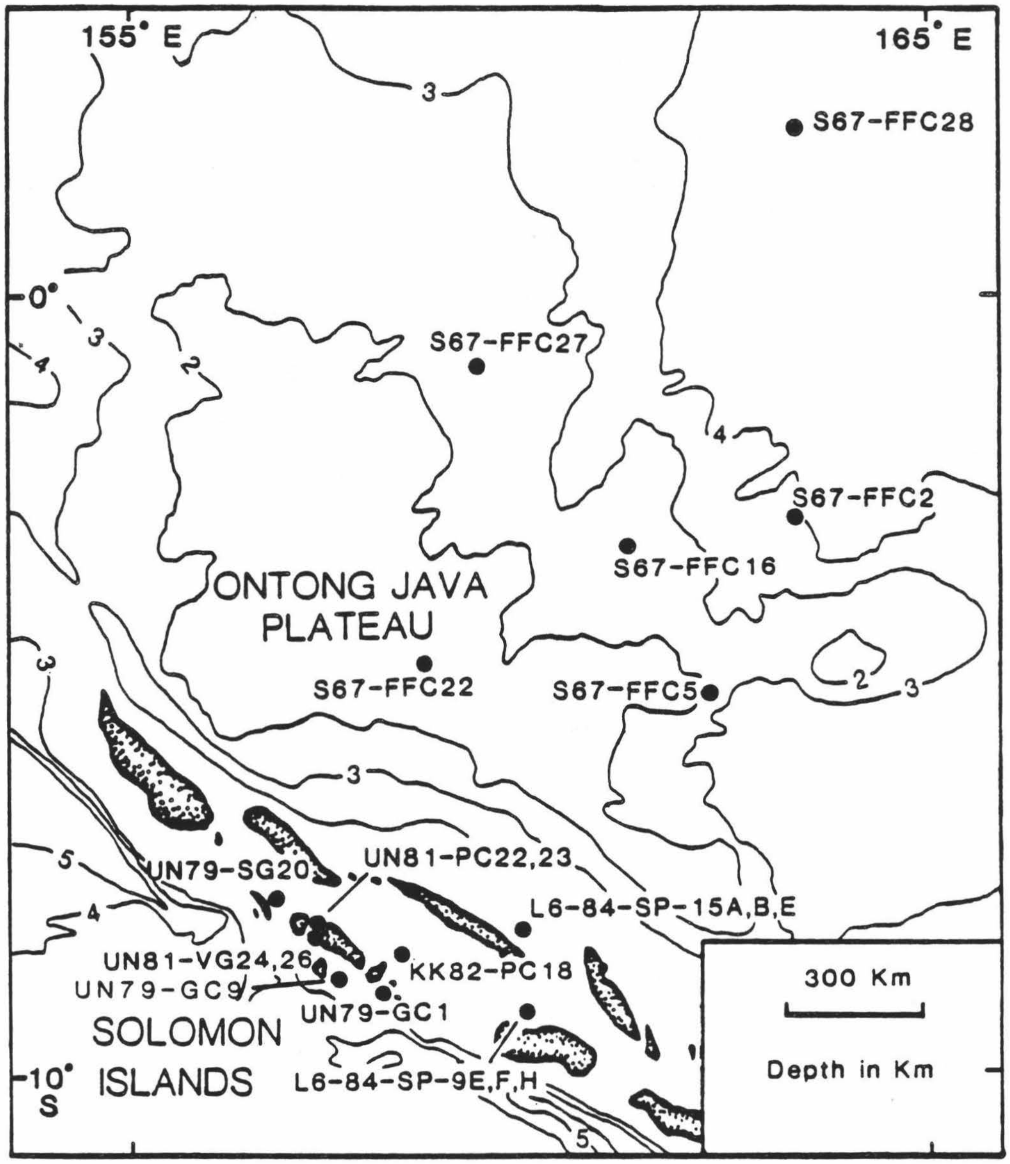


Figure 3. Map of core locations. Cores with prefixes S67 and KK82 are from the Hawaii Institute of Geophysics, UN79 and UN81 from United Nations-SOPAC, and L-84-SP from the United States Geological Survey.

Because each species inhabits a particular depth range according to the distribution of water mass in the area (Burke, 1981), not all species occurred in all samples, but in some cases two or more of the species chosen for analysis occurred in the same sample.

Chemical compositions were determined using the techniques described in Chapter 2. Magnesium and calcium were analyzed on separate spectrometers; dolomite was used as a standard for magnesium and calcite was used as a standard for calcium. Each specimen was analyzed at 3 to 12 points, depending on the availability of suitable surfaces for probing. The Miliolina normally provided large areas for probing because of the lack of pores in the test wall. The only factor limiting probing area was the size of the test. On the other hand, the area available for probing on the Rotaliina depends on the number, size and distribution of pores as well as the size of the test. The perforate species chosen for microanalysis had large tests that were ideal for probing.

The variability of the concentration of $MgCO_3$ in the standard serves as a measure of the precision of the analyses. The standard deviation of $MgCO_3$ in the dolomite standard was 0.46 or 1% of the mean value of 45.51 weight percent. The accuracy of the microprobe measurements is indicated by the differences between the analyzed and given compositions in the standards. The concentration given for $MgCO_3$ in the dolomite standard (45.55 weight percent) differs from the averaged analyzed concentration by 0.04 weight percent (or 0.1% of the given value).

Statistical Analysis and Partition Coefficients -- Temperature of the water from which the specimens were collected was estimated by linear interpolation between data points from the NODC temperature curve. These temperature estimates were used in bivariate plots to compare magnesium content in foraminifera and seawater temperature. As a measure of the degree of relationship between temperature and magnesium content, separate correlation coefficients were computed for low- and high-magnesium groups. To test the significance of the correlations, the Student's t statistic was computed.

At constant temperature, the proportion of a minor element found substituting for a major element in a mineral precipitated from solution is related by a constant to the ratio of these elements in the solution. This constant is known as the partition coefficient. For the substitution of magnesium for calcium in calcite precipitated in seawater by foraminifera, the partition coefficient (P) may be expressed as:

$$P = \frac{[Mg^{++}]/[Ca^{++}]_{\text{foraminiferal calcite}}}{[Mg^{++}]/[Ca^{++}]_{\text{seawater}}}$$

The molar ratio $[Mg^{++}]/[Ca^{++}]$ for foraminiferal calcite may be computed by dividing the weight percents from microprobe analysis by the cation weights.

The computation of the partition coefficients is simplified by considering the value of $[Mg^{++}]/[Ca^{++}]$ for seawater as constant over the world ocean. Although the ratios of magnesium and calcium to seawater chlorinity do vary (Riley and Tongudai, 1967), variations are so small that these elements may, for the purpose of partition coefficient computations, be considered conservative. For the computation of partition coefficients in this study, the ratios of magnesium and calcium to chlorinity measured by Riley and Tongudai (1967) for the world ocean were converted to a molar ratio which was used as an estimate of $[Mg^{++}]/[Ca^{++}]$ in seawater.

The partition coefficient is a function of temperature because the amount of magnesium substituting in the calcite lattice of the tests of foraminifera is a function of temperature. An equation for the relationship between the partition coefficient and temperature may be derived by fitting a regression line:

$$P = mT + P_o$$

where P_o is the partition coefficient at $T = 0°$ C, and m is the slope of the line determined by regression. In this analysis, temperature has been chosen as the independent variable and the magnesium partition coefficient as the dependent variable because the investigation proceeds on the premise that temperature controls magnesium content. Whereas the Student's t statistic for correlation tests if the relationship between temperature and magnesium is significantly nonzero (or nonrandom), the significance of the linear model produced by regression was tested by computing the F statistic to compare the variance explained by regression with the unexplained variance.

To facilitate the use of the relationship between magnesium and temperature for paleotemperature determination from fossil foraminifera, an equation for temperature as a function of magnesium concentration in foraminiferal calcite is desired. Although it is inappropriate to simply reverse the regression analysis to yield an equation where temperature is the dependent variable (Sokal and Rohlf, 1969), an equation for temperature may be derived by solving for T in the original regression equation. If the definiton of the partition coefficient is also included in the equation, the formula for temperature as determined by magnesium in foraminifera may be expressed as:

$$T = \frac{[Mg^{++}]/[Ca^{++}]_{f.c.}}{([Mg^{++}]/[Ca^{++}]_{s.w.}) \times m} - P_o/m$$

The value of P_o/m is constant for the equation. The denominator of the first term is also a constant in this case because of the conservative nature of magnesium and calcium in the ocean. This equation was used to recompute magnesium-based temperatures which were compared to the NODC temperatures.

RESULTS

Microanalysis -- The highest concentrations and widest range of variation of $MgCO_3$ among the low-magnesium foraminifera occurred in the species Cibicidoides pseudoungerianus (Table 3). This species was collected from water depths less than 778 m. Lowest concentrations

TABLE 3.-- Chemistries of the tests of some calcareous-perforate foraminifera from the Solomon Islands. N = number of spot analyses averaged. Standard deviations are based on sample (n-1).

Species	Core	N	Depth (m)	Wt. % $MgCO_3$	Std. Dev.	Wt. % $CaCO_3$	Std. Dev.
Cibicidoides pseudoungerianus	UN79-SG20	5	102	0.75	0.09	101.02	0.94
C. pseudoungerianus	UN81-VG26	12	150	0.87	0.14	101.71	1.15
C. pseudoungerianus	UN81-VG24	13	260	0.79	0.25	101.46	0.82
C. pseudoungerianus	L6-84-SP-9H	12	399	0.13	0.06	102.01	1.18
Pullenia bulloides	L6-84-SP-9H	3	399	0.36	0.00	97.45	2.57
C. pseudoungerianus	L6-84-SP-15D	12	458	1.22	0.15	100.14	1.34
Cassidulina subglobosa	L6-84-SP-15D	12	458	0.16	0.07	101.06	1.35
C. pseudoungerianus	L6-84-SP-15B	13	614	0.09	0.09	101.29	2.14
P. bulloides	L6-84-SP-15B	10	614	0.24	0.07	99.31	2.38
C. pseudoungerianus	L6-84-SP-9C	11	685	0.07	0.05	101.88	0.71
P. bulloides	L6-84-SP-9C	8	685	0.22	0.03	99.69	1.59
C. pseudoungerianus	L6-84-SP-15A	12	778	0.11	0.07	101.31	1.05
P. bulloides	L6-84-SP-15A	11	778	0.17	0.06	98.87	1.92
P. bulloides	L6-84-SP-15E	12	895	0.18	0.08	99.31	2.35
P. bulloides	KK82-PC18	11	1320	0.30	0.09	99.03	2.19
P. bulloides	S67-FFC15	12	2222	0.14	0.05	98.84	2.18
P. bulloides	S67-FFF16	13	2712	0.11	0.06	100.00	1.55
P. bulloides	S67-FFC14	11	2876	0.17	0.07	99.78	1.76
C. subglobosa	S67-FFC14	11	2876	0.09	0.04	97.39	2.00
C. subglobosa	S67-FFC15	12	4245	0.01	0.02	99.86	1.22

of $MgCO_3$ occurred in the species Cassidulina subglobosa, which was collected from depths greater than 458 m.

Sigmoilina sp. occurred below 458 m and contained the lowest concentrations of $MgCO_3$ among the imperforate foraminifera (Table 4). Quinqueloculina lamarckiana from 260 m to 102 m depth had the highest concentrations of $MgCO_3$ of all foraminifera studied. A single specimen of Pyrgoella sphaera from 458 m contained a magnesium concentration intermediate between the ranges of $MgCO_3$ in Q. lamarckiana and Sigmoilina sp. Figures 4a, b, and c compare the magnesium-depth distribution with the distribution of temperature with depth.

Data Analysis -- The correlation coefficient between the magnesium concentration and temperature is 0.72 for the twenty low-magnesium specimens, and 0.96 for the eight high-magnesium specimens (Figure 5). Both correlations are significant at 95% confidence (alpha = 0.05). The paucity of data between 10° and 20° C is a result of the steepness of the thermocline through water depths with these temperatures. In contrast, many samples were collected in water that is less than 10° C because most of the deep ocean is cold.

An unusually high $MgCO_3$ concentration occurred in a specimen of Cibicidoides pseudoungerianus from 458 m. The species is represented in this sample by only a few,

TABLE 4. -- Chemistries of the tests of some calcareous-imperforate foraminifer from the Solomon Islands. N = number of spot analyses averaged. Standard deviations are based on sample (n-1).

Species	Core	N	Depth (m)	Wt. % $MgCO_3$	Std. Dev.	Wt. % $CaCO_3$	Std. Dev.
Quinqueloculina lamarckiana	UN79-20	12	102	11.99	0.28	87.98	1.74
Q. lamarckiana	UN81-26	10	150	11.03	0.69	88.46	2.31
Q. lamarckiana	UN81-24	11	260	11.76	0.77	88.26	2.40
Sigmoilina sp.	UN79-09	5	344	8.60	0.34	88.34	0.90
Pyrgoella sphaera	L6-84-SP-15D	5	458	7.85	0.28	89.54	2.63
Sigmoilina sp.	L6-84-SP-15D	10	458	7.39	0.31	90.10	1.29
Sigmoilina sp.	L6-84-SP-15B	8	614	7.32	0.30	90.84	1.98
Sigmoilina sp.	L6-84-SP-15A	7	778	6.92	0.24	91.12	2.19
Sigmoilina sp.	L6-84-SP-15E	8	895	6.55	0.19	91.31	3.03

Figure 4. Comparison of the distribution of magnesium in the tests of calcareous foraminifera and the distribution of temperature with depth. Scale bars = 0.2 mm. A) Weight percent MgCO in perforate tests. B) Weight percent MgCO in imperforate tests. Error bars indicate standard deviations of spot analyses.

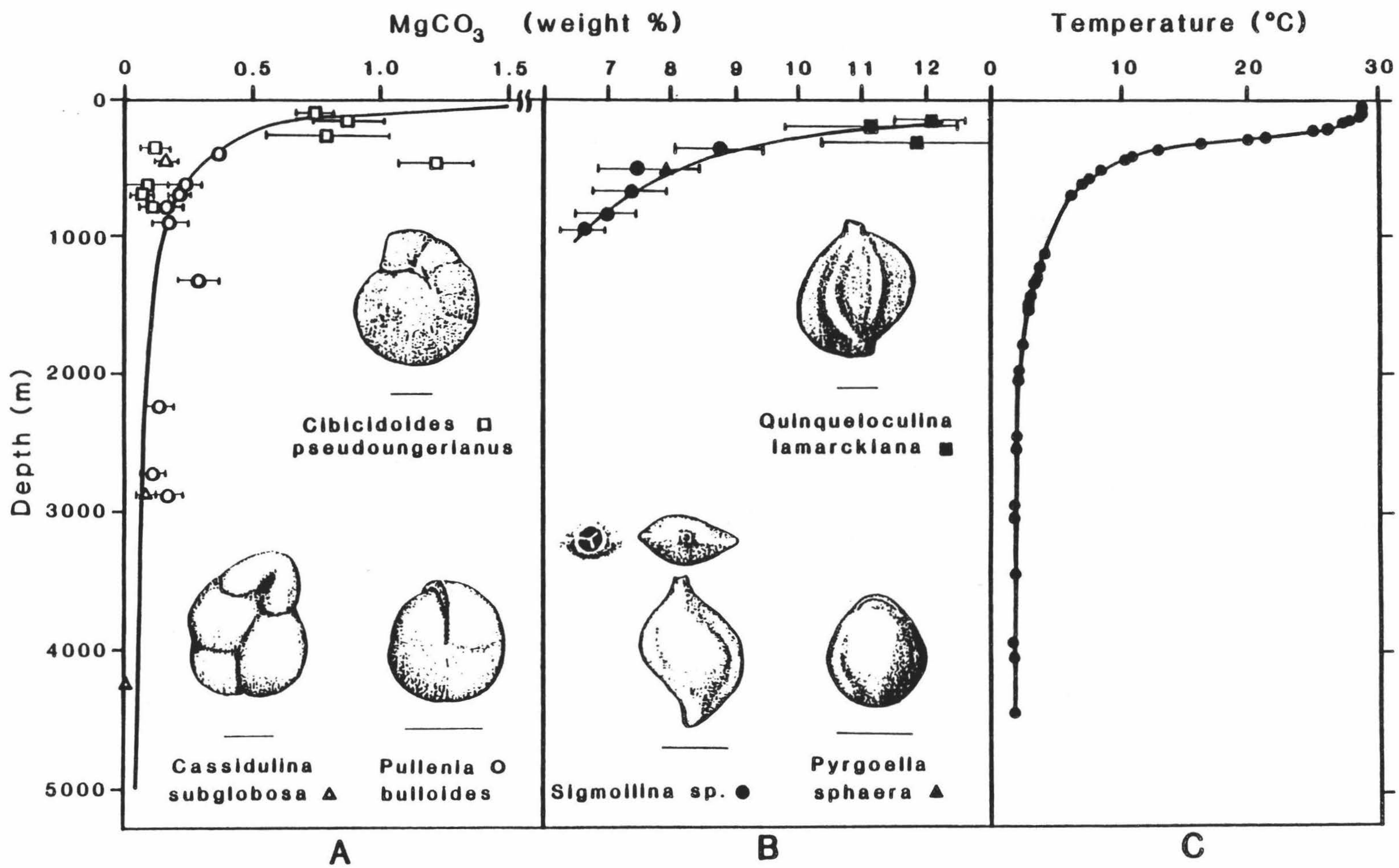
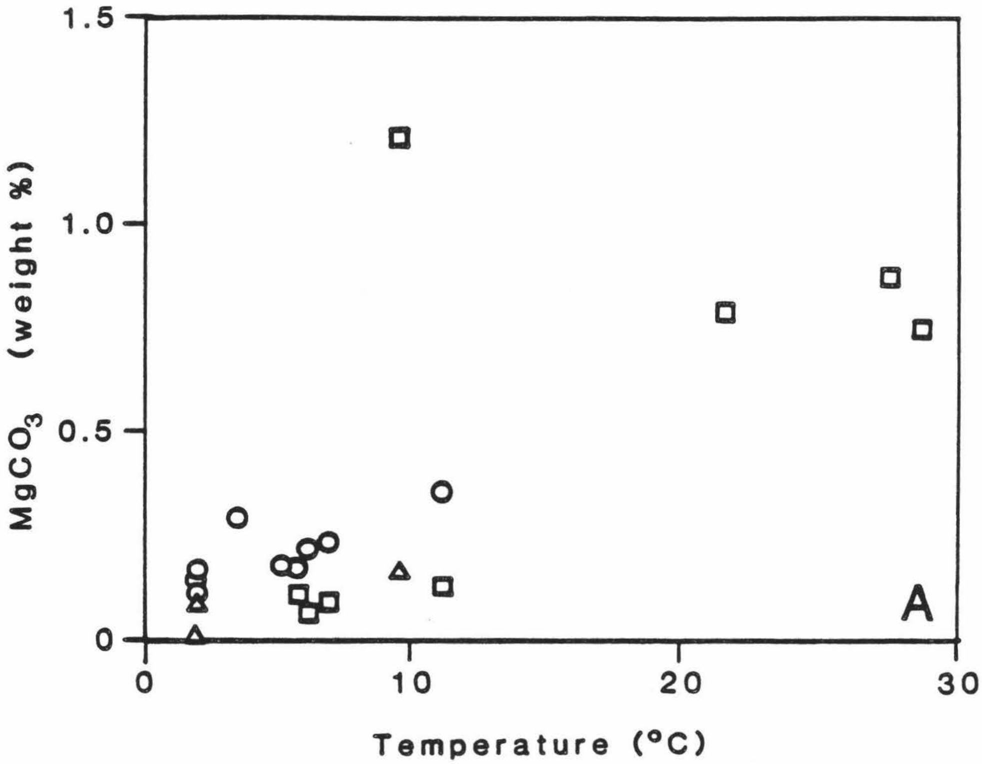
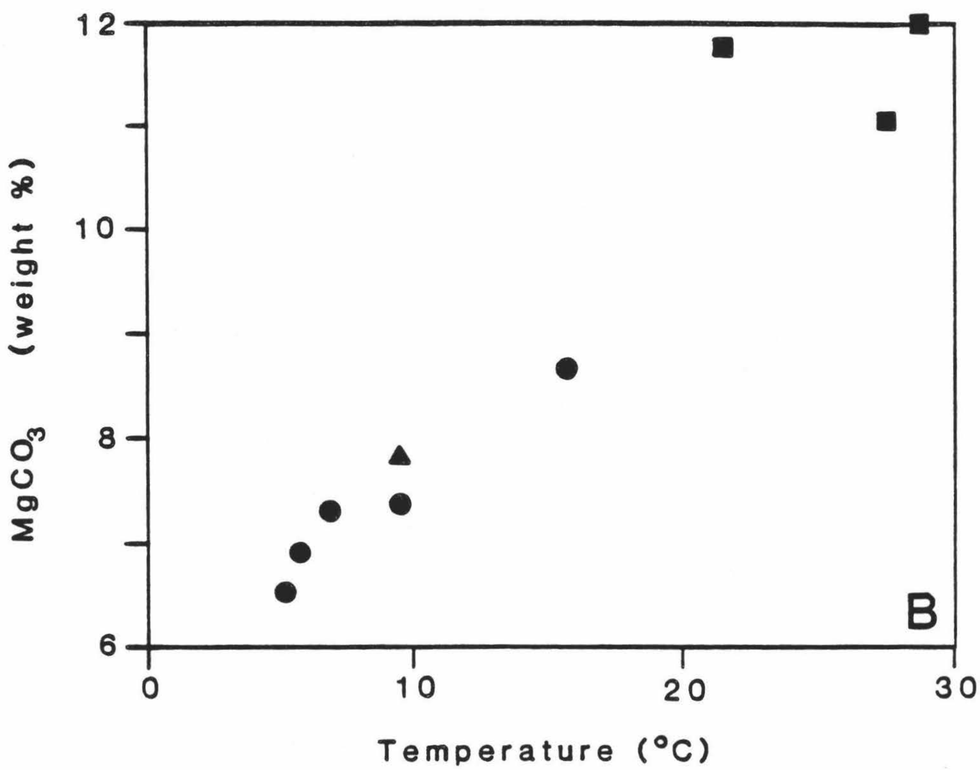

MgCO3 (weight %)
Temperature (°C)
0 0.5 1.0 1.5
7 8 9 10 11 12
0 10 20 30
Depth (m)
0
1000
2000
3000
4000
5000
Cibicidoides pseudoungerianus □
Quinqueloculina lamarckiana ■
Cassidulina subglobosa △
Pullenia bulloides ○
Sigmoilina sp. ●
Pyrgoella sphaera ▲
A
B
C

Figure 5. Relationship between temperature and magnesium concentration in A) low-magnesium foraminifera (correlation coefficient R = 0.72) and B) high-magnesium foraminifera (correlation coefficient R = 0.95). Symbols indicate species as in Figure 4.


1.5
1.0
0.5
0
MgCO3 (weight %)
A
0
10
20
30
Temperature (°C)


12
10
8
6
MgCO3 (weight %)
B
0
10
20
30
Temperature (°C)

large, poorly preserved specimens. The specimens may have been have been transported or altered, thus yielding the anomalously high magnesium concentration. Because of this possibility, and the fact that the magnesium concentration of this specimen lies distant from the rest of the magnesium analyses, this anomalous concentration was eliminated from the computation of the paleotemperature formula for low-magnesium foraminifera.

The partition coefficients of the high-magnesium foraminifera are about 1.5 orders of magnitude greater than those of the low-magnesium foraminifera for comparable temperatures (Tables 5 and 6, Figure 6). The slope of the regression line for the high-magnesium foraminifera is greater than the slope of the line for the low-magnesium foraminifera, which reflects the greater range of magnesium variation in the high-magnesium foraminifera. Both of the regression models are significant at 95% confidence (alpha = 0.05). The formula derived from regression analysis of low-magnesium foraminiferal data is:

$$T(^\circ C) = \frac{[Mg^{++}]/[Ca^{++}]_{f.c.}}{3.22 \times 10^{-4}} - 0.73 .$$

TABLE 5.-- Temperatures (T) of seawater (interpolated from NODC data), partition coefficients (P), regression statistics and water temperatures recalculated using the formula for temperature based on magnesium content in perforate foraminifera (Tm).

Depth	T (° C)	P (x 10^{-4})	Tm (°C)	Tm - T (°C)
102	28.83	17.06	26.12	-2.72
150	27.63	19.65	30.20	2.57
260	21.51	17.89	27.42	5.91
399	10.95	2.92	3.87	-7.07
399	10.95	8.48	12.62	1.68
458	9.46	3.63	4.99	-4.47
614	6.84	2.04	2.48	-4.36
614	6.84	5.55	8.00	-1.17
685	6.10	1.57	1.75	-4.34
685	6.10	5.07	7.25	1.15
778	5.66	2.49	3.19	-2.47
778	5.66	3.95	5.49	-0.17
895	5.10	4.16	5.82	0.72
1320	3.37	6.96	10.22	6.85
2222	2.07	3.25	4.39	2.32
2712	1.94	2.52	3.24	1.30
2876	1.92	3.91	5.42	3.51
2876	1.92	2.12	2.61	0.69
4245	1.90	0.23	-0.37	-2.27

Regression Statistics:

Number of observations = 19
Slope (m) = 0.64 x 10^{-4}
Y intercept = 4.65 x 10^{-5}
R^2 = 0.84

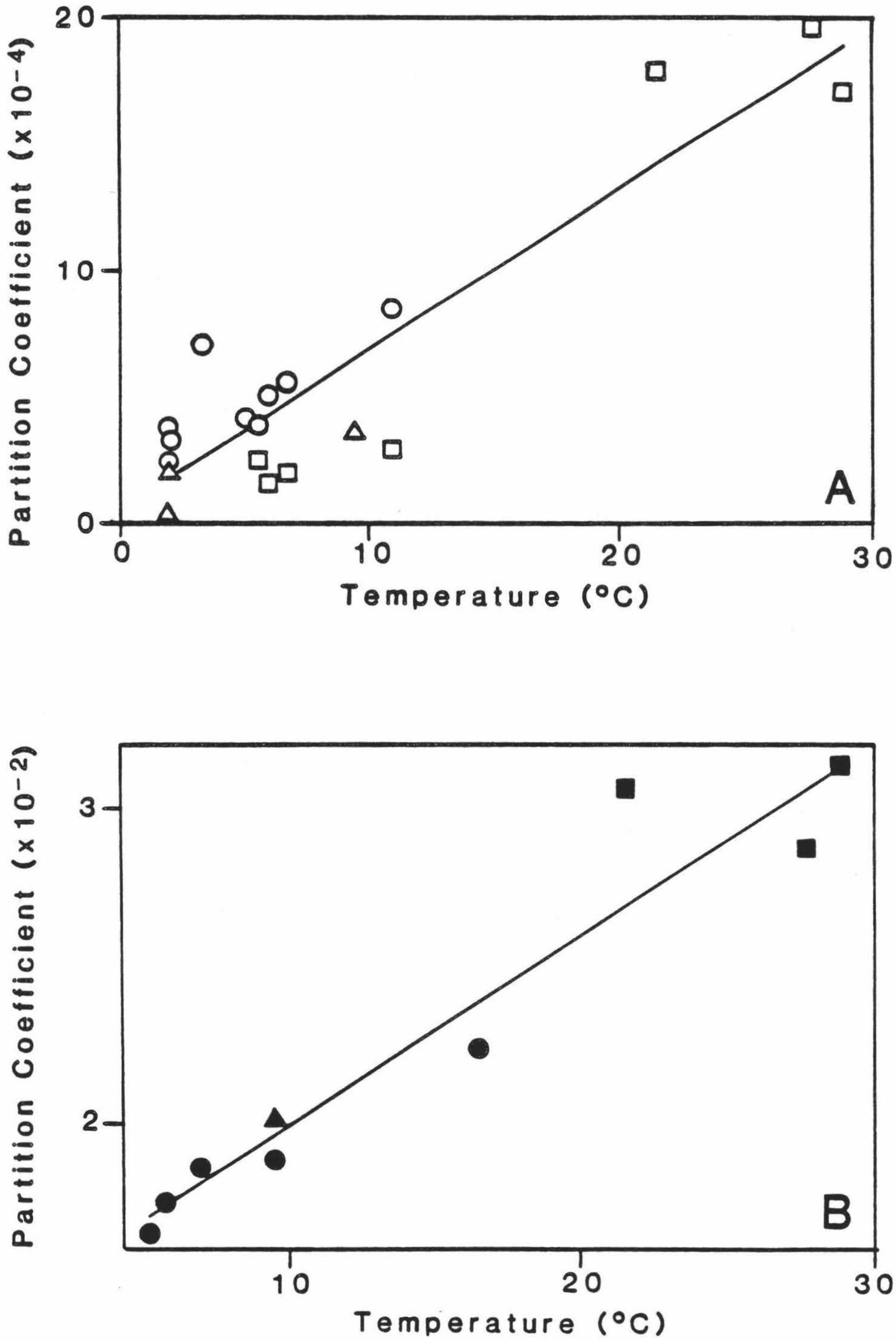
TABLE 6. -- Temperatures (T) of seawater (interpolated from NODC data), partition coefficients (P), regression statistics and water temperatures recalculated using the formula for temperature based on magnesium content in imperforate foraminifera (Tm).

Depth	T (°C)	P (x 10^{-2})	Tm (°C)	Tm - T (°C)
102	28.84	3.13	28.87	0.03
150	27.63	2.87	24.44	-3.19
260	21.51	3.06	27.71	6.20
344	16.40	2.24	14.01	-2.39
458	9.46	2.01	10.31	0.85
458	9.46	1.88	8.15	-1.31
614	6.84	1.85	7.60	0.76
778	5.66	1.75	5.83	0.27
895	5.10	1.65	4.23	-0.87

Regression Statistics:

Number of observations = 9
Slope (m) = 6.02×10^{-4}
Y intercept = 1.40×10^{-2}
$R^2 = 0.92$

Figure 6. Regression line for relationship between water temperature and partition coefficient for A) low-magnesium foraminifera and B) high-magnesium foraminifera. Regression statistics are given in Tables 5 and 6. Symbols correspond to species as in Figure 4.



20
10
0
Partition Coefficient (x10-4)
0
10
20
30
Temperature (°C)
A
3
2
Partition Coefficient (x10-2)
10
20
30
Temperature (°C)
B

The formula for temperature based on high-magnesium foraminiferal data is:

$$T(^\circ C) = \frac{[Mg^{++}]/[Ca^{++}]_{f.c.}}{3.11 \times 10^{-2}} - 23.16 .$$

Differences between the magnesium-based temperatures and the NODC temperatures (Tables 5 and 6) range from 0.69 C to 7.07 C in the low-magnesium foraminifera and from 0.03 C to 6.20 C in the high-magnesium foraminifera.

DISCUSSION

Analyses of individual specimens plot along two separate curves in a graph of depth versus magnesium concentration (Figure 4a, b). As expected from the results of Blackmon and Todd (1959), all perforate species plot on the low-magnesium curve whereas all imperforate species plot along the high-magnesium curve. Separation of the lines of the plot is in agreement with the phylogenetically-linked bimodality of the distribution of foraminiferal species in terms of their magnesium contents.

The bimodal magnesium concentrations in the tests of foraminifera require separation of high-and low-magnesium foraminifera in the correlation analysis and in the partition-coefficient computations. Individuals from the high-magnesium group may grow at the same temperature as individuals from the low-magnesium group, yet precipitate calcite of a different composition. Clearly, the variations in the high- and low-magnesium groups are not described by the same partition coefficients. This difference suggests that the precipitation of calcite from seawater by foraminifera is not governed entirely by the physical properties of the seawater. The chemical microenvironment for the precipitation of skeletal calcite that is provided by the living foraminifer may be a modification of the external physical environment, but is apparently affected by temperature.

Organic material secreted prior to chamber formation controls precipitation of calcite by foraminifera (Arnold, 1964; Angell, 1967; Sliter, 1970; Spindler and Röttger, 1973), but the manner in which the organic material is formed and how the new crystals are arranged differs between perforate and imperforate species. Towe and Cifelli (1967) suggest that for radial and granular walls (in the Rotaliina), growth of crystals proceeds epitaxially after nucleation on organic layers, whereas for porcellaneous walls (in the Miliolina), crystal formation takes place in an organic matrix or "colloid".

The difference in manner of calcification may be the cause of the observed difference in chemical composition between imperforate and most perforate tests, but cannot account for the high magnesium contents (more than 10 mol %) measured in some perforate foraminifera (Blackmon and Todd, 1959). Alternatively, the difference between high- and low-magnesium tests may reflect the ability of the foraminifera to provide a solution from which high- or low-magnesian calcite may be precipitated.

Temperature effects -- Although the foraminifera are divided into two groups with distinctly different magnesium compositions, the parallel between the high- and low-magnesium curves and the temperature-depth curve supports the conclusion that the magnesium content in the calcite of foraminifera is related to temperature. Despite individual deviations, all low-magnesium specimens appear to plot along a single curve, irrespective of taxonomic classification (Figure 4a). The curve is also congruent with the curve from previous analyses of *Cassidulina subglobosa* and *C. oriangulata* from the same Solomon Islands/Ontong Java Plateau samples (Chapter 2). The magnesium concentrations in the three species, *Cibicidoides pseudoungerianus*, *Pullenia bulloides*, and *Cassidulina subglobosa*, analyzed in this study, as well as *C. oriangulata* analyzed in Chapter 2, behave similarly under the same temperature conditions. The high-magnesium species also plot along a single curve, which suggests that magnesium concentration in the calcite of the tests of the three imperforate species Quinqueloculina lamarckiana, Pyrgoella sphaera, and Sigmoilina sp. behave similarly under the same temperature conditions. The temperature effects described here are variations within the low- and high-magnesium groups, and are not responsible for the difference between these groups.

Whether temperature actually affects the calcite composition directly or by means of some temperature-related parameter such as growth rate, as suggested for other organisms by Moberly, 1968, and Weber, 1973, is not certain. Although temperature has been shown to have an effect on the rate of chamber addition in foraminifera (Bradshaw, 1957), it is not known whether temperature causes changes in the rate of precipitation of test calcite. Whereas growth rate for organisms that secrete calcite continually during growth may serve as a measure of the rate of precipitation of calcite by the organism, the growth rate in foraminifera is not necessarily a measure of precipitation rate because growth proceeds by periodic addition of chambers to the test.

Calcite formed physiochemically from seawater (cement and recrystallized material) show a depth trend similar to the curve for the imperforate foraminifera. In contrast, the perforate foraminiferal species in this study have magnesium contents much lower than physiochemically precipitated calcite from comparable depths and temperatures (compare, for example, calcites studied by Schlager and James, 1978, and Land and Moore, 1980). The magnesium-temperature relationship of the high-magnesium foraminifera is also similar to the magnesium-temperature relationship described for calcites that were artificially precipitated from seawater by Burton and Walter (1987). It is possible that the high-magnesium foraminifera are precipitating calcite that is at or near equilibrium with the surrounding water, whereas the low-magnesium foraminifera are precipitating calcite that is not in equilibrium with the seawater. Still, temperature controls the amount of magnesium (higher temperatures result in higher magnesium) in calcites precipitated artificially from seawater (Mackenzie and others, 1983) and may also control the concentration of magnesium within a foraminiferal skeleton, even though the protoplasm of the organism is able to create a microenvironment suitable for precipitating calcites that would otherwise be metastable in the surrounding seawater.

As the R^2 statistic ("goodness of fit") indicates, the fit of the data to the regression line is better for the high-magnesium foraminifera (Figure 6b) than for the low-magnesium foraminifera (Figure 6a). Expressed as a percentage, the R statistic may be interpreted as the amount of the total variance explained by the regression. For the low-magnesium foraminifera, the value of R is 0.84; only 84% of the total variation is explained by linear regression. On the other hand, the value of R^2 for the high-magnesium foraminifera is 0.92; 92% of the total varance is explained by linear regression. Although linear models for both data sets are significant, the model for the high-magnesium foraminifera fits its data far better than the model for the low-magnesium foraminifera fits the low-magnesium data.

The small range over which the low-magnesium foraminifera vary (only about 1.2 weight percent difference between the lowest and highest $MgCO_3$ concentrations in this group of foraminifera) and the accuracy of the microprobe (explained above) accounts for some of the unexplained variance in that regression. Small variations resulting from analytical errors are amplified because the total variance is small. In contrast, the large range of magnesium concentrations in the high-magnesium foraminifera (about 5.5 weight percent difference between the lowest and highest $MgCO_3$ concentrations) accounts for such a large part of the total variance that small variation resulting from analytical errors are not apparent.

A second possible source of unexplained variation is diagenetic alteration. Chemical alteration in fossil and subfossil specimens of foraminifera may occur even where specimens showing no recrystallization or other visible evidence of alteration (Krinsley, 1960; Towe and Hemleben, 1976; Lorens and others, 1977). Effects such as overgrowths of higher- or lower-magnesium calcite on preexisting skeletal calcite (Morse and others, 1979) or selective crystal solution (Lorens and others, 1977) or cation exchange without microsolution-reprecipitation (Towe and Hemleben, 1976) are surficial and were avoided in the present study by probing sites distant from external surfaces of the specimens.

The better fit of the high magnesium data to its regression model is also reflected in the magnesium temperatures recomputed by application of formulas derived from the regression analysis. Magnesium-based temperatures from high-magnesium foraminifera correspond more closely to the NODC temperatures than temperatures derived from the formula for low-magnesium foraminifera (Tables 5, 6). The average of the absolute value of the difference between NODC and magnesium-based temperatures is only 2.55° C in the high-magnesium data, but is 4.40° C in the low-magnesium data. The formula derived for temperature based on high-magnesium foraminifera therefore more accurately reproduces the original temperature data.

High-magnesium foraminifera are preferred over low-magnesim foraminifera as paleotemperature indicators because they are less affected by experimental errors, but the majority of high-magnesium foraminifera belong to the Miliolina, which are most abundant in shallower-water environments, or to shallow-water genera of the Rotaliina (Blackmon and Todd, 1959). The low-magnesium perforate foraminifera occur over a greater depth range and may become useful where the high-magnesium foraminifera do not occur.

Conclusions

The foraminifera studied in this investigation show temperature-linked variation in magnesium concentration in the calcite of their tests. The species studied plot along two separate magnesium-depth curves, one with high-magnesian calcite and the other with low-magnesian calcite, but both curves parallel the temperature-depth curve for the area from which the specimens were collected.

All three imperforate species studied plot on the single high-magnesium curve, which suggests that the magnesium concentrations in these three species vary similarly with temperature. This similarity is particularly important where species have small depth ranges, as it permits several species to be used together in reconstruction of paleotemperature of sediments that have accumulated at various depths. If the relationship of temperature to magnesium of other species may be considered the same, the depth range over which paleotemperature may be determined, without phylogenetic overprints, is expanded to include the combined ranges of the species.

Similarly, the variation of magnesium with temperature in the three perforate foraminifera is the same, which suggests that the three species vary similarly with temperature and that their magnesium compositions can be treated the same in paleotemperature determinations. These foraminifera, however, all fall in the low-magnesian calcite range, and therefore as a group do not react to temperature exactly as do the high-magnesium foraminifera. Thus, although either high- or low-magnesium foraminifera could be used to determine paleotemperature, the two groups must be treated separately. A fundamental difference in the nature of calcite precipitation exists between the high- and low-magnesium forminifera, and these differences are apparent in the partition coefficients.

The use of high-magnesium foraminifera in the study of paleotemperatures is preferred over the use of low-magnesium foraminifera, because the wider range of magnesium is less susceptible to analytical error and recomputation of temperature using the formula derived for high-magnesium foraminifera more accurately reproduces original temperature data. Whereas the foraminifera with high-magnesian calcite belong mainly to the Miliolina which become rarer in deeper water, it may be necessary to use the low-magnesium foraminifera to determine paleotemperature where the high-magnesium foraminifera do not occur.

The partition coefficients presented here and the relationship of these coefficients to water temperature can be refined with more measurements of temperature and magnesium concentration in foraminifera. As the data base increases with future studies, the relationship between temperature and magnesium will become more reliable as a measure of paleotemperature.

CHAPTER 4

EFFECTS OF PALEOTEMPERATURE AND DIAGENESIS ON MAGNESIUM AND IRON CONCENTRATIONS IN THE TESTS OF BENTHIC FORAMINIFERA FROM SELECTED HOLES OF ODP LEG 112, PERUVIAN CONTINENTAL MARGIN

SYNOPSIS

Concentration of magnesium in the calcite of benthic foraminiferal tests from Leg 112 of the Ocean Drilling Program (Peruvian continental margin) show both intrasample and intersample variations. Mixing and time averaging of foraminifera that lived within the thermocline probably accounts for much of the intrasample variation, whereas changes in water temperature through time accounts for variation between samples. Part of the variation may be due to diagenesis. The down-hole record of foraminiferal magnesium contents of sites that have remained above the thermocline (e.g. Site 681) are characterized by high intrasample variability, whereas sites that have remained in cold water below the thermocline (e.g. Site 684) show little variation both within and between samples. Sites that have passed into and out of the thermocline because of sea-level changes or tectonism (e.g. Sites 680, 686, and 687) show intervals

of high intrasample variation (shallow periods) alternating with intervals of low intrasample variation (deep periods). Concentrations of iron in benthic foraminifera are generally less than 0.10 weight percent, but some fossil foraminifera have greater concentrations. High iron concentrations occur in specimens with pyrite contaminants, but microanalyses suggest that iron may be incorporated in foraminferal calcite in amounts greater than previously thought.

INTRODUCTION

Results of studies of the relationship between water temperature and the magnesium content of calcite in the tests of foraminifera suggest that the variation in magnesium of fossil foraminifera may be used as paleotemperature indicators (Chave, 1955; Savin and Douglas, 1973; Bender and others, 1975; Duckworth, 1979; Cronblad and Malmgren, 1981; Chapter 2). Benthic foraminifera provide ideal material for the study of temperature effects on magnesium content in biogenic calcite because they live (and their remains accumulate) at a variety of depths and temperatures. Modern benthic foraminifera show magnesium variation that parallels the temperature structure with depth in the oceans (Chapter 2). If preserved in the fossil record, the magnesium-temperature relationship in benthic foraminifera could be used to reconstruct paleoenvironments. The temperature relationship is not a simple one, however, because it is obscured by effects from other factors unrelated to temperature including phylogenetic or "vital" effects and diagenesis. The objectives of the present study include testing if the relationships between temperature and magnesium content in modern benthic foraminifera can be applied to the fossil record and identification of the limitations of utilizing foraminiferal magnesium content as paleotemperature indicators.

Diagenesis may alter the composition of fossil tests such that the original magnesium contents are lost. Physiochemical alteration may occur very early after necrolysis of the protective organic covering on foraminiferal tests (Krinsley, 1960; Lorens and others, 1977; Towe and Hemleben, 1976; Berger, 1970). The possibility also exists of physiochemical precipitates forming on the surface of the foraminiferal calcite (Morse et al., 1979). After burial, tests may be exposed to porewaters with chemistry different from the seawater from which the living foraminiferan secreted its test. These porewaters may further alter the chemical compositions of foraminiferal remains and render them unsuitable for paleotemperature analysis.

The presence of iron in foraminiferal calcite has been reported by previous workers (Emiliani, 1955; Lipps and Ribbe, 1967; Chapter 2). Although iron probably occurs as a contaminant on the tests of some foraminifera, small concentrations (less than 0.10 weight percent) may actually occur in the crystal lattice of foraminiferal calcite (Lipps and Ribbe, 1967). The environmental significance of the presence of iron in foraminiferal tests is unclear. The variation of this element in foraminifera is difficult to measure with the microprobe because concentrations are so small. Unusually high concentrations of iron (greater than about 0.10 weight percent) may, however, be a useful indicator of diagenetic alteration or the influence of contaminants on the apparent concentrations of minor elements in chemical analyses of foraminiferal remains (Lipps and Ribbe, 1967).

METHOD

A total of 115 specimens representing 16 different benthic species (Table 7) were picked from sieved samples from holes 680B, 681A, 684A, 686A, and 687A of ODP Leg 112 (Figure 7). The holes were selected because benthic foraminiferal census data indicate that the sites had undergone changes in depth and temperature (Resig, 1988, pers. commun.). Most specimens were picked from

TABLE 7. -- List of species selected for microanalysis. Numbers on the left correspond to nembers in Figure 9.

1. *Angulogerina carinata* Cushman
2. *Bolivina plicata* d'Orbigny
3. "*Bolivina*" sp.
4. *Bolivinellina seminuda* (Cushman) var. *humilis* (Cushman and McCulloch)
5. *Brizalina interjuncta* (Cushman)
6. *Brizalina spissa* (Cushman)
7. *Buliminella subfusiformis* Cushman
8. *Cancris inflatus* (d'Orbigny)
9. *Cassidulina detierraensis* McCulloch
10. *Cassidulina pulchella* d'Orbigny
11. *Epistominella afarensis* McCulloch
12. *Hanzawaia nitidula* (d'Orbigny)
13. *Nonionella auris* (d'Orbigny)
14. *Nonionella chiliensis* Cushman and Kellett
15. *Uvigerina peregrina* Cushman
16. *Uvigerina striata* d'Orbigny

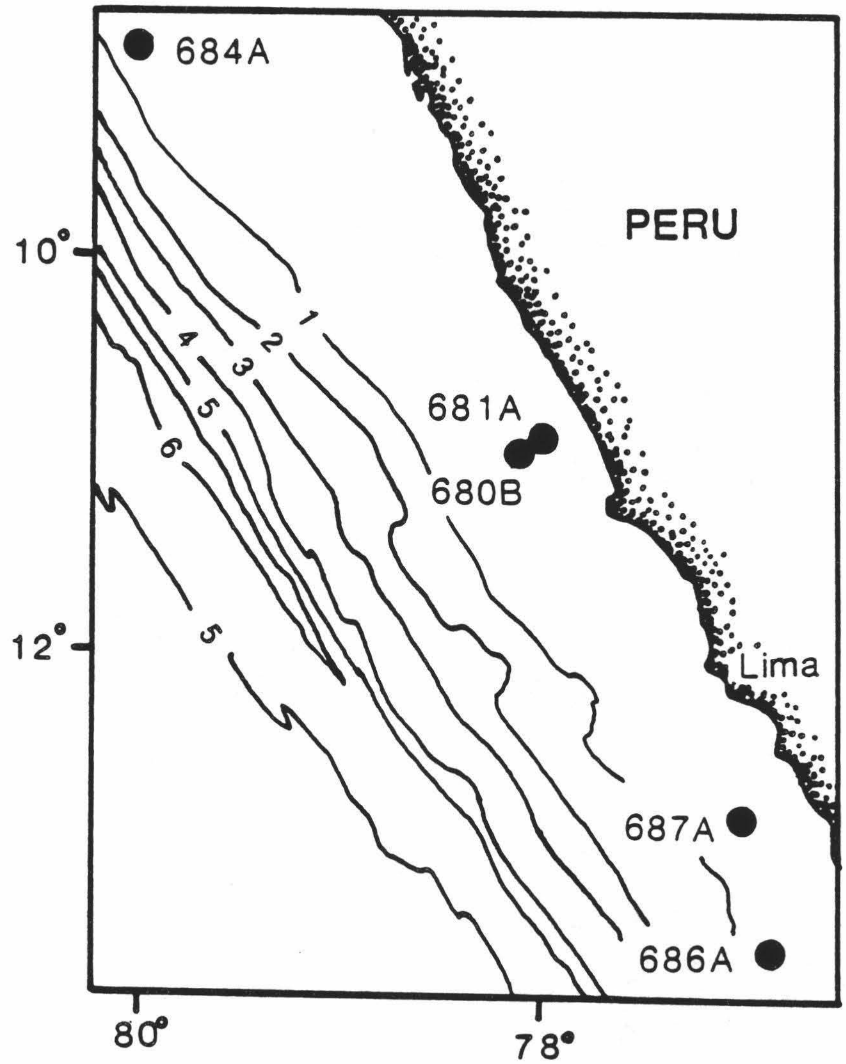


Figure 7. Map of O.D.P. Leg 112 drill sites used in this study. Bathymetric contour interval = 1,000 m.

core-catcher samples, but a few specimens were picked from samples taken from sections within the cores.

The criteria for selecting which species would be analyzed were size and abundance. Larger species are easier to probe than small species; abundant species are more representative of the environment and easier to find than rare species. To reduce phylogenetic effects, however, the total number of species used in the analysis was limited to only 16 belonging to genera that have low-magnesian calcite (Blackmon and Todd, 1959). These species were not necessarily the most abundant species but ones that occurred in relatively high proportions in many samples. Not all samples yielded specimens that were suitable for microanalysis. In some samples the foraminifera were too small to probe; some other samples were barren.

Concentrations of magnesium, iron and calcium in the foraminiferal calcite were measured using the techniques described in Chapter 2. As many as 20 spots were analyzed on a single specimen; multiple analyses on a specimen were averaged. The number of spots analyzed on each specimen depended on the availability of well-polished surface areas free of pores and other surface imperfections. The amount of optimum surface area was determined by the size of the specimen, the thickness of the wall, the density of pores, and the orientation of the test in the mount.

Variability of the concentration of $MgCO_3$ and $FeCO_3$ in their respective standards serves as a measure of the precision of the analyses. The standard deviation of the $MgCO_3$ in the dolomite standard was 0.61 or 1.34 percent of the mean value of 45.53 weight percent; the standard deviation of $FeCO_3$ in the siderite standard was 1.33, or 1.40 percent of the mean value of 95.25 weight percent. Microprobe accuracy is indicated by the differences between the analyzed and given compositions in the standards. The concentration given for $MgCO_3$ in the dolomite standard (45.55 weight percent) differs from the average analyzed concentration by 0.02 weight percent or 0.04 percent of the given value. The difference between the analyzed and given (95.25 weight percent) concentrations in the siderite standard was less than 0.01 weight percent.

Because magnesium is the cation of principal interest in this study, it is helpful to know the precision of the microprobe at concentrations of magnesium near the range expected for low-magnesian foraminiferal calcites (between 0.0 and 1.0 weight percent). The microprobe consistently measured $MgCO_3$ in the siderite sample within a range of 0.11 to 0.46 weight percent. Although no value was given for $MgCO_3$ in the wet-chemical analysis of the siderite (Jarosewich and MacIntyre, 1983), the precision of the measurements is indicated by the mean (0.34 weight percent) and standard deviation (0.07 or 21 percent of the mean) of the microprobe analyses of the siderite standard.

RESULTS

Hole 680B

All 23 specimens yielded low-magnesian calcite compositions of 0.07 to 1.25 weight percent $MgCO_3$ (Table 8). The two highest magnesium contents occur in specimens of Nonionella auris from sample 2CC (15.2 mbsf), which also has the highest degree of variability within a sample. Sample 1CC also contains considerable variation of magnesium content among specimens collected from that sample; other samples exhibit relatively little intrasample variation. Except for sample 6CC all samples from Hole 680B from 1CC (5.3 mbsf) through 7CC (62.4 mbsf), where the major portion of sediment was recovered, contained specimens large enough to probe. Sample 6CC contained a fairly large number of Bolivinellina seminuda var. humilis, but the specimens were too small for microanalysis.

Iron concentrations in the calcite of foraminifera from Hole 680A are all low (less than about 0.10 weight

Table 8. -- Results of microanalyses of fossil benthic foraminifera from Hole 680B. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 680B

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(° C)
Sample 1CC (5.3 mbsf)								
Cassidulina pulchella	1	0.43	--	102.54	--	0.09	---	14.72
Cassidulina pulchella	4	0.08	0.06	97.78	1.58	0.07	0.08	2.28
Cassidulina pulchella	6	0.11	0.02	97.20	1.22	0.10	0.05	3.36
Cancris inflatus	10	0.24	0.27	97.64	1.21	0.04	0.06	8.36
Sample 2CC (15.2 mbsf)								
Nonionella auris	5	1.03	0.13	96.14	2.16	0.03	0.04	36.53
Nonionella auris	6	1.25	0.27	95.32	1.91	0.06	0.07	48.96
Cancris inflatus	12	0.22	0.14	97.66	1.68	0.03	0.06	7.09
Sample 3CC (24.7 mbsf)								
Cancris inflatus	19	0.22	0.30	101.70	1.28	0.04	0.05	7.09
Cancris inflatus	11	0.08	0.07	100.73	2.50	0.04	0.05	2.27
Brazilina interjuncta	12	0.18	0.13	101.18	0.87	0.05	0.06	5.75
Brazilina interjuncta	15	0.11	0.07	101.34	1.12	0.04	0.06	3.31
Cassidulina detierraensis	13	0.17	0.10	101.46	0.98	0.04	0.06	5.26
Cassidulina detierraensis	10	0.12	0.05	101.72	1.06	0.05	0.06	3.65
Sample 4CC (34.1 mbsf)								
Cassidulina detierraensis	13	0.09	0.04	99.22	1.30	0.01	0.03	2.69
Cancris inflatus	13	0.11	0.08	98.88	1.80	0.01	0.03	3.37
Angulogerina carinata	3	0.13	0.06	97.50	2.24	0.01	0.01	4.18

TABLE 8. (Continued) -- Results of microanalyses of fossil benthic foraminifera from Hole 680B. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 680B

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
		Sample 5CC (43.6 mbsf)						
Bolivinellina humilis	3	0.08	0.02	95.79	0.91	0.01	0.02	2.46
Cancris inflatus	10	0.13	0.08	98.32	2.04	0.02	0.05	3.96
Cancris inflatus	8	0.07	0.05	99.42	1.69	0.03	0.03	1.82
Cassidulina pulchella	3	0.07	0.04	96.60	0.62	0.03	0.05	2.05
		Sample 7CC (62.4 mbsf)						
Nonionella auris	8	0.24	0.05	98.24	3.22	0.36	0.09	8.27
Nonionella auris	9	0.23	0.08	100.12	2.65	0.50	0.29	7.77
Nonionella auris	10	0.26	0.06	98.50	2.02	0.29	0.09	8.84

percent) except for those from 7CC, where individual iron concentrations range from 0.29 to 0.50 weight percent. Small yellow (in reflected light) crystals of pyrite are present as physiochemical precipitates in the chambers of some specimens from this sample.

Hole 681A

The 26 specimens from Hole 681A measured low-magnesian calcite between 0.08 (Cancris inflatus from 110.9 mbsf) and 0.42 (Nonionella auris from 44.6 mbsf) weight percent $MgCO_3$ (Table 9). All samples for which more than one specimen was analyzed exhibit moderate intra-sample variation, with the exception of 13CC (115.0 mbsf) where the two data points are relatively close together.

The highest iron concentraton in specimens from this hole (0.15 weight percent) occurred in a specimen of Nonionella auris from 8CC (73.3 mbsf). All other specimens, including two specimens from sample 8CC, had concentrations of $FeCO_3$ less than 0.10 weight percent. Variability within samples, except in 8CC, is small.

Hole 684A

Only three samples between 1CC (5.2 mbsf) and 5CC (43.2 mbsf) from Hole 684A yielded specimens that could be

TABLE 9. -- Results of microanalyses of fossil benthic foraminifera from Hole 681A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 681A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(° C)
Sample 1CC (6.3 mbsf)								
Cassidulina pulchella	8	0.24	0.06	101.57	2.06	0.06	0.05	7.90
Sample 5CC (44.6 mbsf)								
Hanzawaia nitidula	10	0.15	0.07	99.68	1.47	0.07	0.07	4.92
Nonionella auris	9	0.42	0.16	97.51	2.31	0.07	0.05	15.29
Nonionella chiliensis	11	0.22	0.06	98.33	1.26	0.05	0.07	7.44
Sample 6CC (45.0 mbsf)								
Cancris inflatus	5	0.10	0.06	97.09	1.44	0.09	0.10	3.06
Nonionella chiliensis	9	0.24	0.08	98.51	1.74	0.06	0.09	8.10
Hanzawaia nitidula	10	0.16	0.08	100.38	0.61	0.06	0.04	5.18
Sample 7CC (63.1 mbsf)								
Cassidulina pulchella	8	0.19	0.05	101.63	2.43	0.02	0.03	6.01
Cassidulina detierraensis	12	0.09	0.04	101.94	1.69	0.07	0.08	2.67
Cancris inflatus	8	0.13	0.08	101.64	2.84	0.04	0.04	3.98
Sample 8CC (73.3 mbsf)								
Nonionella auris	2	0.28	0.00	96.04	0.30	0.09	0.12	10.01
Nonionella auris	8	0.25	0.07	98.38	2.69	0.15	0.10	8.66
Hanzawaia nitidula	15	0.16	0.10	102.23	1.56	0.04	0.06	4.85

TABLE 9. (Continued) -- Results of microanalyses of fossil benthic foraminifera from Hole 681A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 681A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
	Sample 9CC (82.7 mbsf)							
Nonionella auris	2	0.30	0.03	95.91	0.49	0.07	0.09	10.79
	Sample 10CC (88.2 mbsf)							
Epistominella afueraensis	9	0.26	0.10	102.64	1.55	0.02	0.05	8.64
Epistominella afueraensis	3	0.16	0.04	99.99	4.61	0.03	0.02	5.27
	Sample 11CC (99.2 mbsf)							
Buliminella subfusiformis	9	0.16	0.12	98.68	3.03	0.02	0.03	5.39
Buliminella subfusiformis	6	0.23	0.11	98.90	2.22	0.03	0.06	7.76
Buliminella subfusiformis	3	0.12	0.04	97.29	0.61	0.06	0.07	3.70
	Sample 12CC (110.9 mbsf)							
"Bolivina" sp.	5	0.09	0.05	102.60	2.04	0.01	0.02	2.36
Buliminella subfusiformis	7	0.19	0.10	98.71	1.89	0.02	0.06	6.25
Nonionella auris	6	0.28	0.07	99.49	0.70	0.03	0.03	9.34
Cancris inflatus	8	0.08	0.08	100.58	1.03	0.02	0.04	2.24
	Sample 13CC (115.0 mbsf)							
Buliminella subfusiformis	3	0.34	0.15	96.29	0.41	0.02	0.04	12.38
Buliminella subfusiformis	1	0.32	----	97.75	----	0.00	----	11.32
	Sample 14CC (124.8 mbsf)							
Buliminella subfusiformis	5	0.18	0.11	99.04	1.65	0.06	0.05	6.04

probed (Table 10). All species from this sample contained low concentrations of magnesium. Sample 1CC yielded specimens with the highest as well as the lowest magnesium contents, but the difference between these concentrations is small (the lowest concentration, 0.16 weight percent, occurred in Cancris inflatus; highest concentration, 0.25 weight percent, occurred in Cassidulina pulchella). The distribution of magnesium in foraminiferal tests from Hole 684A exhibits the least variation of all the holes studied.

The 7 specimens of foraminifera from Hole 684A measured between 0.02 and 0.05 weight percent $FeCO_3$ (Table 10). Foraminifera from this hole varied least in iron concentration, both within as well as among samples, of all holes in this study.

Hole 686A

As in the holes discussed previously, all foraminiferal tests from Hole 686A (Table 11) were formed of low-magnesian calcite. The lowest magnesium concentration (0.06 weight percent $MgCO_3$) occurred in a specimen of Bolivinellina seminuda var. humilis from sample 17CC (148.7 mbsf); the highest concentration (0.81 weight percent $MgCO_3$) occurred in the same species from sample 16CC (139.2 mbsf). Variation of analyses in

TABLE 10. -- Results of microanalyses of fossil benthic foraminifera from Hole 684A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 684A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(° C)
Sample 1CC (5.2 mbsf)								
Cancris inflatus	10	0.16	0.08	101.99	1.60	0.03	0.04	4.87
Cassidulina pulchella	6	0.25	0.09	99.09	2.49	0.02	0.03	8.67
Sample 4CC (33.7 mbsf)								
Bolivina plicata	9	0.18	0.14	98.43	1.98	0.04	0.05	6.01
Uvigerina peregrina	8	0.22	0.27	98.94	2.16	0.02	0.05	7.31
Brizalina spissa	10	0.22	0.13	101.00	1.16	0.02	0.02	7.19
Sample 5CC (43.2 mbsf)								
Uvigerina peregrina	8	0.18	0.08	97.03	2.94	0.05	0.05	6.10
Bolivina plicata	8	0.20	0.10	100.55	1.39	0.04	0.07	6.56

TABLE 11. -- Results of microanalyses of fossil benthic foraminifera from Hole 686A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 686A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
Sample 1-1 (0.0 mbsf)								
Cassidulina detierraensis	10	0.07	0.05	102.28	1.13	0.03	0.05	1.86
Brazilina interjuncta	7	0.08	0.03	99.35	2.16	0.06	0.08	2.28
Sample 2-7 (13.0 mbsf)								
Brazilina interjuncta	13	0.17	0.11	99.32	1.88	0.07	0.06	5.47
Cassidulina detierraensis	16	0.14	0.07	100.32	1.44	0.03	0.05	4.38
Sample 8CC (64.7 mbsf)								
Epistominella afueraensis	9	0.19	0.18	101.38	1.52	0.11	0.10	6.10
Sample 9CC (71.6 mbsf)								
Cassidulina pulchella	10	0.15	0.07	102.41	0.44	0.07	0.07	4.56
Cassidulina pulchella	12	0.10	0.05	102.18	0.96	0.05	0.07	3.02
Cassidulina pulchella	10	0.10	0.05	101.20	1.72	0.06	0.06	2.76
Sample 13CC (111.1 mbsf)								
Cassidulina pulchella	9	0.16	0.13	100.36	1.16	0.10	0.09	5.21
Cassidulina pulchella	7	0.18	0.05	101.87	2.76	0.09	0.10	5.74
Sample 14CC (113.2 mbsf)								
Cassidulina pulchella	10	0.12	0.08	101.26	1.23	0.03	0.05	3.56

TABLE 11. (Continued) -- Results of microanalyses of fossil benthic foraminifera from Hole 686A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 686A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
Sample 15CC (133.3 mbsf)								
Cassidulina pulchella	7	0.20	0.04	100.57	2.38	0.04	0.05	6.45
Sample 16CC (139.2 mbsf)								
Cassidulina pulchella	4	0.13	0.03	100.64	2.53	0.04	0.31	3.88
Cassidulina pulchella	13	0.13	0.08	100.25	1.83	0.08	0.07	3.93
Cassidulina pulchella	9	0.20	0.14	101.30	3.57	0.08	0.07	6.54
Cassidulina pulchella	9	0.13	0.09	100.39	2.11	0.05	0.08	4.17
Bolivinellina seminuda	5	0.81	0.43	100.15	3.67	0.03	0.04	29.20
Sample 17CC (148.7 mbsf)								
Bolivinellina seminuda	3	0.06	0.04	100.49	2.48	0.06	0.03	1.58
Bolivinellina seminuda	4	0.16	0.02	94.42	1.97	0.02	0.02	5.52
Bolivinellina seminuda	4	0.09	0.06	97.19	1.30	0.05	0.05	2.68
Sample 18-5 (154.5 mbsf)								
Cassidulina pulchella	10	0.15	0.05	98.20	1.09	0.11	0.08	5.01
Sample 18CC (158.7 mbsf)								
Bolivinellina seminuda	9	0.36	0.38	99.67	2.33	0.05	0.06	12.65
Cassidulina pulchella	11	0.15	0.04	101.01	1.14	0.08	0.06	4.60

TABLE 11. (Continued) -- Results of microanalyses of fossil benthic foraminifera from Hole 686A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 686A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
Sample 19CC (167.6 mbsf)								
Cassidulina pulchella	6	0.21	0.05	100.42	2.39	0.04	0.05	6.79
Cassidulina pulchella	11	0.22	0.19	101.41	2.21	0.06	0.08	7.11
Cassidulina pulchella	9	0.19	0.09	99.38	2.38	0.05	0.05	6.24
Bolivinellina seminuda	7	0.20	0.09	97.16	1.42	0.07	0.06	6.89
Sample 20CC (177.2 mbsf)								
Hanzawaia nitidula	10	0.10	0.07	99.48	1.74	0.04	0.04	3.01
Cassidulina pulchella	10	0.21	0.10	100.41	2.80	0.11	0.09	6.94
Sample 21CC (186.7 mbsf)								
Bolivinellina humilis	4	0.24	0.14	101.73	0.65	0.11	0.13	7.78
Sample 22CC (187.1 mbsf)								
Hanzawaia nitidula	15	0.18	0.24	101.63	1.18	0.06	0.07	5.83
Hanzawaia nitidula	12	0.15	0.11	101.31	1.47	0.06	0.08	4.62
Sample 23CC (204.6 mbsf)								
Nonionella auris	8	0.29	0.11	99.99	1.69	0.08	0.09	10.10

samples from Hole 686A is low to moderate, with the exception of sample 16CC where the specimen of _B_. _seminuda_ var. _humilis_ with the highest magnesium content occurs together with specimens of _Cassidulina pulchella_ containing only 0.13 and 0.20 weight percent $MgCO_3$.

Concentrations of iron in specimens from Hole 686A ranged from 0.02 to 0.11 weight percent $FeCO_3$. The majority of the specimens measured less than 0.10 weight percent $FeCO_3$. Variation within samples is small. The interior of the chambers of a specimen of _Epistominella afueraensis_ from sample 8CC (64.7 mbsf) contained small pyrite crystals. This specimen was among three that showed the highest concentrations of iron.

Hole 687A

All nonrecrystallized specimens in Hole 687A measured in the low-magnesian calcite range (Table 12). The highest magnesium content among nonrecrystallized specimens (1.03 weight percent $MgCO_3$) occurred in a specimen of _Nonionella auris_ from 121.2 mbsf; the lowest content occurred in a specimen of _Cancris inflatus_ from 45.4 mbsf. The magnesium data show moderate to low variation except in sample 12CC (104.2 mbsf) where specimens of _Nonionella auris_ and _Bolivinellina seminuda_ var. _humilis_ vary between 0.11 and 0.43 weight percent

TABLE 12. -- Results of microanalyses of fossil benthic foraminifera from Hole 687A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 687A

Species	N	MgCO (wt%)	Std. Dev.	CaCO (wt%)	Std. Dev.	FeCO (wt%)	Std. Dev.	Est. T(C)
Sample 1CC (7.4 mbsf)								
Angulogerina carinata	11	0.17	0.07	99.25	2.07	0.05	0.05	5.47
Uvigerina striata	9	0.39	0.31	97.92	1.96	0.05	0.05	14.05
Cancris inflatus	10	0.33	0.28	99.07	2.70	0.02	0.03	11.35
Sample 4CC (36.1 mbsf)								
Epistominella afueraensis	6	0.27	0.14	98.10	4.63	0.06	0.05	9.48
Buliminella subfusiformis	6	0.16	0.05	98.74	2.78	0.11	0.06	5.05
Cassidulina pulchella	11	0.18	0.04	104.34	1.85	0.04	0.04	5.59
Sample 5CC (45.4 mbsf)								
Nonionella auris	2	0.22	0.00	96.20	2.07	0.15	0.02	7.69
Cancris inflatus	11	0.05	0.04	101.23	3.59	0.03	0.04	1.16
Cassidulina pulchella	14	0.14	0.07	99.19	3.60	0.05	0.07	4.32
Sample 6CC (55.1 mbsf)								
Cassidulina pulchella	5	0.12	0.05	103.79	1.75	0.08	0.05	3.53
Bolivinellina humilis	11	0.12	0.04	99.86	3.46	0.04	0.05	3.85
Bolivinellina humilis	9	0.07	0.03	97.37	1.70	0.05	0.04	1.84
Cancris inflatus	7	0.11	0.09	98.50	1.80	0.03	0.05	3.27
Sample 7CC (57.0 mbsf)								
Nonionella auris	10	39.22	0.79	61.46	1.62	0.01	0.04	----
Nonionella auris	10	38.72	0.97	61.65	1.07	0.02	0.04	----
Buliminella subfusiformis	13	37.98	0.67	62.80	1.28	0.04	0.05	----

TABLE 12. (Continued) -- Results of microanalyses of fossil benthic foraminifera from Hole 687A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 687A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
Sample 9CC (74.0 mbsf)								
Nonionella auris	15	0.25	0.23	109.36	3.51	0.12	0.07	7.72
Sample 10CC (83.5 mbsf)								
Bolivinellina humilis	6	0.19	0.15	102.79	2.73	0.18	0.07	5.94
Cancris inflatus	10	0.09	0.06	113.04	1.33	0.06	0.04	2.11
Sample 11CC (93.0 mbsf)								
Nonionella auris	9	0.11	0.05	99.94	2.22	0.36	0.25	3.25
Sample 12CC (104.2 mbsf)								
Nonionella auris	5	0.42	0.12	100.19	4.57	0.57	0.41	14.64
Nonionella auris	6	0.32	0.06	98.83	2.44	0.39	0.16	11.20
Nonionella auris	4	0.43	0.13	98.10	2.80	0.24	0.17	15.23
Nonionella auris	5	0.18	0.07	99.04	2.99	0.85	0.06	5.89
Bolivinellina seminuda	5	0.11	0.05	102.26	1.34	0.16	0.14	3.23
Sample 13CC (121.2 mbsf)								
Nonionella auris	8	1.03	0.16	117.18	5.79	0.08	0.06	30.33
Nonionella auris	4	0.25	0.06	101.22	3.39	0.07	0.14	8.26
Sample 14CC (127.9 mbsf)								
Uvigerina striata	10	0.36	0.14	109.84	4.54	0.05	0.06	11.38

TABLE 12. (Continued) -- Results of microanalyses of fossil benthic foraminifera from Hole 687A. Column "N" gives number of averaged spot analyses. Estimated paleotemperatures are computed with the formula for low-magnesium foraminifera derived in Chapter 3.

Hole 687A

Species	N	$MgCO_3$ (wt%)	Std. Dev.	$CaCO_3$ (wt%)	Std. Dev.	$FeCO_3$ (wt%)	Std. Dev.	Est. T(°C)
Sample 15CC (133.4 mbsf)								
Buliminella subfusiformis	1	0.43	----	106.51	----	0.00	----	14.14
Sample 17CC (158.3 mbsf)								
Nonionella auris	2	0.24	0.02	105.28	0.43	0.02	0.03	7.49
Buliminella subfusiformis	10	0.22	0.10	108.95	5.97	0.03	0.04	6.68
Sample 18CC (161.7 mbsf)								
Buliminella subfusiformis	4	0.22	0.09	96.77	4.13	0.01	0.02	7.45
Bolivinellina seminuda	4	0.15	0.03	114.60	4.78	0.03	0.04	4.19
Nonionella auris	5	0.26	0.05	116.36	1.80	0.08	0.06	7.50
Sample 19-4 (173.5 mbsf)								
Nonionella auris	5	0.25	0.07	99.15	1.24	0.04	0.07	8.71
Sample 21CC (193.4 mbsf)								
"Bolivina" sp.	5	0.20	0.18	112.68	0.92	0.03	0.06	5.81
Buliminella subfusiformis	5	0.19	0.13	98.61	2.03	0.01	0.02	6.30
Sample 22CC (202.0 mbsf)								
Buliminella subfusiformis	10	0.18	0.07	114.93	4.26	0.06	0.10	4.91
Nonionella auris	11	0.14	0.04	115.21	3.80	0.04	0.04	3.87

$MgCO_3$, and 13CC where two specimens of *N. auris* contain 1.03 and 0.25 weight percent $MgCO_3$. High magnesium contents (37.89 to 39.22 weight percent $MgCO_3$) occurred in recrystallized specimens of *N. auris* and *Buliminella subfusiformis* from sample 7CC (57.0 mbsf). Some specimens from below about 170 mbsf yielded anomalously high calcium concentrations (greater than 105 weight percent $CaCO_3$, if stoichiometry with the carbonate radical is assumed).

Iron concentrations ranged between 0.00 to 0.85 weight percent $FeCO_3$. Crystals of pyrite were present on specimens from samples 10CC (93.0 mbsf), 11CC (102.5 mbsf), and 12CC (112.0 mbsf). These samples also contain specimens with the highest iron concentrations among all holes. Variability of iron within sample 12CC is particularly high (concentrations range from 0.16 to 0.85 weight percent $FeCO_3$). Variations within other samples from which two or more specimens were analysed are low.

DISCUSSION

Diagenesis

Dolomite and Iron

All specimens of foraminifera that were analyzed from sample 7CC, Hole 687A were altered to a composition near dolomite. These tests were recrystallized to the extent that the walls were composed of coarse crystals that almost entirely filled the interior of the chambers. Specimens from this sample are thus easily distinguished from the unaltered specimens of other samples. The concentration of magnesium (37.89 to 39.22 weight percent $MgCO_3$ or 39.29 to 42.82 mole percent), in the fossils is below that of an "ideal" dolomite. Such nonideal dolomites are common in nature (Lumsden and Chimahusky, 1980). Although the mineral in the foraminifera did not show the characteristic dolomite ordering in x-ray diffraction analysis (probably because of small sample size), the composition of the mineral is like other naturally occurring carbonates that have been called calcium-rich dolomites or protodolomites (Graf and Goldsmith, 1956, Gaines, 1977). In the large majority of specimens from the 5 ODP holes in this study, $FeCO_3$ occurs in concentrations less than 0.10 weight percent. The microprobe is able to detect iron in modern foraminiferal calcite (Lipps and Ribbe, 1967), but variations of this cation are too small to be measured with the microprobe (Chapter 2). In foraminifera from Holes 680B-7CC, 687A-11CC and 687A-12CC, however, iron analyses reached as high as 0.80 weight percent. The high iron concentrations of this study occur in specimens that have pyrite crystals on the interior of the chambers. The co-occurrence of high FeCO concentrations and authigenic pyrite suggests that high concentrations may be the result of iron-bearing contaminants, but the microprobe beam was placed entirely on freshly polished surfaces of foraminiferal calcite far from the pyrite crystals. High iron also occurred in specimens of miliolid foraminifera (which do not possess perforate test walls) from Hole 687A sample 10CC. These occurrences of high $FeCO_3$ concentrations in foraminiferal calcite leave open the possibility that the iron has been substituted, either biologically or diagenetically, into the calcite lattice.

Dolomite is a common occurrence in the sediment of Hole 687A (Shipboard Scientific Party, 1988e), but only one sample in this hole showed significant dolomitization of foraminiferal calcite, which suggests that porewater chemistry ideal for dolomite formation does not occur throughout the sediment. Baker and Burns (1985) suggest that dolomitization occurs mainly in the zone of microbial sulfate reduction where magnesium can be diffused from the seawater at the sediment-water interface. Ease of fluid motion through the sediment is probably also required for dolomitization (Land, 1980), and sediment characteristics such as grain size may have controlled the distribution of dolomitization in Hole 687A and other Holes of Leg 112 (Shipboard Scientific Party, 1988a, 1988e).

The three samples that contain pyrite and high $FeCO_3$ concentrations also tend to have higher magnesium concentrations, which suggests that the incorporation of these two cations is related in some of the fossils. Aspects of oxygen-deficient chemical environments are important in the formation of both dolomite and pyrite and possibly in the incorporation of high iron concentrations in some of the fossil tests. The low concentrations of SO_4 in anoxic environments promote dolomite formation (Baker and Kastner, 1981; Baker and Burns, 1985) and the reducing conditions promote the formation of pyrite (Calvert, 1976). The possibility exists that reducing conditions causing formation of the pyrite seen in the samples with high iron concentrations may also be altering the concentration of magnesium in the foraminifera. In laboratory experiments, however, Baker and Kastner (1981) did not find evidence that alteration of calcite to dolomite produced a magnesian calcite precursor. The fossil foraminifera in this study also showed no intermediate compositions that might suggest a trend. Further, the dolomitized foraminifera from 687A-7CC contained less than 0.05 weight percent $FeCO_3$. Thus, although dolomite and pyrite may be produced in reducing environments, no evidence exists to indicate that the pyrite-producing environment has altered any of the nondolomitized species.

Anomaluosly High Calcium

Calcium concentrations in specimens collected from below 57.0 mbsf in Hole 687A were as high as 117.18 weight percent $CaCO_3$ after the carbonate radical was stoichiometrically added to the weight percent of the calcium ion. The high totals suggest that not all calcium is stoichiometrically linked with the carbonate radical. A calcium-bearing mineral other than calcite may exist as a contaminant or alteration product. Analysis of specimens from this hole by X-ray diffraction revealed nothing about the unknown mineral because the size of the powdered samples was too small. Because the mineral remains unknown, the magnesium data of specimens that have anomalously high $CaCO_3$ concentrations should be used only with caution for the purposes of paleotemperature determinations, but the high calcium concentrations do not appear to be related to variations in magnesium concentrations.

Variation Within Samples

The degree of compositional variation exhibited by specimens collected from one sample may be the result of one or a combination of factors such as interspecific variations, time averaging, mixing of faunas by bioturbation or transportation, diagenesis, and experimantal errors. Inaccuracies in microprobe analyses, discussed in the previous section, are random and small and cannot be responsible for consistently high or low measurements within a specimen. The procedure of averaging replicate analyses on each specimen reduces the effects of random errors in the microprobe analyses.

Differences Between Species

The strong compositional similarity between the species analyzed in this study is apparent from inspection of data in Tables 8 through 12. Concentrations of $MgCO_3$ in all unaltered specimens fall within a narrow low-magnesian calcite range. Differences may be suspected, however, between some of the more disparate species. The significance of the differences in magnesium compositions from one species to the next may be tested by comparing the distributions of the magnesium concentration in the 12 species. An analysis of variance, precisely designed for such a comparison, was computed to test if the chemical analyses of any of the species was statistically different from the others. The analysis showed significant at a 95% confidence (alpha = 0.05), which suggests that the magnesium-content distribution of at least one of the species differs significantly from the other species.

To determine which species were different, the Student's t statistic was computed to compare selected species to each other. One comparison that showed significant difference at the 95% (alpha = 0.05) confidence level was between Cassidulina pulchella and Nonionella auris, both represented by large numbers of analyses. The possibility of a phylogenetic effect between N. auris and other species is also indicated by anomalously high paleotemperatures (over 40° C) obtained from the magnesium contents of some specimens of this species.

Mixing and Time Averaging

Evidence of bioturbation and transportation (e.g mottling, burrowing, graded laminations) are evident in the cores of all the holes used in this study (Shipboard Scientific Party, 1988a-e). These processes may mix specimens that lived in different environments or at different times. Because aspects of the environment control the concentration of magnesium in the tests of the foraminifera, a mixture of tests from various environments should produce variable magnesium concentrations. The degree of variability resulting from this mixture depends on the difference in the temperatures in which the component faunas lived. The distribution of magnesium concentrations in benthic foraminifera from the western side of the Pacific mimics the temperature structure of that region (Chapter 2, 3). Surface ocean temperatures off the Peruvian coastline, however, are generally cooler than ocean temperatures at the same latitude on the western side of southern Pacific (Reid, 1969; Dietrich, et al., 1975). Because the contrast between surface and deep temperatures is not as great, the thermocline is less steep than in the western Pacific, but the difference between surface temperatures and temperatures at about 300 m depth may still be as much as 15° to 20 ° C (Figure 8). The temperature structure is made more complex by upwelling in the region which brings to the surface cooler water from the thermocline via discreet eddies (Dietrich, et al, 1975). Annual temperature variations on the surface may be greater than 5° C (Figure 8). The temperature structure of the ocean off the Peruvian coastline is thus characterized by a juxtaposition of environments with relatively large temperature differences that fluctuate with time. The differences are most pronounced in the upper oceanic layers from the surface to the bottom of the thermocline. Any process of mixing or time averaging could produce an assemblage of fossils

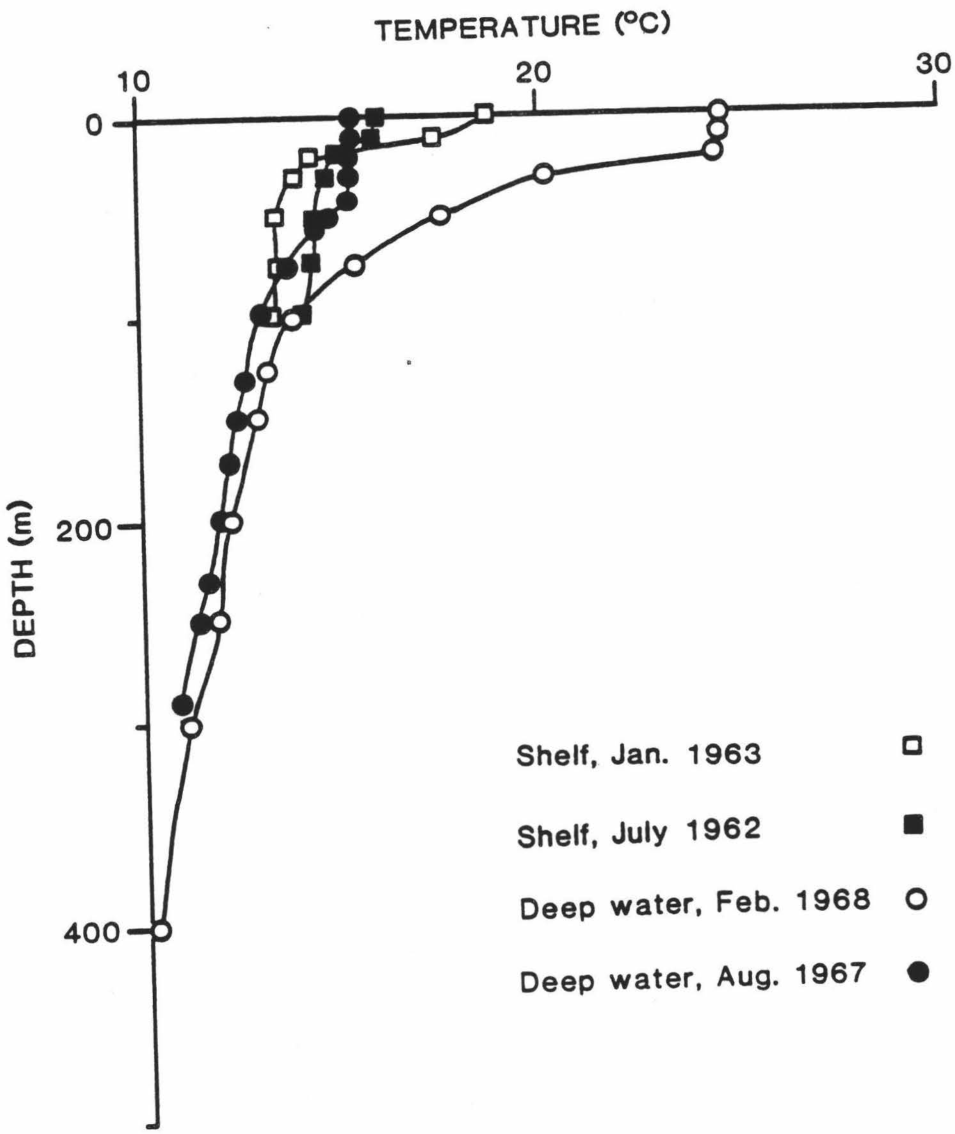


Figure 8. Variability of the distribution of temperature with depth in the Peruvian continental margin region. Temperatures for winter and summer months are shown for both shelf and deep-water locations. Based on ocean station data from the National Oceanographic Data Center.

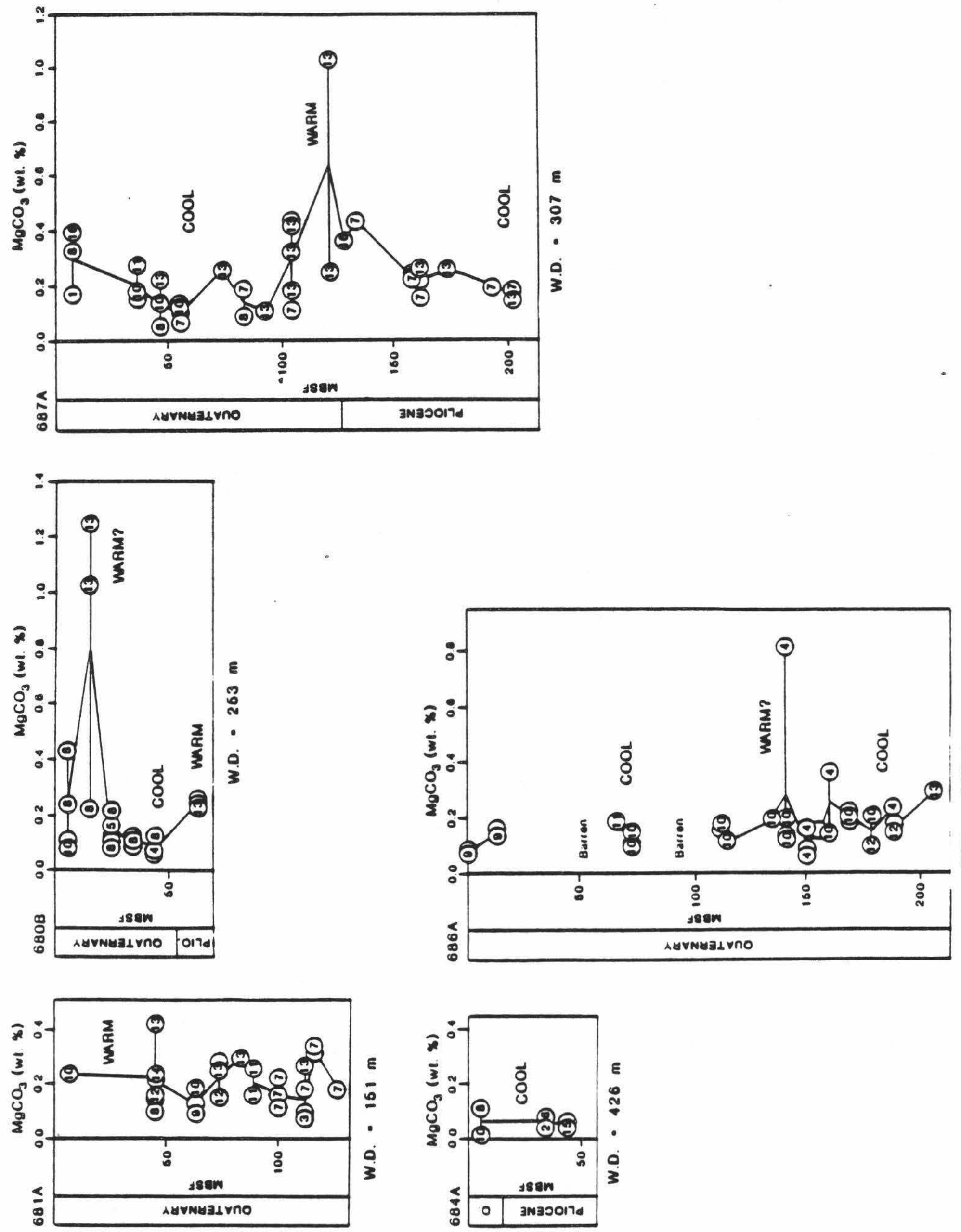
grown in water temperatures that differ by several degrees. Considerable variation in the magnesium contents of specimens is therefore expected from a mixed assemblage from within the thermocline and may be used as an indicator of time averaging or mixing. All of the holes in this study were sited in water deepths that show little seasonal variation today (Figure 8 and 9), but the downhole variation in magnesium content in some holes indicate periods when the sites may have existed in shallower water where temperatures are more variable.

Paleotemperatures

Holes 680B and 681A

Hole 680B was sited in 253 m and Hole 681A in 151 m of water on the shallow end of a transect across the continental shelf at approximately 11° S (Figure 7). The down-hole magnesium concentrations of benthic foraminifera from the Hole 680B indicate at least one warming trend in the water at the site during the Quaternary and one in the late Pliocene (Figure 9). The large variation in magnesium contents of specimens from sample 2CC may be the result of short-term fluctuations in temperature or mixing of specimens from warm, shallower water with indigenous foraminifera. Temperature variations within short timespans (i.e. seasonal or year to year) are more

Figure 9. Downhole variation of magnesium contents in fossil foraminifera. Numbers correspond to species listed in Table 1. Horizontal cross bars join specimens from one sample; tie lines connect the means of samples. Interpretations of relative cool and warm periods are indicated.


687A
W.D. = 307 m
680B
W.D. = 263 m
686A
W.D. = 447 m
681A
W.D. = 151 m
684A
W.D. = 426 m
MgCO3 (wt. %)
MBSF
QUATERNARY
PLIOCENE
WARM
COOL
WARM?
Barren

pronounced within the thermocline and the shallow mixed layer than in deep water (Figure 8), and magnesium contents of populations of foraminifera grown in the thermocline should reflect this variability. On the other hand, the highest magnesium concentrations in 2CC occurred in specimens of shelf-dwelling Nonionella, whereas the lowest concentration occurred in the upper-bathyal species Cancris inflatus (Bandy, 1961, Ingle and Keller, 1980), which suggests that mixing may have caused the intrasample variation. The temperatures indicated by the compositions of the foraminifera from this sample are, however, anomalously high (36° to 48° C), which suggests that the high intrasample variation may be due to phylogenetic effects separating N. auris from the other species studied.

Hole 681A, which was sited in 253 m of water on the continental shelf, shows moderate intrasample variation throughout the portion of the hole sampled in this study (Figure 9). The degree of intrasample variation suggests that the site has remained in the steep part of the thermocline throughout the Quaternary, but variations in upwelling (which is most intense over the continental shelf) in the past probably also added to the complexity of the picture. As in Hole 680B, specimens with the highest magnesium concentrations in samples from Hole 681A belong to the shelf-dwelling species Nonionella auris, which suggests that transportation may have an important effect on the intrasample variation. Despite the intrasample variations, the down-hole magnesium concentrations in the tests of benthic foraminifera from Hole 681A suggest some oscillation in water temperature of a few degrees at the site during the Quaternary. Two cooling events, one peaking near 63 mbsf and the other at about 110 mbsf, and at least one warming trend between them are apparent. The oscillations are not simply random variations from sample to sample but trends in the magnesium contents that can be traced from one sample to the next.

Hole 684A

Low-magnesium concentrations and small down-hole variation of Hole 684A contrasts with the higher variation in Holes 680B and 681A. The small variations suggest that the site, which today lies in 426 m of water, well beneath the steep part of the thermocline (Figure 8), has remained in relatively cold water (5° to 7° C) through part of the Pliocene and Quaternary section that was analyzed (Figure 9). At this depth, water temperature is uniformly cold and does not vary greatly with depth. Fluctuations in sea level of as much as 100 m may not have affected the foraminiferal magnesium concentrations because temperature changes would have been small. Also, mixing of faunas may not have produced the same degree of intrasample variation as in shallower sites because environments of greatly different temperatures were not nearby.

Hole 686A

The drill site of Hole 686A today lies at 447 m water depth near the seaward margin of the Pisco basin (Shipboard Scientific Party, 1988d). The site is presently situated below the thermocline, but oscillations in the down-hole foraminiferal magnesium content suggest periods when the water may have been warmer. The signal is not as clear as in the previously-discussed holes, however, because the data are discontinuous where sections are barren of foraminifera. An increase in $MgCO_3$ is apparent between the surface and 13 mbsf. In the interval between 64.7 mbsf and 71.6 mbsf, magnesium concentrations in foraminiferal calcite decrease. This change of downhole magnesium concentration corresponds to a temperature change of about 3° C.

Below 111.1 mbsf, the magnesium data are scattered, indicating that the site may have come close to the steep part of the thermocline where variable temperatures result in variable magnesium contents in the foraminifera.

Sample 16CC (139.2 mbsf) shows the greatest intrasample variation because one specimen of *Bolivinellina seminuda* var. *humilis* with a high concentration (0.81 weight percent) of $MgCO_3$ occurs with several specimens of *Cassidulina pulchella* that measured between 0.13 to 0.20 weight percent $MgCO_3$. The magnesium concentration of *B. seminuda* var. *humilis* indicates a temperature of 29 ° C, but the large error associated with the magnesium measurement indicates that the estimated temperature is inaccurate. The magnesium concentrations continue to oscillate down core to sample 23CC (204.6 mbsf) but the oscillations show no trends and the magnesium contents are not, generally speaking, any lower or higher than the most of the rest of the samples from this hole. Small-scale oscillations in magnesium content may exist, but these cannot be resolved at the sampling intervals used in this study.

Hole 687A

As discussed previously, cautious paleotemperature interpretation of the foraminiferal magnesium data in Hole 687A is advisable because of the suspected presence of calcium- and possibly magnesium-bearing mineral contaminants. The down-hole trends in magnesium contents may indicate paleotemperature changes, provided contaminant mineral phases do not have an appreciable effect on the magnesium contents of the foraminiferal tests. The interpretations that follow are thus provisionary, pending identification of the source of the anomalously high $CaCO_3$ concentrations measured in samples from below 57.0 mbsf. Excluded from the interpretations are specimens from sample 7CC (63.1 mbsf) which were clearly replaced by dolomite.

Hole 687A was sited in 307 m of water on the Lima Platform which is tectonically stable (Shipboard Scientific Party, 1988c). The down-hole foraminiferal magnesium content in Hole 687A shows a cooling trend from an average estimated temperature of 10° C in sample 1CC (7.4 mbsf) to 3° C in sample 6CC (55.1 mbsf). The magnesium content rises again between sample 9CC (74.0 mbsf) and sample 13CC (121.2 mbsf), indicating a rise in temperature to approximately 10 ° C. Samples 12CC (104.2 mbsf) and 13CC show great intrasample variation, indicating that the assemblage in the sample consists of a mixture of specimens grown in different water temperatures. The high magnesium trend peaks near sample 13CC and continues to drop toward sample 22CC (202.0 mbsf). The foraminiferal magnesium profile thus indicates one period of warming (possibly shallowing of the site) that peaks in the lower-middle part of the hole (13CC) and another trend beginning at cool temperatures in 6CC and warming to the top of the present sediment surface.

CONCLUSIONS

The interpretation of magnesium concentrations in the tests of foraminifera from ODP Holes 680B, 681A, 684A, 686A, and 687A, in terms of paleotemperature is hampered by the variability in shallow-water temperatures that is caused by the ocean circulation characteristic of the Peruvian continental margin and the weak thermocline. The concentration of magnesium and iron in the calcite of benthic foraminiferal tests show variation both within and between samples. Part of the intrasample variation may be attributed to diagenesis. Dolomitization occurred in one sample, but the effects of recrystallization of the original foraminiferal calcite are obvious and clearly identify the altered specimens. Pyrite occurs as a contaminant in some samples but the effect of this mineral on the analysis of magnesium (and paleotemperature interpretations) is insignificant. Iron may be combined in the foraminiferal calcite lattice in greater amounts than was previously thought. A study of living foraminifera from oxygen-deficient environments may shed light on this possibility.

The paleotemperatures estimated from the fossil foraminiferal magnesium content are generally lower, with a few noted exceptions, than modern temperatures, even after allowances are made for sea-level changes in position of the thermocline. The low temperatures may reflect a Quaternary environment cooler than present, or the inaccuracy of the magnesium paleotemperature formula. Phylogenetic or "vital" effects may be responsible for the inaccuracy of the formula, particularly in the case of Nonionella auris. Although paleotemperatures may be inaccurate in detail, however, trends in magnesium concentration may still reflect paleotemperature fluctuations.

Mixing and time averaging of foraminifera that were grown in different environments and at different temperatures probably accounts for much of the intrasample variation. Foraminiferal remains that accumulate within the thermocline where temperatures vary greatly both with space and time show the greatest intrasample variation. The foraminiferal magnesium content of Hole 681A serves as an example of such a site. On the other hand, sites that have remained in cold, deep water below the thermocline will show very little foraminiferal magnesium variation both within samples and between samples because temperatures at that depth are uniformly cold. Hole 684A illustrates such a record. The down-hole record of magnesium contents at sites that have passed into and out of the thermocline because of sea-level changes or tectonism be show intervals of high intrasample variation (shallow periods) alternating with intervals of low intrasample variation (deep periods). The oscillations in intrasample variability in Holes 680B, 686A, and 687A illustrate this condition.

CHAPTER 5

GENERAL CONCLUSIONS AND AVENUES FOR FUTURE RESEARCH

This research into the aspects of magnesium and other minor elements in the calcite of the tests of modern and fossil benthic foraminifera supports the concept that foraminiferal magnesium contents vary in response to the temperature of the water in which the organisms precipitated their tests. Although previous inconclusive results have raised skepticism regarding the validity of the magnesium-temperature relationships, the depth distribution of foraminiferal magnesium contents parallels the depth distribution of ocean temperatures when phylogenetic relationships are eliminated (Chapter 2).

Constraining the phylogenetic effect does not necessarily require limitation of a temperature study to one or two very closely related species. As shown in Chapter 3, several species of low-magnesium foraminifera may react to temperature in a similar manner and their magnesium contents may be combined in foraminiferal magnesium-temperature studies. Although a strong, phylogenetically linked chemical disparity separates low-magnesium foraminifera from high-magnesium foraminifera, the high magnesium foraminifera themselves exhibit a magnesium-temperature relationship. The two observed relationships thus suggest that at least two different equations, one for high-magnesium foraminifera and another for low-magnesium foraminifera, are required to describe the response of magnesium concentration in foraminifera to water temperature. Either of the relationships could be used in paleotemperaure determinations, but the high-magnesium relationship is less prone to analytical error (and therefore preferred) because the variation of magnesium with temperature is greater than in the low-magnesium foraminifera. The high-magnesium foraminifera, however, become rare in deeper colder water. In deeper water (below about 900 m), therefore, it may be necessary to use the low-magnesium relationship for paleotemperature determinations even though the results may be less accurate.

The analysis of fossil benthic foraminifera reveals the effects of transportation, bioturbation, and time-averaging, as well as diagenetic processes such as recrystallization and precipitation of external contaminants. Still, down-hole foraminiferal magnesium variations record changes in water temperature through time. Indeed, the intrasample magnesium variation itself provides some information. Sites that have remained below the thermocilne show little intrasample variation, sites that have remained above the thermocilne show greater variation, and sites that have passed into and out of the thermocline show alternations of intervals with high and low intrasample variation.

This study has resulted in a better understanding of the previously questioned relationship between temperature and the magnesium content in foraminifera, but several directions for future research are suggested as well. Investigations into the paleoceanography of other regions and other oceans will test the reliability of foraminiferal magnesium content as a paleotemperature indicator. For example, whereas the magnesium contents of foraminifera from Peruvian sites in Chapter 4 reflects the complexity of the circulation and temperature distribution of the region, a similar down-hole study of cores from the western side of the ocean basin should reflect the differences in circulation and temperature distributions between eastern and western ocean margins.

The effects of early diagenesis on the remains of benthic foraminifera can be studied by comparing the compositions of living foraminifera to the compositions of empty tests from the nearby sediment surface. Except for a few laboratory culture experiments such as those of Delaney (1983), very little information is available on the chemical content of living foraminifera, particularly benthic foraminifera. Some workers have concluded that early diagenesis can significantly alter the chemical composition of foraminifera without visible alteration of the microstructure of the test (e.g. Towe and Hemleben, 1976) but these conclusions were based on analyses of empty tests without comparison to analyses of the tests of living foraminifera. Until the range of compositions in living foraminifera is known, the changes attributed to early diagenesis remain speculative.

An investigation into the ultrastructure, growth, and phylogeny of foraminifera may reveal the basis of the difference between the high and low-magnesium foraminifera. Little is known about the differences in the rates of precipitation of the calcite of miliolid and rotaliid tests, yet rates of precipitation have been shown to cause variation in the concentration of magnesium incorporated into physiochemical calcites (Mackenzie, et. al, 1983) as well as biochemical calcites of organisms other than foraminifera (Moberly, 1968; Weber, 1973).

Finally, in order to use foraminiferal magnesium contents in quantitative paleotemperature determinations, more studies of the magnesium content in modern foraminifera are required. Small-scale phylogenetic effects may be responsible for anomalous paleotemperatures determined by use of magnesium-temperature relationship in modern foraminifera. These small vital effects can only be identified as the magnesium-temperature relationships of more species are studied.

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