1984

Diagenesis of Cenozoic Limestones on Enewetak Atoll (Dolomite, Neomorphism, Radial).

Arthur Henry Saller
Louisiana State University and Agricultural & Mechanical College

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DIAGENESIS OF CENOZOIC
LIMESTONES ON ENEWETAK ATOLL

A dissertation
Submitted to the Graduate Faculty of
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy
in
The Department of Geology

by
Arthur Henry Sailer
B.S. Geology, University of Kansas, 1977
M.S. Geology, Stanford University, 1980
May, 1984
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ABSTRACT

Cores from Enewetak Atoll afford an excellent opportunity to study diagenetic alteration in carbonates from the modern sediment-water interface to burial depths of over 1,300 m. Intensity of diagenetic alteration in Cenozoic carbonates on Enewetak is largely a function of time which strata have been in diagenetic environments with active water circulation. In Pleistocene strata deposited in back-reef environments, diagenesis is dominated by meteoric processes including dissolution of aragonite, calcite cementation, and alteration of aragonite and high-magnesian calcite (HMC) to low-magnesian calcite (LMC). Petrographic and stable isotope data suggest that aragonite neomorphism occurred by a process of partial delicate intrafabric dissolution of aragonite followed by calcite infilling. Meteoric alteration in Pleistocene strata is intense both in intervals immediately below subaerial exposure surfaces and in intervals affected by meteoric-phreatic environments for significant amounts of time. Cenozoic carbonates (including some Pleistocene strata), away from exposure surfaces and out of ancient meteoric-phreatic zones, generally exhibit little meteoric alteration.

Marine diagenesis on Enewetak is most intense in permeable strata near the seaward margin of the atoll. In Lower Miocene strata of the Enewetak F-1 well (375 - 850 m),
extensive aragonite dissolution and radiaxial calcite cementation occurred in relatively deep marine waters circulating through the atoll. These radiaxial calcites apparently precipitated directly from marine water without any subsequent neomorphism. Dolomite is common in deeper parts of Upper Eocene strata on Enewetak Atoll (1,150 - 1,380 m deep). Petrography, stable isotope analyses, and strontium isotope analyses consistently indicate dolomitization probably occurred in deep marine waters between the Middle Miocene and the present. The products of marine diagenesis within Enewetak Atoll vary according to depth and carbonate saturation. In shallow marine waters above the HMC and aragonite saturation depths, diagenesis consists primarily of HMC and aragonite cementation. In actively circulating marine waters between the aragonite and calcite saturation depths (300 - 1,000 m), aragonite dissolution and radiaxial calcite cementation are pervasive. Below the calcite saturation depth (1,000 m), calcite dissolution and dolomitization have apparently occurred in marine waters.
INTRODUCTION

The ultimate porosity of ancient limestones and dolomites is determined by (1) depositional (primary) porosity, (2) the degree to which cementation and compaction have filled or destroyed those primary pore spaces, and (3) the amount of secondary porosity generated by dissolution and fracturing. Because post-depositional (diagenetic) processes commonly create and obliterate porosity in carbonate rocks, understanding those diagenetic changes is vital to predicting porosity and locating potential hydrocarbon reservoirs.

Diagenetic alteration of carbonates occurs in many different environments. During the last 15 years, numerous studies have examined the diagenetic alteration of Holocene and Pleistocene carbonate strata by shallow marine and nearsurface meteoric waters. In addition, many diagenetic studies have examined ancient carbonates after they have been through significant burial. However, few studies have attempted to examine the continuum of diagenetic processes affecting carbonate rocks from the period shortly after deposition through nearsurface diagenesis to deep burial. The main objective of this study is to trace the diagenetic evolution of carbonate rocks on Enewetak from nearsurface conditions through burial and establish a link between nearsurface and burial diagenesis on the Enewetak Atoll.

A major problem in studying ancient carbonates is
distinguishing between the products of marine, meteoric, and burial diagenesis. Studies by Moore and Druckman (1981), Wagner and Matthews (1982), and Moore and Brock (1983) have demonstrated that it is often difficult to distinguish between diagenetic alteration in meteoric and deep burial environments in ancient rocks. A secondary objective of this study is to develop criteria for distinguishing between marine, meteoric, and, to a lesser extent, burial diagenesis on Enewetak.

Enewetak Atoll was selected for this project because Enewetak cores contain a long, fairly continuous record of tropical carbonate deposition and diagenesis from Late Eocene to the present. The position of these strata in the middle of the Pacific Ocean is advantageous because it removes them from depositional and diagenetic complexities associated with terrigenous sediments. Enewetak's general history of subsidence since Upper Eocene is also fortuitous because it is similar to the subsidence observed in many ancient sedimentary basins (Schlanger, 1963; Mattes and Mountjoy, 1980). It is quite possible that the diagenetic evolution of carbonates on Enewetak may be used as a model for diagenetic evolution of limestones in ancient atolls, bioherms, and continental margins that have not been affected by terrigenous material. Most major types of diagenetic modifications present in ancient carbonate are found in Cenozoic carbonates on Enewetak.
PREVIOUS STUDIES ON ENEWETAK

Between 1948 and 1958, the U.S. Atomic Energy Commission tested nuclear weapons on Enewetak Atoll (Goter, 1979). To monitor the effects of nuclear testing, the United States government has sponsored numerous hydrologic, geochemical, and geological studies of Enewetak since 1950. Between 1950 and 1952, 21 shallow wells (less than 61 m deep) and 3 deep wells (390 – 1411 m deep) were drilled. Extensive geological analyses of well cores and cuttings are described in U.S. Geological Survey Professional Papers 260A-260II. Emery et al. (1954) describe the topography and surface geology of Enewetak. Professional Paper 260-Y (Ladd and Schlanger, 1960) discusses the early 1950's drilling operation on Enewetak. Extensive descriptions and chemical analyses of samples from the 3 deep wells are found in Schlanger (1963). Paleontologic studies on foraminifera and calcareous algae in deep Enewetak cores are summarized in Cole (1957), Todd and Low (1960), and Johnson (1961). Numerous geophysical studies associated with that early 1950's drilling project are described in Swartz (1958, 1962). Samples from the 3 deep Enewetak wells (E-1, F-1, K-1) are re-examined as a part of this study.

Between 1971 and 1974, the U.S. Air Force Weapons Laboratory conducted two more drilling programs on Enewetak.
During the second drilling project called "The Exploration Program on Enewetak" (EXPOE), 46 cored boreholes were completed, to depths of 73 - 91 m. Samples from 3 EXPOE wells (XAR-1, XEN-1, and XRI-1) are examined in this study. Other geological studies incorporating information from these EXPOE cores include Ristvet et al. (1974), Tracey and Ladd (1974), Couch et al. (1975), Videtich and Tremba (1978), and Goter (1979). Schmalz (1971) discusses the formation of modern beachrock on islands of the Enewetak Atoll. Results of hydrologic studies on several Enewetak islands conducted during and after Project EXPOE are reported in Buddemeier (1976), Buddemeier and Holladay (1977), and Wheatcraft and Buddemeier (1981). Goff (1979) studied groundwater chemistry and its relation to diagenesis on the island of Engebi in the Enewetak Atoll.

PHYSICAL SETTING OF ENEWETAK

Enewetak Atoll is located in the equatorial Pacific Ocean (Fig. 1) and is the westernmost member of the Marshall Islands. Enewetak is a classic atoll with islands and shallow reefs surrounding a central lagoon which has a maximum depth of 64 m (Fig. 1; Emery et al., 1954). The sea floor surrounding the atoll is 4,572 to 5,852 m deep (Emery et al., 1954, p. 19). The margin of the atoll is
Figure 1.
Location and map of Enewetak Atoll. Note the location of the E-1, F-1, XAR-1, XEN-1 and XRI-1 wells. Modified from Goter (1979).
quite steep, sloping seaward at an average grade of 567 m per km between 914 m and sea level (Fig. 2; Emery, et al., 1954; Ladd and Schlanger, 1960, Fig. 285). Stratigraphically, Enewetak Atoll consists of roughly 1,400 m of Upper Eocene through Holocene carbonates stacked on a slowly subsiding volcanic basement (Fig. 2). Seismic refraction studies reveal that the upper surface of the volcanic basement slopes gently to the northwest (Raitt, 1957).

Enewetak has a humid tropical climate characterized by annual temperatures ranging from 22° to 34°C, relative humidities between 73% and 80%, and a mean annual rainfall of approximately 150 cm most of which occurs between July and November (Goff, 1979). Relatively constant trade winds blow across Enewetak from the northeast. Tides are mixed semidiurnal with a mean tidal range of 0.8 m (Tracey and Ladd, 1974) and spring tidal range of 1.8 m (Wheatcraft and Buddemeier, 1981). Throughout most of the year, ocean currents in the vicinity of Enewetak come from the east. This westward current, called the "North Equatorial Current", is caused by the prevailing trade winds (Emery et al., 1954, p.19). The prevailing trade winds also generate waves and swells that come from the east-northeast during most of the year (Emery et al., 1954, p. 19).
Figure 2.
Cross-section of Enewetak Atoll. All strata above the volcanic basement are carbonates. Adapted from Ladd and Schlanger (1960).
ENEWETAK ATOLL

NW        SE

F-1

PLIO-PLEISTOCENE

MIocene

UPPER EOCENE

VOLCANIC BASEMENT

Cased Interval

0 8 km

0 300 m
HYDROLOGY

Well data consistently indicate that the Enewetak Atoll is underlain by an extremely permeable sequence of carbonates (Buddemeier and Holladay, 1977; Swartz, 1958). Monitoring tidal fluctuations in pits and shallow wells, Buddemeier and Holladay (1977) and Wheatcraft and Buddemeier (1981) demonstrated that Quaternary limestones in the upper 76.2 m of Engebi Island (and Enewetak Atoll as a whole) are very permeable (Fig. 1). Engebi is the largest island in the northern part of the atoll, covering approximately 1.1 square kilometers (Fig. 1; Goff, 1979). On Engebi, Buddemeier and Holladay (1977) and Wheatcraft and Buddemeier (1981) found that subsurface transmission of tidal forces through Quaternary strata is not dependent on the lateral distance of wells from the ocean; rather, tidal forces are apparently transmitted horizontally through deep, permeable aquifers and then vertically up through less permeable strata. Therefore, within Quaternary strata below Engebi, the horizontal permeability of some deep intervals is enormous; however, vertical permeabilities are great enough to allow tidal signals to be transmitted vertically from deeper, extremely permeable intervals instead of being transmitted laterally from the ocean.

Extensive vertical mixing of fresh and marine waters
has prevented the development of large fresh water lenses on Engebi and probably other Enewetak islands during modern times. Most of the groundwater on Engebi (Fig. 1) is brackish to saline (Buddemeier and Holladay, 1977; Goff, 1979, p. 39). Minimum chloride concentrations are found at the top of the modern water table near the middle of the island and range from 500 - 1,000 ppm Cl\(^-\) (Goff, 1979, p. 39). Salinities increase rapidly with depth in the phreatic zone. At approximately 9 m below the water table in the middle of Engebi, groundwater is approximately 50% fresh and 50% marine (Buddemeier and Holladay, 1977). Mixing of meteoric and marine waters is basically a vertical process on Engebi because of the vertical transmission of the tidal pressure (Wheatcraft and Buddemeier, 1981). Another important observation is that lower permeability strata on Engebi are able to attenuate tidal signals and hence retain larger freshwater inventories than more permeable strata (Buddemeier and Holladay, 1977).

Observations involving tidal fluctuations and temperature profiles in the deep E-1 and F-1 wells (see Figure 1 for locations) indicate that marine water circulates freely through deep carbonate strata. After being solidly cased to a depth of 601 m, the water-level in the F-1 well fluctuated in phase and at the same amplitude as the adjacent open ocean (Swartz, 1958, p. 729; Fig. 2). The E-1 well was cased solidly to 1,252 m. After casing, the water level
in that well fluctuated with a 2.54 cm amplitude at a 9 1/2 hour lag relative to surface tides (Swartz, 1958, p. 729 - 731). Tidal fluctuations in the F-1 well indicate that Lower Miocene strata penetrated by this well are extremely permeable and are in close communication with the open ocean water over 3 km away from the well (Fig.2). Tidal fluctuations in the E-1 well suggest that Upper Eocene strata (1,250 m deep) around the E-1 well are significantly less permeable than Lower Miocene strata (580 m deep) surrounding the F-1 well. However, the fact that the deep E-1 strata do "feel" oceanic tides suggests some significant communication of those deep strata with open oceanic waters. Temperature profiles from the E-1 and F-1 wells confirm that marine waters are circulating more freely in the vicinity of the F-1 well than the E-1 well (Fig. 3; Swartz, 1958).

METHODS

To prevent potential complexities associated with exposure and alteration of outcrop, subsurface (core) material was exclusively used in this study. Samples from 3 shallow wells (less than 80 m deep; XRI-1, XAR-1, and XEN-1; see Figure 1 for locations) came from a collection procured by C.H. Moore and stored at Louisiana State University. Average sampling intervals for the XRI-1, XAR-1, and XEN-1
Figure 3.

Degree of carbonate saturation for Pacific ocean water and temperature profiles for the E-1 well, F-1 well, and Pacific ocean water. At left, stratigraphy from the Enewetak F-1 well with bars indicating the location of cores. F-1 well stratigraphy modified from Schlanger (1963). Carbonate saturation curves from Li et al. (1969) and Scholle et al. (1983). Temperature profiles from Swartz (1958).
F-1 WELL  CARBONATE SATURATION  TEMPERATURE PROFILE

Depth (meters)

0 m
Pleistocene
Pliocene

200
400

Miocene

600
800

Upper Eocene

1000
1200
1400
Basalt
Volcanic Basement

- Aragonite
- Calcite  - Dolomite
(Cored intervals)

After Scholle et al. (1983)

After Swartz (1958)
wells were 1.2 to 1.5 m. Cores from the deep Enewetak E-1, F-1, and K-1 wells (Fig. 1) are stored at the U. S. National Museum in Washington, D. C. and were sampled by the author (with permission) in the Fall of 1981.

The deep Enewetak F-1 and E-1 wells penetrated the entire Cenozoic carbonate section on Enewetak and encountered volcanic basement rock over 1,280 m below sea level (Figs. 1 and 4; Ladd and Schlanger, 1960). Fifteen cores of carbonate rock were taken in the F-1 well, but only 3 cores were taken in the carbonate section of the E-1 well (Fig. 4). Each core from the E-1 and F-1 wells penetrated an average of 6 m; however, average recovery was only 2.1 m. Therefore, only 30 m out of a 1,278 m Miocene and Upper Eocene section was recovered from the F-1 well, and only 7.2 m of core was recovered from 1,067 m of Miocene and Eocene carbonates in the E-1 well.

While cores recovered from the F-1 well represent only a small fraction of the stratigraphic section, the cores have a relatively even distribution through the Upper Eocene and Lower Miocene section (Fig. 4). Petrographic analysis of samples shows that adjacent cores frequently have very similar depositional and diagenetic features suggesting that much of the intervening, uncored strata is similar. For example, cores 3 through 6 between 375 and 819 m in the F-1 well show very similar depositional and diagenetic textures. Likewise, cores 9, 10, 11, and
Figure 4.
Stratigraphy of Upper Eocene through Holocene carbonates on Enewetak. Tops of Tertiary b, c, and g are based on larger foraminifera (Cole, 1957). Diagram modified from Schlanger (1963).
DEEP ENEWETAK STRATIGRAPHY

<table>
<thead>
<tr>
<th>Depth (feet)</th>
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<tbody>
<tr>
<td>0</td>
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<tr>
<td>1000</td>
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<tr>
<td>4000</td>
<td></td>
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<tr>
<td>1200 Cored Intervals</td>
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K-1  F-1  E-1

Top of Tertiary e  Top of Tertiary e  Top of Tertiary e

Pleistocene  Pliocene  Middle to Upper Miocene

Lower Miocene

Upper Eocene

Basalt

Aragonite  Calcite  Dolomite
part of 12 (1,114 - 1,317 m) are very similar. Therefore, some generalizations can be made regarding large portions of the Lower Miocene and Upper Eocene sections in the F-1 well. The 3 cores from the E-1 well are quite different from each other; therefore, little can be inferred regarding intervening uncored strata. The E-1 cores do, however, provide some valuable comparisons to parts of the F-1 section.

Petrography, trace elements, and stable isotopes were systematically used in this study to identify and characterize different diagenetic products. Initially, all samples were examined using standard petrography to note patterns of cementation, dissolution, neomorphism, compaction, and dolomitization. Petrography served as a guide to the diagenetic components that could and should be examined in later geochemical analyses. Geochemical analyses were performed almost exclusively on individual textural and diagenetic components in order to minimize complexities and uncertainties introduced by multiple components present in "whole rock" samples. Trace element and stable isotope data were systematically collected for several textural components of interest including cements, neomorphic spar, coralline algae, echinoderm fragments, and internal sediments.

Trace element data were obtained using electron microprobe analyses and atomic absorption spectrophotometry. Magnesium and strontium concentrations of numerous diagenetic components were determined using an ARL - EMX electron microprobe
at Louisiana State University. Atomic absorption spectrophotometry was used (1) to check magnesium and strontium concentrations determined by microprobe analyses and (2) to determine iron, manganese, and sodium concentrations of a few selected components which had sufficient separable material (more than 0.3 grams). Analytical techniques, accuracy, and precision of elemental analyses are discussed in detail in Appendix.

Samples of diagenetic components used in stable carbon and oxygen isotope analyses were separated by scraping the desired components out of polished slabs and thick thin sections with needles and microknives. The resulting powder was then sent to the Coastal Science Laboratories in Austin, Texas for extraction and mass spectrometry. Accuracy and precision of stable carbon and oxygen analyses are discussed in Appendix.

STRATIGRAPHY

After the early 1950's drilling program, the gross stratigraphy of Enewetak Atoll was outlined by Cole (1957), Ladd and Schlanger (1960), and Todd and Low (1960). Cole (1957) and Todd and Low (1960) recognized carbonate strata of Upper Eocene, Miocene, Pliocene, and Pleistocene age on the basis of foraminifera (Fig. 4).

The increased data base provided by EXPOE borings
has allowed a much more detailed stratigraphic evaluation of the upper 80 m of Quaternary limestone on Enewetak, with divisions based largely on subaerial exposure surfaces. Each surface represents a hiatus in deposition when previously deposited marine sediments emerged above sea level and were exposed to subaerial, usually meteoric processes.

Criteria for recognition of subaerial exposure have undergone extensive evolution over the last 35 years. Ladd, Tracey, and Lill (1948, p. 52) initially suggested that leached zones in the subsurface of Bikini Atoll formed during emergence and subaerial exposure. Schlanger (1963) used zones of leached aragonite and sparry calcite cement to identify 2 Pleistocene unconformities on Enewetak, at depths of 21 - 32 m and 85 - 95 m in the E-1, F-1, and K-1 wells. Using some of the first EXPOE cores, Tracey and Ladd (1974) proposed a third Enewetak unconformity at well depths of 8 to 12 m.

Because of increased core recovery, workers of the EXPOE drilling project were able to recognize 5 subaerial exposure surfaces between well depths of 0 and 76.2 m (Couch et al., 1975; Ristvet et al., 1978; Goter, 1979). Subaerial exposure surfaces in the EXPOE wells were identified on the basis of paleosols (terra rosa), soil alteration structures, abrupt irregular truncations of strata, and/or prominent changes in mineralogy, chemical composition, and cementation in adjacent strata (Couch et al., 1975, p. 45). Unfortunately,
our samples from the XRI-1, XAR-1, and XEN-1 wells are not extensive enough to re-evaluate the location of each subaerial exposure surface described in Couch et al. (1975). However, the diagenetic patterns observed in our samples are generally consistent with the location of exposure surfaces as proposed by Couch et al. (1975).

The 5 exposure surfaces (0 - 80 m deep) recognized in the EXPOE borings have been traced from core to core and island to island across Enewetak Atoll (Couch et al., 1975). Presumably each exposure surface formed during low stands of sea level associated with glaciation. During interglacial times, sea level would rise and deposit new sequences of carbonate sediment on top of the atoll. Goter (1979) correlated the five unconformities with the terminations of the last 5 interglacial stages whose ages were inferred from isotopic chronostratigraphy of deep sea cores from the Western Pacific (Shackleton and Opdyke, 1976; Fig. 5).

**Depositional Facies in Quaternary Strata**

Descriptions and facies interpretations of the XRI-1, XAR-1, and XEN-1 cores by Couch et al. (1975) are shown in Figures 6 and 7. In addition, all samples examined as a part of this study were described petrographically and in hand sample by the author (Figs. 6 and 7). Couch et al. (1975) provided a general description of 5 - 10
Figure 5.
Stratigraphy of Quaternary limestones of the XRI-1, XAR-1, and XEN-1 wells based on subaerial exposure surfaces (unconformities). Modified from Couch et al. (1975) and Goter (1979).
QUATERNARY STRATIGRAPHY

Package | Unconformity | Average Depth | Glacial Terminations, years BP*
--- | --- | --- | ---
I | A | 12 m (40 ft) | 13,000 BP
II | B | 24 m (80 ft) | 128,000 BP
III | C | 38 m (125 ft) | 347,000 BP
IV | D | 49 m (163 ft) | 440,000 BP
V | E | 68 m (225 ft) | 502,000 BP
VI | | | 592,000 BP

* from Shackleton and Opdyke (1976)
Figure 6.
Depositional facies model for Quaternary strata on Enewetak (left) and depositional textures of the XEN-1 well (right). Depositional facies model is modified from Couch et al. (1975). Dots in diagram on right indicate textures present in samples examined in this study. Lines indicate textural descriptions and facies interpretations of the XEN-1 well from Couch et al. (1975).
DEPOSITIONAL FACIES

XEN-1 WELL

- Coral
- Coralline Algae
- Foraminifera
- Halimeda
- Molluscs
- Sample Texture (this study)
- Textural descriptions and facies interpretation of Couch et al. (1975)
- Exposure Surface
Figure 7.
Depositional textures and environments in Quaternary strata of the XRI-1 and XAR-1 wells. See Figure 6 for Legend and Depositional Model. See Figure 5 for Pleistocene stratigraphy of the wells. Dots indicate textures present in samples examined as a part of this study. Lines indicate textural descriptions and facies interpretations from Couch et al. (1975).
m intervals. The author, however, described smaller samples (less than 30 cm long), which may account for many inconsistencies between the two studies. Virtually every sample examined in this study was analyzed in thin section. Thin section analyses of carbonate textures are more accurate in the recognition of mud and in determining "grain-support" than the examinations of slabbed cores. Most descriptions of Couch et al. (1975) are based on examination of slabbed cores. Couch et al. (1975, p. 45) noted a good correlation between subsurface and surface facies and concluded that there has been little lateral shifting of reef and associated environments during deposition of the upper 90 m of Quaternary strata.

With only a few exceptions, Couch et al. (1975) described the XRI-1, XAR-1, and upper 40 m of the XEN-1 wells as bioclastic packstones and grainstones (Figs. 6 and 7). Most of these bioclastic packstones and grainstones contain interbedded coralline boundstones or interbedded coral and coralline algae clasts (Figs. 6 and 7). Goter (1979) suggested that bioclastic sands interbedded with boundstones are the result of patch reefs growing in areas with sandy bottoms, and considered bioclastic sands with some in situ coral and coralline algae to be typical of back-reef depositional environments (Fig. 6). In contrast, bioclastic sands containing almost no in situ coral or coralline algae are considered to be typical of marginal lagoonal environments
(Fig. 6). Therefore, most of the sediments in the XRI-1, XAR-1, and upper XEN-1 wells were probably deposited in back-reef or marginal lagoonal environments.

Depositional Facies of Lower Miocene and Upper Eocene Strata

Lower Miocene and Upper Eocene strata in the F-1 well have been divided into 2 distinct lithologic groups. Lower Miocene strata between 366 and 853 m in the F-1 well are primarily boundstones and reef-related grainstones formed in or adjacent to a reef (Schlanger, 1963; Fig. 8). Upper Eocene strata between 853 and 1,400 m in the F-1 well include wackestones, packstones, and grainstones deposited mainly in fore-reef and slope environments (Fig. 8; Schlanger, 1963). Clionid galleries are common in cores 3 - 6 (375 - 819 m; Fig. 8). The coarse nature of the sands, abundance of Clionid galleries, and the presence of significant amounts of in situ coral and coralline algae indicate deposition of Lower Miocene strata of the F-1 well in high energy waters near a reef at the seaward margin of the atoll (Fig. 9). The presence of many planktonic foraminifera in core 6 (811 - 819 m) suggests deposition in deeper more seaward reefs; whereas the presence of significant amounts of miliolid foraminifera in core 3 (375 - 380 m) suggests deposition in the more lagoonward parts of a reef complex (Todd and
Figure 8.
Depositional textures of the E-1 and F-1 wells. Solid line indicates the dominant texture. Dashed lines indicate subordinate textures. See Figure 9 for depositional model of E-1 and F-1 well.
Figure 9.
Depositional model for Cenozoic carbonates in the E-1 and F-1 wells. Depositional facies show primarily vertical growth. A large-scale progradation of facies is present in the F-1 well and probably in the E-1 well. Note that almost all carbonate strata in the E-1 well were apparently deposited in shallow atoll-top environments. However in the F-1 well, most Upper Eocene strata and lower portions of Lower Miocene strata were probably deposited in deeper marine waters.
CARBONATES ON ENEWETAK ATOLL

DEPOSITIONAL MODEL FOR CENOZOIC
Low, 1960; Schlanger, 1963).

Between 930 and 1388 m in the F-1 well, cores 7 and 9 - 15 include wackestones, packstones, and grainstones (Fig. 8). Core 8 was not available for sampling. Core 7 is a bioclastic wackestone with large rotaline foraminifera and abundant globigerinids which suggest deposition in over 180 m of water (Todd and Low, 1960). Cores 9 - 11 and the upper part of 12 are primarily grainstones composed dominantly of free-living rotaline foraminifera and fragments of coralline algae with a few large clasts of boundstones and well-cemented grainstones. Paleontologic evidence, as well as textural evidence, suggests deposition of these strata in fore-reef and slope environments over 180 m deep (Todd and Low, 1960; Schlanger, 1963). Most of the larger foraminifera, coral, and coralline algae were probably derived from reef and shallow atoll-top environments (Fig. 9).

Between 1,320 and 1,388 m in the F-1 well, the lower parts of core 12 and cores 13 - 15 are composed predominantly of bioclastic packstones (Fig. 8). Carbonate mud is significantly more abundant in these cores than in cores 9 - 11 and the upper part of 12. Large clasts of coral and boundstones are present, especially in core 15 (Fig. 4). Paleontologic and textural evidence suggests that these rocks were also deposited in fore-reef and slope environments (Fig. 9; Todd and Low, 1960; Schlanger, 1963).

Only three cores were taken in the E-1 well. Core
Core 1 (610 - 618 m deep in the E-l well) consists mainly of bioclastic grainstones including coralline algae, foraminifera, and molluscs (Fig. 8). The presence of many pelecypods and miliolid foraminifera suggests deposition of these sands in shallow water in or near a lagoon (Schlanger, 1963). Core 2 (845 - 855 m) includes bioclastic grainstones as well as wackestones and packstones. As in core 1, the abundance of pelecypods and miliolids in core 2 suggests deposition in a lagoonal environment. Core 3 (1,243 - 1,250 m in E-l well) is primarily a boundstone consisting of coral and muddy internal sediments. Coralline algae and molluscs are also common. Evidence indicates that core 3 was deposited in a shallow reefal environment (Schlanger, 1963).

Deposition in most of the E-l well appears to be shallow marine, suggesting that the location of the E-l well remained high and on top of the atoll from Late Eocene to the present (Schlanger, 1963; Fig. 9). In contrast, most of the Upper Eocene of the F-l well consists of deep marine strata which prograded out into the open ocean (Fig. 9). During Miocene, Pliocene, and Quaternary times, the slow seaward progradation of the atoll continued with reef and reef wall deposition passing upward into back-reef deposition in the F-l well (Fig. 9).
GENERAL DIAGENETIC PATTERNS

The three main diagenetic processes which operate in the subsurface of Enewetak are: cementation, dissolution, and conversion of metastable grains to low-magnesian calcite (LMC). Compaction and dolomitization are also present in some areas. These diagenetic processes vary in intensity in the Cenozoic strata on Enewetak. They will be briefly outlined in this section and discussed in detail in following sections.

Holocene

Diagenetic alteration of Holocene sediments in the XRI-1, XAR-1, and XEN-1 wells is minor (Figs. 10 - 12). Only one Holocene sample (at a depth of 1.5 m in XAR-1) shows significant dissolution or diagenetic alteration of grains. Cements growing on pre-existing grains are very minor in Holocene strata of those three wells (Figs. 10 - 12). Some Holocene boundstones do contain borings and pelleted internal sediments. Based on examination of slabbed core material, Couch et al. (1975) estimated the porosity of most Holocene strata at 20% - 40%.
Figure 10.
Diagenetic alteration in XRI-1 well. Dots at the far left represent sample locations. Abbreviations for cement types are shown at bottom. Many cement types comprise less than 1% of rock sample. Amounts of diagenetic alteration and cementation are based on visual estimates using comparison diagrams in Scholle (1978). Spot checks of visual estimates were made by point-counting thin-sections (300 points). Whole rock mineralogy was estimated from petrographic data. Estimates of % aragonite are based on petrographic recognition of aragonitic fossils and cement. When possible, identification of aragonite grains and cements was confirmed by electron microprobe analyses for strontium. Electron microprobe analyses were used to discriminate between HMC and LMC. Mineralogic analyses of Goter (1979) by X-ray diffraction yield results similar to estimates of mineral composition in this study. The uppermost subaerial exposure surface (17m) separates Holocene from Pleistocene strata.
DIAGENETIC ALTERATION IN XRI-1 WELL

% Diagenetic Alteration

% Cementation

Mineralogy

M = Micrite
Ms = Microporphyritic
e = Equant mosaic
O = Syntaxial echinoderm overgrowth
c = Circumgranular
F = Fibrous
B = Bladed
Eb = Equant-to-bladed

Exposure surface
HMC
Aragonite
LMC

Cementation
Nonmorphosis
Dissolution

Depth (meters)
Figure 11.
Diagenetic alteration in XAR-1 well. Dots at far left represent sample locations. Abbreviations for cement types are shown at bottom. Amounts of diagenetic alteration and cementation are based on visual estimates using comparison diagrams in Scholle (1978). Spot checks of visual estimates were made by point-counting thin-sections (300 points).
Whole rock mineralogy was estimated from petrographic data. Estimates of % aragonite are based on visual estimates of aragonitic fossils and cements. When possible, identifications of aragonitic grains and cements was confirmed by electron microprobe analyses for strontium. Electron microprobe analyses were used to discriminate between HMC and LMC. Mineralogic analyses of Goter (1979) by X-ray diffraction yield results similar to mineralogic estimates in this study. The uppermost subaerial exposure surface (14m) separates Holocene from Pleistocene strata.
DIAGENETIC ALTERATION IN XAR-1 WELL

% Diagenetic Alteration % Cementation

M = Micrite
Ms = Microporar
F = Fibrous
B = Bladed
Eb = Equant-to-bladed

E = Equant mosaic
O = Syntaxial echino-derm overgrowth
C = Circumgranular

M = Micrite
E = Equant mosaic
Exposure surface
HMC
LMC
Aragonite
Circumgranular crusts are common
Figure 12.
Diagenetic alteration in XEN-1 well. Dots at far left represent sample locations. Abbreviations for cement types are shown at bottom. Amounts of diagenetic alteration and cementation are based on visual estimates using comparison diagrams in Scholle (1978). Spot checks of visual estimates were made by point-counting thin-sections (300 points). Whole rock mineralogy was estimated from petrographic data. Estimates of % aragonite are based on visual estimates of aragonitic fossils and cements. When possible, identification of aragonitic grains and cements was confirmed by electron microprobe analyses for strontium. Electron microprobe analyses were used to discriminate between HMC and LMC. Mineralogic analyses of Goter (1979) by X-ray diffraction yield results similar to mineralogic estimates in this study. The uppermost exposure surface (10m) separates Holocene from Pleistocene strata.
DIAGENETIC ALTERATION IN XEN-1 WELL

% Diagenetic Alteration % Cementation

Mineralogy

Depth (meters)

Neomorphism
Cementation
Dissolution

M = Micrite
Ms = Microspar
F = Fibrous
B = Bladed
Eb = Equant-to-bladed
E = Equant mosaic
O = Syntaxial echinoderm overgrowth
c = Circumgranular
crusts are common

Exposure surface
HMC
Aragonite
LMC
Pleistocene

Pleistocene strata in the XRI-1, XAR-1, and XEN-1 wells have very patchy diagenetic alteration (Figs. 10 - 12). Dissolution and cementation are widely distributed between depths of 10 and 80 m. Volumetrically, dissolution is the dominant diagenetic process, although cementation can be locally important (Figs. 10 - 12). Rarely does cement in these strata exceed 20% of a given rock.

Dissolution in Pleistocene strata includes both fabric selective and irregular (non-fabric selective) dissolution. Irregular (non-fabric selective) dissolution is especially common immediately below exposure surfaces (Figs. 10 - 12). Aragonite alteration is quite variable (Saller, 1982). In some strata, aragonite is virtually unaltered, while in other strata, virtually all aragonite has been either dissolved or converted to sparry calcite. Porosity in Pleistocene strata recovered by the EXPOE drilling project is generally estimated at approximately 20 % by Couch et al. (1975).

Lower Miocene: F-1 well

Samples from Lower Miocene strata of the F-1 well are usually well cemented and show pervasive diagenetic alteration. Cements are very abundant, obliterating much primary and secondary porosity (Fig. 13). Fabric selective
Figure 13.
Diagenetic alteration in F-1 well. Column at left shows core locations and approximate bulk mineralogies from Schlanger (1963). Amounts of dissolution, cementation, and dolomitization are based on visual estimates using comparison diagrams in Scholle (1978). Note, dissolution in Upper Eocene strata is often difficult to estimate because aragonite can dissolve without a trace.
DIAGENETIC ALTERATION IN F-1 WELL

% Alteration in Rock

Pleistocene

Pliocene

Middle and Upper Miocene

Lower Miocene

Upper Eocene

<table>
<thead>
<tr>
<th>Depth (meters)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>200</td>
</tr>
<tr>
<td>400</td>
</tr>
<tr>
<td>600</td>
</tr>
<tr>
<td>800</td>
</tr>
<tr>
<td>1000</td>
</tr>
<tr>
<td>1200</td>
</tr>
<tr>
<td>1400</td>
</tr>
</tbody>
</table>

Basalt

F = Compaction fracturing  PS = Pressure Solution

--- Cementation  --- Dissolution  ---- Dolomitization

Aranomite  Calcite  Dolomite

△ Data point for cementation
○ Data point for dissolution
dissolution of aragonite is pervasive. Many aragonite molds have been refilled with cement. Internal sediments are also very common in these strata. In F-l cores 3 - 6 (375 - 819 m), measured porosities vary from 5.8% in well-cemented intervals to 33.9% in poorly cemented strata (Table 1; Swartz, 1962). Average measured porosity is 13.7%.

**Upper Eocene: F-l Well**

Except in zones of intense dolomitization, cementation and probably dissolution are minor in Upper Eocene strata of the F-l well (Fig. 13). Clasts containing abundant cement can often be found in this interval; however, autochthonous calcite cements are restricted to minor fibrous cements and echinoderm overgrowths. Aragonite has been selectively dissolved. Unfortunately, molds of the original aragonite grains are often not present so the amount of aragonite originally present, and subsequently dissolved, is impossible to estimate. Compaction-related fracturing and pressure solution are very common in Upper Eocene grainstones of the F-l well. Dolomitization is present in cores 11 - 15 (1,279 - 1,388 m) and is abundant in cores 11 and 12 (1,279 - 1,323 m). Measured porosity is very high (over 30%) in undolomitized and partially dolomitized grainstones (Table 1). Porosity of a completely dolomitized sample is only 10% (Table 1; Swartz, 1962).
### TABLE 1
POROSITY AND PERMEABILITY
OF DEEP ENEWETAK SAMPLES
(E-1 and F-1 Wells)

<table>
<thead>
<tr>
<th>WELL</th>
<th>CORE-SAMPLE</th>
<th>DEPTH (m)</th>
<th>POROSITY (%)</th>
<th>PERMEABILITY (millidarcies)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E-1</td>
<td>1</td>
<td>611 - 618</td>
<td>47.6</td>
<td>454</td>
</tr>
<tr>
<td></td>
<td>1 - 13</td>
<td>611 - 618</td>
<td>56.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>854 - 856</td>
<td>28.7</td>
<td>619</td>
</tr>
<tr>
<td></td>
<td>3 (5&quot; above base of core)</td>
<td>1,243 - 1,250</td>
<td>11.7</td>
<td>5.9</td>
</tr>
<tr>
<td></td>
<td>3 (6&quot; above base of core)</td>
<td>1,243 - 1,250</td>
<td>15.0</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>3 - 21</td>
<td>1,243 - 1,250</td>
<td>16.6</td>
<td></td>
</tr>
<tr>
<td>F-1</td>
<td>1 - 1</td>
<td>52 - 58</td>
<td>43.0</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>3 - 5</td>
<td>376 - 380</td>
<td>12.1</td>
<td>2.0</td>
</tr>
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<td>3 - 6</td>
<td>376 - 380</td>
<td>18.8</td>
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<td>4 - 1</td>
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<td>6 - 2</td>
<td>811 - 819</td>
<td>13.7</td>
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<tr>
<td></td>
<td>6 - 20</td>
<td>811 - 819</td>
<td>7.6</td>
<td>0.011</td>
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<tr>
<td></td>
<td>10 - 6</td>
<td>1,208 - 1,216</td>
<td>37.1</td>
<td>488</td>
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<tr>
<td></td>
<td>11 - 31</td>
<td>1,279 - 1,287</td>
<td>31.1</td>
<td>112</td>
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<tr>
<td></td>
<td>11 - 31</td>
<td>1,279 - 1,287</td>
<td>33.6</td>
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<tr>
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<td>12 - 6</td>
<td>1,316 - 1,323</td>
<td>8.7</td>
<td>0.022</td>
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<tr>
<td></td>
<td>12 - 6</td>
<td>1,316 - 1,323</td>
<td>12.0</td>
<td></td>
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<td>13 - 5</td>
<td>1,343 - 1,351</td>
<td>19.1</td>
<td>48.8</td>
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<tr>
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<td>14 - 18</td>
<td>1,372 - 1,379</td>
<td>31.8</td>
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<td>14 - 19</td>
<td>1,372 - 1,379</td>
<td>32.7</td>
<td>3.6</td>
</tr>
</tbody>
</table>

Note: Above data from Swartz (1962)
Only 3 cores were taken from the E-1 well and each shows very different patterns of diagenetic alteration. Core 1 is from the Lower Miocene at approximately 610 m and shows very little diagenetic alteration. In core 1, the only diagenetic process identified by petrography is minor intrafabrics dissolution of some aragonitic grains, minor compaction fracturing, and minor pressure solution (Fig. 14). Much aragonite (over 50%) remains intact in these strata and no cement was found. Measured porosity is approximately 50% (Table 1; Swartz, 1962).

Core 2 of the E-1 well (854 - 856 m deep) shows diagenetic textures similar to those observed in Pleistocene strata of the Enewetak Atoll. Major diagenetic features include fabric selective dissolution of aragonitic grains and cementation (Fig. 14). Clear, unevenly distributed equant-to-bladed cements are common. Measured porosity in a sample from core 2 is 28.7% (Table 1; Swartz, 1962).

Strata in core 3 of the E-1 well (1,243 - 1,250 m) were deposited in and around a coral reef. Large amounts of original aragonite have been selectively dissolved and many coral molds have been refilled with bladed cement. Medium to coarse crystalline bladed cement is very abundant filling both primary and secondary voids. A significant amount of dolomite is also present. Measured porosity in core 3 is 11.7 - 16.6% (Table 1; Swartz, 1962).
Figure 14.
Diagenetic alteration in E-1 well. Column at left shows core locations and approximate bulk mineralogies from Schlanger (1963). Amounts of dissolution, cementation, and dolomitization are based on visual estimates using comparison diagrams in Scholle (1978). The intensity of diagenetic alteration between cores is based partly on the drilling rate log (Fig. 38).
DIAGENETIC ALTERATION IN E-1 WELL

% Alteration in Rock

- Pleistocene
- Pliocene
- Middle and Upper Miocene
- Lower Miocene
- Upper Eocene

Depth (meters)

Data point for cementation

Data point for dissolution

Cementation
Dissolution
Dolomitization

Aragonite
Calcite
Dolomite
F = Compaction
fracturing
PS = Pressure
solution
H = HMC

Basalt
Discussion of General Diagenetic Patterns

Figures 10 - 14 illustrate the variability in diagenetic alteration of Cenozoic carbonates on Enewetak. Clearly, cementation and dissolution are not only dependent on burial time and depth. Rather, diagenetic alteration appears to be a product of the diagenetic environments through which the rocks have passed. Cementation, dissolution, and other diagenetic processes observed on Enewetak are known to occur in meteoric, marine, and burial environments (Matthews, 1968; Land, 1970; James et al., 1976; Land and Moore, 1980; Schlager and James, 1978; Moore and Druckman, 1981).

In the following sections, cementation and other types of diagenetic alteration in Cenozoic strata on Enewetak are systematically described. First, cementation on Enewetak will be discussed petrographically and geochemically, and general conclusions will be drawn regarding the environments in which various cements were precipitated. Diagenetic alteration of original grains will then be considered. Conclusions regarding the origin of various cements will aid in the interpretation of dissolved grains and grains inverted or neomorphosed to LMC.

In deeper Enewetak carbonates, compaction and dolomi-
tization are common. Compaction generally occurs after calcite cementation, but before dolomitization. Therefore compaction of rigid grains will be discussed prior to dolomitization so that information provided by compaction can be used to place constraints on the origin of Enewetak dolomite.
CEMENTS

One of the most fundamental processes in carbonate diagenesis is cementation. Cements are essential to the lithification of limestones and often are the main feature obliterating porosity in ancient rocks. The term "cement" is used to include all "passively" precipitated carbonate crystals which grow attached to a free surface and fill open voids (Bathurst, 1975, p. 416). Bathurst (1975) established a number of criteria for the identification of cement, most of which were used in this study. In all samples, cements were petrographically described according to morphology, distribution, and relation to other textural features. Cements in many samples were then analyzed for strontium and magnesium concentrations by an electron microprobe. In addition, cements in some samples were separated for detailed stable carbon and oxygen isotope analyses.

PETROLOGY

Petrologic studies of cement morphology, position, and distribution can yield a great deal of insight into the timing and environment of cementation. Using petrographic relationships, the timing of cementation can often be determined relative to dissolution, compaction, and other generations.
of cementation. Recently, cement morphology and distribution have been correlated to certain nearsurface diagenetic environments of precipitation (Land, 1970; Folk, 1974; Longman, 1980).

**Quaternary Cements**

Quaternary cements on Enewetak include seven main morphologies: (1) micrite, (2) microspar, (3) fibrous, (4) bladed, (5) equant-to-bladed (6) equant mosaic, and (7) echinoderm overgrowths (Folk, 1965).

**Micrite Cements**

Micrite cements are not volumetrically important in Quaternary strata on Enewetak and were only observed in 2 out of 25 Holocene samples from the XRI-1, XAR-1, and XEN-1 wells (Figs. 10 - 12). Micrite cements are widespread in Pleistocene strata, but are not volumetrically important. The only sample studied which contains over 1% micrite cement is from the XRI-1 well at 45 m (less than 0.3 m below an exposure surface; Fig. 10). That sample contains micrite in a structure similar to soil-related structures described by Harrison (1977) and Beach (1982). Early micrite cements in Pleistocene strata often form thin dark crusts around grains which retain the outline of grains even after the original grains are dissolved (Fig. 15a). Micrite
Photomicrographs of Pleistocene cements from Enewetak:

(a) Calcite cements in limestone from a depth of 69 m in XRI-1 well. Note the dark crusts of micrite cement (M) surrounding grains. Micrite crusts are overgrown by clear bladed-to-equant cements. Bar scale at lower left equals 0.1 mm. Crossed nicols.

(b) Microspar (Ms) associated with a root path. See Harrison (1977) for photomicrographs of similar root paths in caliche profile on Barbados. Note how microspar grades into equant-to-bladed cements in some voids (53 m, XAR-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.

(c) Fibrous aragonite cements preferentially growing on aragonite grains. Note that rotaline foraminifera (R) and echinoderm fragment (E) have no fibrous aragonite cement whereas Halimeda plates (H) are surrounded by crusts of fibrous aragonite cement (18 m, XEN-1 well). Bar scale at lower left equals 0.5 mm. Crossed nicols.

(d) Bladed cement (left) grading into travertine (right) suggesting rapid precipitation of bladed cements as well as travertine (73 m, XRI-1 well). Bar scale equals 0.5 mm.

(e) Crust of equant-to-bladed cement. See Figure 23 for electron microprobe traverse C-C' (72 m, XRI-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.

(f) Equant mosaic cement filling intracoralline void (50 m, XRI-1 well). Bar scale equals 0.1 mm. Crossed nicols.
rims formed by endolith algae may superficially appear like crusts of micrite cements. However, micritization associated with endolithic algae can be identified by filaments and borings (often filled with micrite) penetrating into primary grains.

**Microspar**

Microspar (Folk, 1965) is rare in the Pleistocene and absent in Holocene samples from Enewetak. Microspar is found in 2 samples immediately below exposure surfaces, and is associated with what appear to be root paths and soil-related structures similar to those described by Harrison (1977). Clear microspar can also occasionally be found replacing aragonite grains. It is difficult to prove that the microspar is indeed a fine void-fill cement; however, microspars in soil-related structures often grade into clear, coarser void-fill cements (Fig. 15b), suggesting that microspar may occur as a fine crystalline equant, void-fill cement. When replacing aragonite grains, microspar is generally clear and is often surrounded by open void space suggesting that the microspar may also be a cement.

**Fibrous Cement**

In Quaternary strata of the XRI-1, XAR-1, and XEN-1 wells, fibrous cements may be aragonite, high-magnesian
calcite (HMC), or low-magnesian calcite (LMC). Fibrous HMC cements are extremely rare in the XRI-1, XAR-1 and XEN-1 wells, being found only in one Holocene sample. Fibrous LMC cements were found only in a few Pleistocene samples. Fibrous aragonite (identified by SEM and elemental analyses for strontium) occurs more widely in the Quaternary section of Enewetak (Figs. 10 - 12). Fibrous aragonite cements are present in 10 out of 25 samples from Holocene strata; however, no Holocene samples examined in this study contain over 2% fibrous cement. Fibrous aragonite cements are scattered through much of the Pleistocene of Enewetak, but they are volumetrically important in only two intervals (14.0 - 18.3 m in the XEN-1 well; 28.7 m in the XAR-1 well; Figs. 10 - 12). Fibrous aragonite cement may preferentially grow and form isopachous crusts on aragonite rather than calcite grains (Fig. 15c).

**Bladed Cement**

In some Pleistocene strata on Enewetak, bladed cements (Folk, 1965) are quite common and tend to be concentrated in intervals not directly associated with exposure surfaces (Figs. 10 - 12). As used here, bladed cements maintain a relatively constant width while growing into open voids. Bladed cements usually occur as isopachous crusts and have a fairly uniform distribution in the Pleistocene of Enewetak. They are preferentially found in primary intergranular
and larger solution voids, and rarely in primary intragranular voids. At 72.8 m in the XRI-1 well, bladed cements grade laterally into travertine (Fig. 15d).

Bladed cements in Pleistocene strata of the XEN-1 and XRI-1 wells are commonly inclusion-rich. These inclusion-rich cements are present in many samples between 45 and 64 m in the XRI-1 well (Fig. 10) and between 25.6 and 39 m in the XEN-1 well (Fig. 12). Inclusion-rich bladed cements occur as (1) inclusion-rich, isolated bladed crystals which generally do not touch adjacent cement crystals and (2) coalescing bladed crystals with inclusion-rich cores and clear rims and terminations (Fig. 16).

Isolated bladed cements are uniformly inclusion-rich with no clear portions. These cements have irregular terminations and variable orientations relative to the substrate on which they are growing (Fig. 16). Scanning electron microscopy (SEM) reveals that these isolated, inclusion-rich, bladed crystals do not have simple planar faces, but consist of complex composite forms which include multiple knife-like and arrow-shaped projections (Figs. 15c&f). In thin section, inclusions in both isolated and coalescing bladed cement crystals are generally linear and single phase. SEM examination indicates that the inclusions are hollow, suggesting that they may have originally been filled with a fluid. Linear inclusions tend to parallel other linear inclusions within individual bladed crystals (Fig. 15).
Figure 16.

Pleistocene inclusion-rich bladed cements:

(a) Isolated, inclusion-rich, bladed cement (58 m, XRI-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.

(b) Close-up of isolated, inclusion-rich, bladed cement (58 m, XRI-1 well). Bar scale at lower left equals 0.05 mm. Crossed nicols.

(c) SEM photograph of isolated, inclusion-rich, bladed cement. Bar scale at lower right equals 10 microns (58 m, XRI-1 well).

(d) Inclusion-rich bladed cements with inclusion-rich cores and clear terminations. See Figure 23 for electron microprobe traverse A-A' (51 m, XRI-1 well). Bar scale at lower left equals 0.1 mm.

(e) Close-up of inclusion-rich cores of bladed cements. Note that within cement crystals, linear inclusions are parallel to each other (48 m, XRI-1 well). Bar scale at lower left equals 0.05 mm.

(f) SEM photograph of isolated, inclusion-rich bladed cement. Bar scale at lower right equals 10 microns (58 m, XRI-1 well).
Equant-to-bladed cement

Equant-to-bladed crusts of cement begin as equant cements (Folk, 1965) and become bladed as they grow outward. In contrast to simple bladed cements, equant-to-bladed cements become significantly wider as they grow toward the center of voids (Fig. 16). Equant-to-bladed cements are the most widespread and abundant type of void-fill cement in the Pleistocene of Enewetak (Fig. 10 - 12), but are not observed in Holocene samples. These cements are commonly found filling large and small intergranular, intragranular, and solution voids and, in some samples, occur as isopachous crusts with a fairly uniform distribution. In other samples, equant-to-bladed cements are unevenly distributed (Dunham, 1971) and may be restricted to small intergranular voids and intragranular voids. Equant-to-bladed cements are generally clear and may grade locally into equant mosaic or bladed cements.

Equant mosaic cement

The main difference between equant mosaic and equant-to-bladed cements is that equant mosaic cements are wider, (perpendicular to the original void wall) probably because they grew with less competition and interference from adjacent cements. In the Pleistocene of Enewetak,
equant mosaic cements are less widespread and significantly less abundant than equant-to-bladed cements (Figs. 10-12). Equant mosaic cements were not found in Holocene strata. In the Pleistocene, equant mosaic cements are most commonly found in primary intragranular voids and in fossil molds (Fig. 15f).

**Echinoderm Overgrowths**

In Quaternary strata on Enewetak, neither echinoderm fragments nor echinoderm overgrowths are volumetrically significant (less than 1% of any given rock). While echinoderm overgrowths are scattered through much of the Pleistocene, they were not observed in Holocene samples. The lack of echinoderm fragments in many Quaternary samples makes generalizations regarding overgrowth characteristics and distribution difficult. Echinoderm overgrowths are usually found in rocks containing both echinoderm fragments and significant calcite cement (Figs. 10-12). At 17.7 m in the XEN-1 well, thick isopachous crusts of aragonite cement cover most aragonite grains; however, neither aragonite cement nor calcite overgrowths were observed on most echinoderms fragments (Fig. 15c).

**Cement Distribution in Quaternary strata**

Quaternary cements are common in primary intragranular,
primary intergranular, and solution voids. Immediately below subaerial exposure surfaces, calcite cements are patchy and range from rare to very common. Cements associated with exposure surfaces are variable in thickness and preferentially fill intragranular and small intergranular voids (Fig. 17a). In poorly cemented intervals not directly associated with an exposure surface, calcite cements generally have an uneven distribution preferentially filling intragranular and small intergranular voids (Fig. 17a & b). Distinct meniscus and microstalagtitic (pendant) cements are rare in Pleistocene samples from Enewetak.

In well-cemented zones not directly associated with exposure surfaces, intergranular cements often form isopachous crusts within individual voids (Fig. 17d). However, on a mesoscopic scale, those intergranular cements are often variable in thickness (are patchy; Figs. 17d & e). In some well-cemented intervals, small intergranular voids have the thickest cements; whereas, in other well-cemented intervals larger intergranular and solution voids have thicker crusts. Cement distribution relative to dissolution and neomorphism will be discussed later.

Cements in Lower Miocene Strata
of the F-1 Well

Samples from Lower Miocene strata of the F-1 well
Figure 17.
(a) Pleistocene calcite cements (c) preferentially filling small voids while large void (V) at right contains no visible cement (45 m, XRI-1 well). Bar scale at lower left equals 0.1 mm.
(b) Pleistocene calcite cements preferentially fill intra-foraminiferal chambers while intergranular voids contain little or no cement (45 m, XAR-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(c) Micrite root-structure (?) at top of core 3, 375 m, F-1 well. Bar scale at lower left equals 0.1 mm.
(d) Circumvoid crusts of equant-to-bladed calcite cement (69 m, XRI-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(e) Grainstone less than 10 cm away from (d). Note (d) has much thicker cement as a result of patchy cementation. Bar scale at lower left equals 0.5 mm. Crossed nicols.
(f) Microcodium (M) at top of core 3 (375 m), F-1 well. Bar scale at lower left equals 0.1 mm.
contain abundant cement (often 20 - 30%; Fig. 13). Radial calcite is the dominant cement type, although fibrous and finer bladed cements are also present in most samples. Echinoderm overgrowths are present and will be discussed in the radiaxial section. In the upper part of core 3 (F-1 well at 375 m), an assemblage of cements and diagenetic features that are not observed elsewhere in Lower Miocene strata of the F-1 well are present and include micrite cements, microspar, equant-to-bladed cements, and Microcodium (Figs. 17 c & f; Johnson, 1961). Micrite cements and microspar are found in structures similar to those described and are given a root or soil-related origin by James (1972), Harrison (1977), and Beach (1982). The equant-to-bladed cements are fine, clear, and uneven in their distribution. Calcite spars identified as Microcodium were initially described in these samples by Johnson (1961). Microcodium structures in core 3 tend to cross cut and truncate original depositional features. It is not clear whether the calcite spar filling the Microcodium structures is a true void-fill cement.

Fibrous Cement

In Lower Miocene strata of the F-1 well, fibrous LMC cements are widely scattered occurring (1) as thin crusts in voids without radiaxial calcite, (2) as early cements overgrown by much coarser radiaxial spar, and (3) in chambers
of rotaline foraminifera (Fig. 18a). These fibrous cements preferentially grow on and in rotaline foraminifera, primary intergranular voids, and aragonite molds. When overgrown by radiaxial calcite, fibrous cements generally retain their own optical identity (Fig. 18b). Coralline algae in these Lower Miocene strata are also LMC suggesting that fibrous cements as well as coralline algae may have lost some original magnesium.

**Fine to medium crystalline bladed cement**

Fine to medium crystalline bladed cements occur in small voids adjacent to radiaxial calcite. Presumably, those bladed LMC crystals grew at roughly the same time as radiaxial spar but apparently did not have enough space to develop extinction features characteristic of radiaxial spar. Fine to medium crystalline bladed cements are common in narrow voids created by the dissolution of some types of coral.

**Radiaxial calcite**

Radiaxial calcite cement is abundant in Lower Miocene strata of the F-1 well. Bathurst (1959, 1975) petrographically describes radiaxial calcite as having "a peculiar combination of curved twins, convergent optic axes and diverging subcrystals within a single cement crystal". Kendall (1984) discusses
Figure 18.
Photomicrographs of calcite cements in Lower Miocene strata of the F-1 well. All bar scales at lower left equal 0.1 mm.
(a) Fibrous LMC cement preferentially growing on rotaline foraminifera (F) (524 m, F-1 well). Crossed nicols.
(b) Clear radiaxial calcite cement. Note undulose extinction of the radiaxial spars. At left, radiaxial calcite has overgrown fibrous LMC cement which retain their crystallographic identity (378 m, F-1 well). For electron microprobe traverse B-B', see Figure 24. Crossed nicols.
(c) Radiaxial calcite cement infilling a dissolved *Halimeda* flake (379 m, F-1 well). Crossed nicols.
(d) Radiaxial calcite cement infilling a dissolved coral. Dark micritic material is internal sediment which filled primary intracoralline voids (378 m, F-1 well). Crossed nicols.
(e) Radiaxial calcite (R) filling a Clionid boring. Note scalloped edges of the boring (379 m, F-1 well). Crossed nicols.
(f) Radiaxial calcites with rhombic to scalenohedral crystal faces. Note that the boundary between clear and inclusion-rich radiaxial calcite is roughly parallel to the existing radiaxial termination (379 m, F-1 well).
the crystallography and growth patterns of radiaxial calcite in terms of master crystals composed of numerous converging and coalescing subcrystals with slightly different optical orientations. Kendall's master crystals are usually bladed or equant-to-bladed, while subcrystals are generally fibrous. Enewetak radiaxial calcites are very similar to those described by Bathurst (1959, 1975), Kendall and Tucker (1973), and Kendall (1984) except that Enewetak radiaxial calcites generally lack twinning.

In Lower Miocene strata of the F-1 well, radiaxial calcites are the dominant type of cement consisting of bladed or equant-to-bladed master crystals which generally become wider away from original cavity walls. Radiaxial spars have sharp boundaries with original depositional grains at the edge of voids. On Enewetak, master radiaxial crystals have an undulose extinction which often covers 25° of stage rotation (Figs. 18b-e). Enewetak radiaxial crystals are generally length-fast with long axes oriented perpendicular to the cavity walls. Intercrystalline boundaries are sharp and often irregular, rather than planar (Fig. 18).

Present radiaxial cement terminations have acute scalenohedral, jagged rhombic, jagged scalenohedral, rounded, and jagged rounded forms (Figs. 18 and 19). SEM observations reveal that jagged terminations appear as composites of numerous fibrous subcrystals which often coalesce into larger roughly rhombohedral or scalenohedral terminations (Fig. 19). Individual fibrous subcrystals may be anhedral
Figure 19.
Radiaxial calcites in Lower Miocene strata of the F-1 well.  
(a) Bladed radiaxial cement. Note inclusion-rich bands that apparently define former crystal faces and are similar in shape to existing cement terminations (607 m, F-1 well). Bar scale at lower left equals 0.1 mm. 
(b) Equant-to-bladed radiaxial cement with jagged, rhombic-to-scalenohedral terminations. Note that inclusion-rich bands mimic existing cement terminations (814 m, F-1 well). Bar scale at lower left equals 0.1 mm. 
(c) Banded radiaxial cement. Note that some growth bands have shapes that apparently define crystal faces similar to existing radiaxial terminations (526 m, F-1 well). Bar scale at lower left equals 0.1 mm. 
(d-f) SEM photographs of jagged radiaxial cement terminations. Note that fibrous subcrystals tend to coalesce with growth (603-611 m, F-1 well). Bar scales equal 100 microns (0.1 mm).
or may have small rhombic terminations (Figs. 19d-f).

Radial crystals vary from clear to very inclusion-rich (Figs. 18-20). Individual inclusions may be roughly linear, jagged or irregular in shape. Videtich (1982) has documented that some tubular and irregular inclusions are the result of organic (fungal?) infestations. SEM examination indicates that other inclusions now are hollow and were probably originally filled with a fluid. Inclusions do not fluoresce under ultraviolet light suggesting that they are not currently filled with organic material.

In Enewetak radial cements, inclusion-rich and inclusion-poor bands often alternate with the final band generally being clear (Figs. 18-20). Inclusion-rich and inclusion-poor bands are usually continuous around a given void (Figs. 19-20). Inclusion-rich radial laminations (bands) commonly have straight, rounded, rhombic, or acute scalenohedral outlines that closely resemble existing termination patterns (Figs. 18-20). Frequently, small jagged inclusion patterns are superimposed on the larger outlines (Figs. 18 and 19).

Distribution

On Enewetak, radial cement is only found in Lower Miocene strata of the F-1 well. In those strata, the thickest radial spars are found in large open voids. In smaller adjacent voids and other voids with more restricted fluid flow, radial spars are often thin or absent. Clearly,
Figure 20.
Cements in Lower Miocene strata, F-1 well.
(a) Internal sediments (I) containing a small foraminifera alternate with cements related to radiaxial calcite (815 m, F-1 well). Bar scale at lower left equals 0.5 mm.
(b) Banded radiaxial calcite partially filling a Clionid gallery. Note irregular and scalloped lower boundary of dark internal sediments in upper third of photo (813 m, F-1 well). For electron microprobe traverse C-C', see Figure 24. Bar scale at lower left equals 0.5 mm.
(c) Dolomite cement (D) overgrowing radiaxial calcite (C). Calcite is dark (red) due to staining with Alizarin-Red-S. Note a band of dolomite within radiaxial calcite (D) that generally parallels growth laminations; however that dolomite cross-cuts radiaxial cement laminations at far right (378 m, F-1 well). Bar scale at lower left equals 0.1 mm.
(d) Echinoderm fragment (E) with syntaxial LMC cement overgrowth. Inclusion-rich bands can be traced from adjacent radiaxial calcite cements (R) into the echinoderm overgrowth (814 m, F-1 well). Bar scale equals 0.1 mm. Crossed nicols.
(e) Radiaxial calcite cement filling intergranular voids (608 m, F-1 well). For electron microprobe traverse A-A', see Figure 24. Bar scale at lower left equals 0.1 mm.
(f) SEM photograph of dolomite overgrowing radiaxial cement. See (c) for photomicrograph of same dolomite overgrowing radiaxial calcite (378 m, F-1 well).
radial cementation is associated with, and enhanced by, open, unobstructed fluid flow.

Relation to other diagenetic features

Radial spars are commonly observed filling voids created by aragonite dissolution, such as coral and Halimeda molds (Figs. 18c-d). In some cases, primary intracoralline voids are filled with one generation of radial spar, while another generation of radial spar can be observed infilling the coral mold. The intracoralline radial cement may have formed prior to aragonite dissolution; however, the radial cement filling the coral mold had to precipitate after dissolution of the coral.

Radial spars commonly fill irregular voids apparently formed by Clionid sponges (C.H. Moore, 1984, pers. comm.; Figs. 18e and 20b). Clionid galleries may be partially filled with rotaline forams, coralline algal fragments, and pelleted internal sediments. Often radial cements grow on fossil fragments and above pelleted internal sediments that partially fill those Clionid galleries. Clionid galleries are never observed truncating radial spar, indicating that bioerosion occurred prior to the formation of radial spar. Fossil fragments are almost never observed resting on radial spar indicating that radial spars formed after fossils were deposited in the irregular voids. Radial spars are found over internal sediments in geopetal structures. However, in a single sample (Fl-6-13), cements associated
with poorly-developed radiaxial calcite alternate with several generations of pelleted internal sediments which also contain small foraminifera tests (Fig. 20a).

In Lower Miocene strata of the F-1 well, calcite overgrowths commonly develop on echinoderm fragments (Fig. 20d). A gradual transition can be observed between proximal echinoderm overgrowths, which have straight monocristalline syntaxial extinction, and distal overgrowths with more undulose, radiaxial-type extinction. Inclusion-rich bands can be traced from radiaxial spars into the echinoderm overgrowths, indicating that the overgrowths and radiaxial calcites grew simultaneously (Fig. 20d).

In a few Lower Miocene samples (F1-3-20, F1-5-20, F1-6-9), small quantities of dolomite have been found (Schlanger, 1963; Videtich, 1982). In this study, dolomite was found in only one Lower Miocene sample (F1-3-22). In that sample, dolomite cements are observed overgrowing the last (distal) stage of radiaxial cementation (Figs. 20 c & f). Microdolomites were not found in these radiaxial cements (Videtich, 1982).

Cements in Upper Eocene Strata of the F-1 Well

In Upper Eocene strata of the F-1 well, the two main types of autochthonous calcite cement are thin fibrous cements and echinoderm overgrowths, but neither are volumetrically important (Fig. 13). Coarse, often inclusion-rich
fibrous and bladed cements are present in some allochthonous clasts found 1,110 - 1,350 m deep in the F-1 well.

Thin fibrous LMC cements are widespread throughout cores 9 - 15 (1,110 - 1,390 m) of the F-1 well; however, they are never volumetrically important (never more than 2%). These cements are very similar to thin fibrous cements found in the Lower Miocene of the F-1 well. Generally, these thin fibrous cements occur as crusts that are thickest on rotaline foraminifera, thinner or non-existent on coralline algae, and absent on echinoderm fragments. Fibrous cements are also generally absent in former (now dissolved) aragonite grains. In Upper Eocene strata, the fibrous cements are sometimes split by compaction fractures; however, they are never observed growing within compaction-related fractures. Thin fibrous cements can also be found at pressure solution contacts (Fig. 21a), suggesting fibrous cements precipitated prior to significant compaction.

Echinoderm overgrowths are commonly found in Upper Eocene strata of the F-1 well. Their volumetric abundance is limited by the number of echinoderm fragments present. Echinoderm overgrowths are often coarse, preferentially growing parallel to the "c" crystallographic axis of echinoderm fragments. These overgrowths are clear and frequently have multiple euhedral terminations (Fig. 21c). Echinoderm overgrowths in Upper Eocene strata of the F-1 well have unit extinction except where the overgrowths are twinned. Petrographically, syntaxial echinoderm overgrowths appear
Figure 21.
Cements in Upper Eocene strata. All bar scales at lower left equal 0.1 mm.

(a) Compaction (pressure solution) of rotaline foraminifera overgrown by fibrous cements. Note that fibrous cements are involved in compaction and pressure solution (1,315 m, F-1 well).

(b) Patchy, uneven cementation in core 2 (854 - 856 m) of the E-1 well. Note much more intergranular cement at right. Crossed nicols.

(c) Echinoderm overgrowth with multiple clear, euhedral terminations (1,281 m, F-1 well). Crossed nicols.

(d) Bladed cement filling a coral mold in core 3 of the E-1 well (1,243 - 1,250 m). Dark internal sediments have filled primary intra-coraline voids.

(e) Bladed cements filling primary intracoralline voids and coral molds. Bladed cements filling coral molds (C) are generally inclusion-rich. Bladed cements filling primary intracoral voids (I) generally have inclusion-rich proximal portions and clear distal portions (core 3, 1,243 - 1,250 m, E-1 well).

(f) Inclusion-rich bladed cements in an allochthonous clast (1,315 m, F-1 well).

to have precipitated at approximately the same time as fibrous cements. Euhedral echinoderm overgrowths can be found in pressure-solution contact with other grains; however, overgrowths are rarely observed overgrowing compaction-related fractures. Therefore, echinoderm overgrowths generally formed prior to significant compaction.

Clasts containing abundant bladed and fibrous cements are found in cores 9, 12, and 13 in the Upper Eocene of the F-1 well. These bladed and fibrous cements are generally medium to coarsely crystalline and inclusion-rich, differing from radiaxial spar in that (1) they generally do not have radiaxial-type undulose extinction, (2) they generally do not have jagged terminations, (3) they do not have alternating bands of inclusion-rich and inclusion-poor calcite, and (4) sometimes they are fibrous (Fig. 21f). These bladed and fibrous cements can be found radiating out from open aragonite molds suggesting that they precipitated prior to aragonite dissolution.

Cements in Upper Eocene strata of the E-1 well

No cements were found in core 1 of the E-1 well (Lower Miocene; 610 - 618 m; Fig. 14). Clear equant-to-bladed cements are common in core 2 (Upper Eocene; 854 - 856 m) of the E-1 well comprising up to 20% of some samples. These equant-to-bladed cements preferentially fill intragranular voids, small intergranular voids, and molds of dissolved
aragonite grains. Equant-to-bladed cements have a very uneven thickness and distribution throughout core 2 (Fig. 21b). Thin micrite crusts coat most original grains, but are volumetrically minor. Cements filling solution molds tend to be equant mosaics rather than equant-to-bladed. The presence of some equant-to-bladed cements surrounding unfilled molds and other cements filling aragonite molds suggests that cementation has alternated through time with aragonite dissolution.

Cementation in core 3 (1,243 - 1,250 m) of the E-1 well is dominated by precipitation of medium to coarse crystalline, bladed cements. Bladed cements, most inclusion-rich, comprise 20 - 70% of most samples. These cements are similar to bladed cements present in allochthonous clasts in Upper Eocene strata of the F-1 well. Bladed cements are commonly found filling coral molds in core 3 of the E-1 well (Figs. 21d-e). Sometimes a different generation of bladed cement will fill intra-coralline voids; in other cases, the same generation of cement that replaced the coral also fills the intra-coralline voids (Fig. 21e). Therefore, bladed calcite cements may have precipitated prior to aragonite dissolution in a few cases, but after aragonite dissolution in many other cases.

Discussion of Cement Petrography

Correlation of diagenetic environments with cement
Mineralogy, morphology, and distribution has been discussed by Land (1970), Dunham (1971), Matthews (1974), Folk (1974), Steinen (1974), Halley and Harris (1979), Moore (1979), and Longman (1980). Folk (1974) set forth a fundamental correlation between salinity and cement morphology in carbonate environments. Basically, Folk (1974) proposed that cements precipitated from waters with lower Mg$^{2+}$/Ca$^{2+}$ ratios have more rapid sideward growth. Therefore cements precipitated from freshwater (low Mg$^{2+}$/Ca$^{2+}$) should be more equant (lower length/width ratio); whereas cements precipitated from more saline waters (high Mg$^{2+}$/Ca$^{2+}$) should be more fibrous (higher length/width ratio; Folk, 1974). Land (1970), Matthews (1974), Folk (1974), Moore (1979), and Longman (1980) show that the petrography of cements can be used as an initial guide to diagenetic environments of cementation on Enewetak.

*Micrite*

Micrite cements are widely scattered through Cenozoic carbonate strata on Enewetak. In general, micrite cements are volumetrically very minor. In most cases, the environment of micrite precipitation cannot be confidently identified. In Holocene samples, minor aragonite and HMC micrite cements are found (often in boundstones) and can confidently be assigned a marine origin on the basis of mineralogy (Folk,
1974; Longman, 1980). Some micrite cements immediately below Pleistocene and Miocene exposure surfaces and associated with soil-related structures can probably be attributed to a meteoric origin. In Pleistocene grainstones, thin crusts of micrite cement are commonly overgrown by equant-to-bladed, probably meteoric, cements. In those Pleistocene grainstones and other rocks that have been in both marine and meteoric environments, micrite cementation may have occurred in either marine or meteoric waters.

**Microspar**

On Enewetak, the close association of microspar with subaerial exposure surfaces suggests a meteoric vadose origin for the microspar. In Quaternary strata on Enewetak, microspar is invariably found immediately below exposure surfaces and associated with soil structures. In the F-1 well, microspar is present in the upper part of core 3 (375 m) and is associated with *Microcodium* and other apparently soil-related structures. Klappa (1978) and Bodergat (1974) have presented compelling evidence that *Microcodium* forms as a result of soil-related processes. Therefore, formation of most microspar encountered on Enewetak is probably the result of meteoric, soil-related processes.
Fibrous Cement Crusts

Fibrous cement crusts are scattered through Quaternary strata of the 3 shallow Enewetak wells and through Lower Miocene and Upper Eocene strata of the F-1 well. According to generalizations of Land (1970), and Folk (1974), fibrous cement morphologies suggest a marine-phreatic origin. The presence of fibrous cements in Holocene strata that have never been subjected to freshwater tends to confirm a marine origin for most fibrous cements on Enewetak. However, the LMC mineralogy of fibrous cements in Lower Miocene and Upper Eocene strata suggests a meteoric origin. Those fibrous LMC cements may have lost original magnesium during subsequent diagenesis.

Bladed cement crusts

Bladed radiaxial calcite cements are abundant in Lower Miocene strata of the F-1 well. Bladed cements are also locally common in some intervals of Pleistocene strata, in core 3 of the E-1 well (Upper Eocene), and in allochthonous clasts from Upper Eocene strata of the F-1 well (Fig. 21). Almost all bladed cements on Enewetak are isopachous crusts suggesting precipitation in phreatic environments (Land, 1970; Halley and Harris, 1979). As Longman (1980) notes, bladed cements frequently form in marine, meteoric, and mixed marine-meteoric environments. The present study
relies on trace element and stable isotope analyses to distinguish bladed cements precipitated in meteoric waters from those precipitated in marine waters.

**Equant-to-bladed cements**

Equant-to-bladed cements are characteristic of cementation in meteoric environments (Folk, 1974). Clear equant-to-bladed calcite cements in Pleistocene strata and in core 2 of the E-1 well (Upper Eocene) are probably meteoric in origin. Petrographically, those cements are very similar to meteoric cements described by Halley and Harris (1979) and many other carbonate petrologists. The occurrence of those equant-to-bladed cements below subaerial exposure surfaces in Pleistocene strata tends to reinforce a meteoric origin for those cements (Figs. 10 - 12). Likewise core 2 of the E-1 well is immediately below a major unconformity at the top of the Upper Eocene and hence is in a location where subaerial diagenesis would be expected (Ladd and Schlanger, 1960; Fig. 4). In Pleistocene strata of the 3 shallow wells (XRI-1, XAR-1, XEN-1) and in core 2 of the E-1 well, the association with aragonite dissolution also suggests that those equant-to-bladed and equant mosaic cements have a meteoric origin (Land, 1970; Halley and Harris, 1979).

Equant-to-bladed radial calsite is common in Lower Miocene strata of the F-1 well. In contrast with equant-to-
bladed Pleistocene Enewetak cements and other meteoric equant-to-bladed cements (Land, 1970; Halley and Harris, 1979), equant-to-bladed radiaxial calcite (1) is often inclusion-rich, (2) has undulose extinction, and (3) has jagged terminations. These characteristics make a simple meteoric origin for equant-to-bladed radiaxial calcites questionable. The association of radiaxial calcite cement with reef-related boundstones, pelleted internal sediments, and Clionid galleries suggests a marine origin for the radiaxial cements (Macintyre, 1977; Moore and Shedd, 1977). Trace element and stable isotope data which are presented in following sections will support a marine origin for Enewetak radiaxial calcite.

**Equant Mosaic Cements**

Equant calcite mosaic cements (medium-coarsely crystalline) are present in many Pleistocene rocks and in core 2 of the E-1 well. In most cases, equant mosaic cements preferentially fill bioclast molds and intragranular voids. Equant cements commonly form in meteoric (Folk, 1974) and deeper subsurface environments (Moore and Druckman, 1981). On Enewetak, the location of equant mosaic cements and their common association with equant-to-bladed cements are consistent with a meteoric origin. Their uneven distribution and common occurrence in intraparticle voids (where vadose waters would preferentially reside) suggest that
equant mosaic cement may also often be precipitated in vadose environments (Dunham, 1971).

TRACE ELEMENTS

During cement precipitation, trace amounts of many different cations are incorporated into calcite including strontium, iron, manganese, zinc, lead, sodium, potassium, and magnesium. The concentration of trace elements in calcite is dependent on the distribution coefficient of the element between the solid and liquid, and the composition of the fluid precipitating the cement.

For several years, carbonate petrologists and geochemists have attempted to use trace elements to infer chemical compositions of diagenetic waters precipitating cements (Land et al., 1975; Brand and Veizer, 1980; Moore and Druckman, 1981). Unfortunately, the distribution coefficients of most trace elements in calcite (and dolomite) are variable (Brand and Veizer, 1980; Moore and Druckman, 1981; Veizer, 1983). In fact, estimates of distribution coefficients often vary by at least 2 to 3 times and sometimes by an order of magnitude (Brand and Veizer, 1980; Moore and Druckman, 1981; Veizer, 1983). Recent studies (Jacobson and Usdowski, 1976; Brand and Veizer, 1980; Moore and Druckman, 1981; Lorens, 1981; Baker et al., 1982) are beginning to shed light on reasons for the variability of distribution coefficients for trace elements incorporated into calcite.
Trace elements examined in this study include magnesium, strontium, iron, manganese, and sodium. Extensive data regarding the strontium and magnesium concentrations of calcite cements on Enewetak were compiled using an electron microprobe (see Appendix for description of analytical procedure). Limited data on iron, manganese, and sodium concentrations were acquired by atomic absorption spectrophotometry.

**Strontium**

Strontium has been examined in many trace element studies of carbonate diagenesis (Kinsman, 1969; Land et al., 1975; Brand and Veizer, 1980; Moore and Druckman, 1981; and many others). The distribution coefficient (D) for strontium incorporated into calcite is variable (Jacobson and Usdowski, 1976; Lorens, 1981). In experimental studies, estimates of D for strontium incorporated in calcite (at 25°C) range from 0.14 (Kinsman and Holland, 1969) to 0.027 (Lorens, 1981) with other studies (Katz et al., 1972; Jacobson and Usdowski, 1976) obtaining intermediate values. The large discrepancy in $D_{\text{Calcite}}^{\text{Sr}}$ is probably due to the kinetics of calcite precipitation. Both Jacobson and Usdowski (1976) and Lorens (1981) found that $D_{\text{Calcite}}^{\text{Sr}}$ increased with increased rate of calcite precipitation. In general, rates of calcite precipitation in natural systems will be much slower than in most experimental systems. Therefore, it is possible
that data from Enewetak may be useful in empirically deriving approximate distribution coefficients for trace elements (specifically strontium) incorporated into calcites in natural systems.

Mean strontium concentrations in Enewetak calcite cements are shown in Table 2. Strontium concentrations in Lower Miocene and Upper Eocene cements are more consistent than Pleistocene calcite cements (Figs. 22, 23, and 24). Some Pleistocene Enewetak cements have large point-to-point strontium variations while others do not (Fig. 23). Pleistocene cements show no distinct strontium variations relative to depth (Fig. 25); however, Lower Miocene and Upper Eocene cements in the F-1 well do show a slight tendency for strontium concentrations to decrease with depth (Fig. 26). In Pleistocene cements, there are some distinct trends in strontium concentrations relative to cement distribution and cement morphology (Table 2). Pleistocene inclusion-rich bladed cements generally have strontium concentrations slightly greater than clear bladed cements (Fig. 23).

**Magnesium**

Magnesium concentrations are also commonly analyzed in trace element studies of carbonate rocks (Benson et al., 1972; Brand and Veizer, 1980; Moore and Druckman, 1981; and others). Unfortunately experimental distribution coefficients for magnesium in calcite at 25°C are quite
<table>
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<th>Mean Sr Concentration</th>
<th>Mean Mg Concentration</th>
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<td>(weight% ±σ)</td>
<td>(weight% ±σ)</td>
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<td>General sparry cement</td>
<td>0.060 ± 0.017</td>
<td>0.236 ± 0.061</td>
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<td>Intergranular</td>
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<tr>
<td>Bladed</td>
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<td>0.240 ± 0.056</td>
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<tr>
<td>Equant mosaic</td>
<td>0.090 ± 0.038</td>
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<td>(351)</td>
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<tr>
<td>Echinoderm overgrowths</td>
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<td>Fibrous cement</td>
<td>0.034 ± 0.008</td>
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<td>Radial calcite</td>
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<td>0.820 ± 0.100</td>
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<td>(99)</td>
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<td>Sparry, soil-related (?) cements in upper part of F-1 core 3</td>
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<td>Autochthonous fibrous</td>
<td>0.031 ± 0.002</td>
<td>0.540 ± 0.120</td>
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<td>0.025 ± 0.008</td>
<td>0.460 ± 0.140</td>
<td>(126)</td>
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<td>Allochthonous fibrous and bladed</td>
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<tr>
<td>Bladed cements</td>
<td>0.029 ± 0.006</td>
<td>0.359 ± 0.035</td>
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Note: Above data based on electron microprobe analyses.
Figure 22.

Histogram showing strontium concentrations in Enewetak calcite cements. Data from electron microprobe analyses.
STRONTIUM CONCENTRATIONS OF ENEWETAK CEMENTS

Radial Calcite, Lower Miocene F-1 Well

Pleistocene Calcite Cements
Figure 23.
Electron microprobe traverses of Pleistocene calcite cements. Location of traverse A-A' is shown in Figure 16d. Location of traverse C-C' is shown in Figure 15e. Data from point analyses. Note in A-A' that strontium concentrations are generally higher in the proximal inclusion-rich portions of the bladed cement. In B-B', note extremely variable strontium concentrations but relatively consistent magnesium concentrations. In C-C' and D-D', note high magnesium concentrations in proximal portions of cements.
TRAVERSES OF PLEISTOCENE CALCITE CEMENTS

Inclusion-rich bladed cement, XRI-1 Well (51 m)

Coarse, clear, equant-to-bladed cement, XAR-1 Well (71 m)

Clear, equant-to-bladed cement, XRI-1 Well (72 m)

Echinoderm overgrowth, XEN-1 Well (39 m)

× Sr concentration  
• Mg concentration  

Sr background ± S.D.  
Mg background ± S.D.
Figure 24.
Electron microprobe traverses of Lower Miocene and Upper Eocene cements. Location of traverse A-A' is shown in Figure 20e, B-B' in Figure 18b, and C-C' in Figure 20b. In C-C', Mg composition for individual cement bands represent means (±1σ) of 9 different point analyses. Data in A-A', B-B', and D-D' represent point analyses. In A-A' and C-C', note that clear radiaxial spar tends to have higher magnesium concentrations than inclusion-rich parts. In A-A' and D-D', note general decreases in magnesium with growth away from grains. In B-B', note large variations in magnesium in clear cement. In A-A', B-B', and C-C', note the consistency of strontium concentrations.
TRAVERSES OF LOWER MIOCENE AND UPPER EOCENE CEMENTS

Radial cement, Lower Miocene, F-1 Well (607 m)

Radial cement, F-1 Well (379 m)

Banded radial cement, F-1 Well (815 m)

Echinoderm overgrowth, F-1 Well (1,114 m)

x Sr concentration

• Mg concentration

Sr background ± S.D.

Mg background ± S.D.

Mean Mg ± S.D.

(9 pt. analyses)
Figure 25.
Strontium concentration versus depth in Pleistocene calcite cements from the XRI-1, XAR-1, and XEN-1 wells. Data from electron microprobe analyses.
STRONTIUM CONCENTRATIONS OF SPARRY LMC CEMENTS, PLEISTOCENE ENEWETAK
Figure 26.
Strontium concentrations in calcite cements of Lower Miocene and Upper Eocene strata of the F-1 well. Note a slight decrease in magnesium concentration with depth. Data from electron microprobe analyses.
STRONTIUM CONCENTRATION OF CEMENTS IN THE F-1 WELL

Pleistocene Calcite Cements

- △ Echinoderm overgrowths
- ○ Radial calcite
- ■ Bladed cement in allochthonous clasts
- + Other cements

DEPTH IN METERS

WEIGHT % SR
variable ($D_{\text{Calcite}}^{\text{Mg}} = 0.013 - 0.060$; Winland, 1969; Katz, 1973; Veizer, 1983). Experimental work by Katz (1973) shows that $D_{\text{Calcite}}^{\text{Mg}}$ is temperature dependent. Lorens (1981) concluded that if the distribution coefficient of an element is less than 1.0, that distribution coefficient will increase with an increased rate of calcite precipitation. $D_{\text{Calcite}}^{\text{Mg}}$ is certainly less than 1.0. A re-evaluation of Katz's $Mg$ (1973) data also indicates that the distribution coefficient of magnesium for his experimental calcites increased with increased rates of calcite precipitation in his experiments.

Fortunately the difference in $Mg^{2+}/Ca^{2+}$ ratios in fresh and marine waters and subsurface brines can be more than an order of magnitude. North American river (meteoric) waters have $Mg^{2+}/Ca^{2+}$ molar ratios of 0.082 - 0.89 (Livingstone, 1963). Ocean water has a $Mg^{2+}/Ca^{2+}$ ratio of 5.3 (Riley and Skirrow, 1965). Theoretically, subsurface brines may have extremely variable $Mg^{2+}/Ca^{2+}$ ratios, however, most subsurface brines have quite low $Mg^{2+}/Ca^{2+}$ ratios. For example, subsurface Gulf Coast brines from the Jurassic Smackover Formation have $Mg^{2+}/Ca^{2+}$ ratios of 0.05 - 0.52 (Collins, 1974). Hence, magnesium levels in calcites may be useful as a tool to help distinguish some environments of cement precipitation.

Mean magnesium concentrations of Cenozoic calcite cements from Enewetak are shown in Table 2. Calcite cements in Pleistocene strata have distinctly lower magnesium concentrations than radiaxial calcites and most other Lower Miocene
and Upper Eocene cements (Fig. 27; Table 2). Magnesium concentrations in sparry Pleistocene cements have no significant correlation with depth (Fig. 28); whereas magnesium concentrations of cements in Lower Miocene and Upper Eocene strata of the F-1 well generally decrease with depth (Fig. 29). Inclusion-rich radiaxial calcite alone has a better inverse correlation between magnesium and depth ($r = -0.82$) than combined clear and inclusion-rich radiaxial calcite ($r = -0.58$; Fig. 30).

Clear radiaxial calcites consistently have higher magnesium concentrations than inclusion-rich radiaxial spars (Table 3; Fig. 24; Videtich, 1982). It should also be noted that there are significant variations in magnesium concentrations within clear radiaxial calcites (Fig. 24). Clear and inclusion-rich parts of Pleistocene bladed cements have no systematic differences in magnesium concentration (Fig. 23).

Magnesium concentrations in radiaxial calcites tend to decrease away from original void walls (Table 3; Fig. 24); however, that tendency is often obscured by magnesium variations superimposed by alternating clear and inclusion-rich spars. In some Pleistocene LMC cements, the magnesium concentrations in the proximal portions of cements are relatively high and decrease away from grains (Fig. 23); however, most sparry LMC Pleistocene cements have no consistent pattern of magnesium concentration with growth (Fig. 23). Likewise, fibrous and bladed cements in Lower Miocene and Upper Eocene...
Figure 27. Histogram showing magnesium concentrations in Enewetak cements. Note that most radiaxial calcite cements contain distinctly more magnesium than Pleistocene calcite cements. Data from electron microprobe analyses.
Figure 28.
Magnesium concentration versus depth for Pleistocene calcite cements in the XRI-1, XAR-1, and XEN-1 wells. Data from electron microprobe analyses.
Figure 29. Magnesium concentration versus depth for calcite cements in the F-l well. Note that magnesium concentrations tend to decrease with depth below 375 m in the F-l well. Data from electron microprobe analyses.
MAGNESIUM CONCENTRATION OF CEMENTS IN THE F-1 WELL

Pleistocene calcite cements

△ Echinoderm overgrowths  ○ Radial calcites  + Other cements
■ Bladed cements in allochthonous clasts

Intensely dolomitized
Figure 30.
Magnesium concentrations versus depth for radiaxial cements. Note that magnesium concentrations in radiaxial cements tend to decrease with depth (in meters). Inclusion-rich radiaxial cements (triangles) display the most consistent magnesium concentrations and have the best correlation between magnesium concentration and depth ($r = -0.82$). Clear radiaxial cements have less consistent magnesium concentrations and poorer correlation between magnesium and depth ($r = -0.56$). Data from electron microprobe analyses.
MAGNESIUM CONCENTRATIONS OF RADIAXIAL CEMENTS, F-1 WELL

LEGEND:
+ Clear
□ Slightly Inclusion-rich
△ Inclusion-rich

Pleistocene calcite cements
TABLE 3

Strontium and Magnesium Concentrations of Radiaxial Calcites

<table>
<thead>
<tr>
<th>n</th>
<th>Mean Sr (wt. % ± 1 σ)</th>
<th>Mean Mg (wt. % ± 1 σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>General radiaxial calcite</td>
<td>69 0.033 ± 0.009</td>
<td>0.799 ± 0.280</td>
</tr>
<tr>
<td>1. Clear</td>
<td>36 0.032 ± 0.010</td>
<td>0.921 ± 0.295</td>
</tr>
<tr>
<td>2. Slightly inclusion-rich</td>
<td>7 0.037 ± 0.007</td>
<td>0.772 ± 0.189</td>
</tr>
<tr>
<td>3. Inclusion-rich</td>
<td>25 0.032 ± 0.006</td>
<td>0.642 ± 0.188</td>
</tr>
<tr>
<td>4. First bands</td>
<td>15 0.037 ± 0.007</td>
<td>0.893 ± 0.280</td>
</tr>
<tr>
<td>5. Second bands</td>
<td>17 0.035 ± 0.007</td>
<td>0.893 ± 0.322</td>
</tr>
<tr>
<td>6. Third bands</td>
<td>15 0.029 ± 0.008</td>
<td>0.679 ± 0.191</td>
</tr>
</tbody>
</table>

Notes: (1) Above Sr and Mg data from electron microprobe analyses.
(2) "n" is the number of samples analyzed.
(3) More inclusion-rich bands generally contain less magnesium than clear bands.
(4) Earlier, more proximal cements (first bands) generally contain more magnesium than later, more distal cements (third bands).
strata show no consistent change toward the center of voids. Echinoderm overgrowths in Pleistocene strata and Upper Eocene strata of the F-l well frequently have decreasing magnesium concentrations away from the original echinoderm fragment (Fig. 24). While magnesium in radiaxial calcites shows a slight correlation to strontium (r = 0.44), Pleistocene LMC cements show no significant correlation between magnesium and strontium (Fig. 31 and 32).

Iron and Manganese

Iron and manganese concentrations are often examined in conjunction with cathodoluminescence to help determine cement stratigraphy in ancient carbonate sequences (Frank et al., 1982; Grover and Read, 1983). In other studies, variations of iron and manganese concentrations in cements and grains have been used in attempts to reconstruct the diagenetic history of carbonate rocks (Pingitore, 1978; Brand and Veizer, 1980; Moore and Druckman, 1981; Moore, 1984).

Ancient carbonates often have distinctly higher iron and manganese concentrations than modern carbonate sediments (Brand and Veizer, 1980). Modern, shallow marine carbonate sediments generally have iron concentrations of approximately 10 - 100 ppm and manganese concentrations of 0 - 80 ppm (Stehli and Hower, 1961; Milliman, 1974). In contrast, many ancient carbonates have iron in excess of 200 ppm.
Figure 31.
Strontium versus magnesium concentration for Pleistocene calcite cements of the XRI-1, XAR-1, and XEN-1 wells. Data from electron microprobe analyses.
STRONTIUM AND MAGNESIUM CONCENTRATIONS IN SPARRY LMC CEMENTS, PLEISTOCENE ENEWETAK

+ Sparry LMC cement  ▲ Echinoderm Overgrowth
Figure 32.
Strontium versus magnesium concentration for radiaxial calcites in Lower Miocene strata of the F-1 well. Data from electron microprobe analyses.
STRONTIUM VERSUS MAGNESIUM CONCENTRATIONS OF RADIAXIAL CALCITES ON ENEWETAK
and manganese in excess of 100 ppm (Brand and Veizer, 1980; Frank et al., 1982; Grover and Read, 1983). These changes suggest that iron and manganese concentrations may be powerful tools in unraveling the diagenetic history of many carbonate rocks.

As with other trace elements, incorporation of iron and manganese into calcite is dependent on the concentration of those elements in the precipitating fluid and their distribution coefficients. Oxidation state plays an important part in determining the amount of iron and manganese that are incorporated into calcite because iron and manganese can occur in different oxidation states (Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, Mn\textsuperscript{2+}, Mn\textsuperscript{3+}, Mn\textsuperscript{4+}). Only the reduced states of iron and manganese (Fe\textsuperscript{2+}, Mn\textsuperscript{2+}) will readily substitute for Ca\textsuperscript{2+} in calcite.

As with other trace elements, distribution coefficients for iron and manganese are quite variable. Experimental distribution coefficients for iron (D\textsubscript{Calcite}\textsubscript{Fe}) are between 1 and 20 (Veizer, 1983). Experimental distribution coefficient for manganese (D\textsubscript{Calcite}\textsubscript{Mn}) range from 5.4 to 30 (Lorens, 1981). Lorens (1981) demonstrates that increased rate of calcite precipitation decreases the D\textsubscript{Calcite}\textsubscript{Mn}. Lorens (1981) concludes that for elements whose D > 1.0, decreased rates of calcite precipitation will increase the distribution coefficient of those elements. Therefore, D\textsubscript{Calcite}\textsubscript{Fe} should also increase with decreasing rate of calcite precipitation.

Only five samples of cement from Enewetak were analyzed for iron and manganese (2 samples from the Pleistocene
and 3 samples from the Lower Miocene of the F-1 well; Table 4). All five samples show consistently low manganese concentrations (7 - 15 ppm). Iron concentrations in two Pleistocene cements (17 - 40 ppm) are significantly lower than in the 3 samples of Lower Miocene cement (78 - 137 ppm; Table 4).

Manganese concentrations in these cements do not change significantly relative to modern carbonate sediments, Nor do they exhibit any clear relationship to strontium concentration in these cements (Table 4). In Pleistocene strata of Enewetak, cements show no distinct enrichment in iron relative to modern sediments. In contrast, the iron concentration in Lower Miocene cements does appear to be slightly greater than most marine sediments and Pleistocene cements (Table 4). There appears to be an inverse correlation between iron concentration and strontium concentration in Enewetak cements (Table 4).

Discussion of Trace Elements

Because distribution coefficients of trace elements in calcite are so variable, it is often difficult to use trace elements as indicators of diagenetic environments. However, when combined with other data, trace element concentrations can give substantial insight into geochemical changes in diagenetic waters through time, relative to depth (or burial), and relative to other nearby pores.
### TABLE 4

**ELEMENTAL ANALYSES OF ENEWETAK CEMENTS**

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Sr</th>
<th>Fe</th>
<th>Mn</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pleistocene calcite cements</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coarse, equant-to-bladed (XAR-1; 71.3 m)</td>
<td>2180</td>
<td>1042</td>
<td>17</td>
<td>7</td>
<td>-</td>
</tr>
<tr>
<td>Travertine (XRI-1; 72.4 m)</td>
<td>425</td>
<td>540</td>
<td>40</td>
<td>11</td>
<td>88</td>
</tr>
<tr>
<td><strong>Lower Miocene cements (F-1 Well)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Radialcalcite (F-1; 607 m)</td>
<td>8395</td>
<td>347</td>
<td>131</td>
<td>9</td>
<td>328</td>
</tr>
<tr>
<td>Radialcalcite (F-1; 815 m)</td>
<td>5890</td>
<td>257</td>
<td>137</td>
<td>9</td>
<td>302</td>
</tr>
<tr>
<td>Fine-to-medium crystalline bladed cement replacing coral (F-1; 818 m)</td>
<td>7768</td>
<td>236</td>
<td>78</td>
<td>15</td>
<td>197</td>
</tr>
</tbody>
</table>

Note: Above data based on atomic absorption spectrophotometry.
Strontium

Strontium concentrations are relatively consistent in calcite cements in Cenozoic strata on Enewetak. The mean strontium concentrations of Lower Miocene radiaxial calcites and Upper Eocene coarse bladed and equant-to-bladed cements are between 0.025 and 0.035 weight % Sr (Table 2). In addition, the modal strontium concentration of Pleistocene calcite cements is approximately 0.030 weight % Sr (Fig. 22). Except for Pleistocene calcite cements, the standard deviations (1σ) of strontium concentrations are less than 0.012 weight % Sr; however, strontium concentrations in Pleistocene LMC cements are quite variable.

Strontium concentrations in Pleistocene calcite cements increase systematically with crystal width (Table 2). Bladed cements generally have the lowest mean strontium concentration and equant mosaic cements the highest (Table 2). As circulation of diagenetic fluids decreases, a diagenetic system should become more stagnant and the growth rate of cement crystals should become slower. As crystal growth slows, cements should become less fibrous and more equant (Kendall and Broughton, 1978). Therefore, higher strontium concentrations and greater crystal width in Pleistocene calcite cements can probably be correlated to precipitation in more closed and stagnant diagenetic systems. Intragranular
voids should have more restricted circulation than most intergranular voids; therefore high strontium concentrations in intragranular cements is also consistent with the notion that strontium concentrations are higher in more stagnant (more closed) diagenetic systems (Brand and Veizer, 1980).

In Lower Miocene and Upper Eocene strata of Enewetak, the low and relatively consistent strontium concentrations of cements suggest precipitation in systems with consistently open circulation. Most cements in Lower Miocene and Upper Eocene strata of the F-1 well exhibit a slight decrease in strontium concentrations with depth (Fig. 26). That decrease may well be related to decreases temperatures and calcite saturation with depth in the F-1 well. These possibilities will be discussed in detail in later sections.

**Magnesium**

Magnesium concentrations show some distinct large-scale vertical variations in Cenozoic limestones on Enewetak as well as more subtle, internal variations. Pleistocene cements have quite low magnesium concentrations; whereas radiaxial calcites in Miocene strata have relatively high magnesium concentrations. In addition, magnesium concentrations in cements generally decrease with depth in Lower Miocene and Upper Eocene strata of the E-1 and F-1 wells.

The low magnesium concentrations of Pleistocene bladed,
equant-to-bladed and equant mosaic cements support a meteoric origin for those Pleistocene cements. In Pleistocene strata, the mean Mg/Ca molar ratio for sparry non-fibrous cements is 0.0036 (Table 4). Using the $\gamma_{\text{Calcite}}^{\text{Mg}}$ of Katz (1973) at 25°C (0.057), a Mg$^{2+}$/Ca$^{2+}$ ratio (molar) of 0.063 is calculated for waters precipitating cements with a Mg/Ca ratio of 0.0036. Using Winland's (1969) $D_{\text{Calcite}}^{\text{Mg}}$ of 0.02, a Mg$^{2+}$/Ca$^{2+}$ (molar) ratio of 0.18 is calculated for waters precipitating cements with a Mg/Ca ratio of 0.0036. According to Livingstone (1963), North American river waters commonly have Mg/Ca ratios of 0.089 - 0.89. On Barbados, most meteoric groundwaters in Pleistocene limestones have Mg$^{2+}$/Ca$^{2+}$ molar ratios between 0.05 and 0.20 (Harris, 1971). Therefore, the magnesium concentrations of sparry Pleistocene cements are indicative of calcite precipitation from meteoric waters. This conclusion is supported by the morphology and distribution of Pleistocene equant-to-bladed and equant mosaic cements (see Discussion of cement petrography). The mean magnesium content of bladed cements is even less than the mean for other sparry cements, suggesting that bladed cements in Pleistocene strata are meteoric in origin (Table 2). The low magnesium concentrations of equant-to-bladed cements in core 2 of the E-1 well also suggest precipitation in meteoric waters.

Radial calcites have magnesium concentrations that are significantly higher than Pleistocene cements, suggesting that they are not meteoric in origin (Fig. 27). However,
the magnesium concentrations in the radiaxial spars are well below HMC cements precipitated in relatively shallow marine waters (Moore, 1973; Milliman, 1974; James et al., 1976; James and Ginsburg, 1979; Land and Moore, 1980). The magnesium concentrations of radiaxial cements (usually 2-4 mole % MgCO₃) are similar to deep marine calcite cements of Schlager and James (1978) which contain 3.5 - 5.0 mole % MgCO₃. Similar magnesium concentrations have also been reported in mixing zone cements (Moore, 1977).

In radiaxial calcites, magnesium decreases relative to (1) depth, (2) abundance of inclusions, and (3) growth into the middle of voids. These systematic decreases in magnesium might be attributed to either of two fundamentally different processes. Different magnesium concentrations could be due to a differential loss of magnesium from HMC cements (Videtich, 1982). Videtich (1982) suggested that more inclusion-rich zones would be more porous and permeable, and thus lose magnesium more efficiently in the HMC to LMC transition. Another way to explain the systematic variations in magnesium concentration within radiaxial spar is that magnesium concentrations are all primary, resulting from geochemical changes in the diagenetic system precipitating radiaxial spars.

The general decrease in magnesium concentration of Lower Miocene and Upper Eocene cements with depth indicates equilibration of calcites with progressively deeper, colder, and less saturated waters. A similar trend in originally
HMC coralline algae supports a progressive loss of magnesium in radiaxial calcite during burial (see Diagenesis of HMC). However magnesium variations of over 0.5 weight % Mg within clear spars suggest that differences in magnesium concentration are not due to a homogeneous alteration of a homogeneous HMC precursor (Fig. 24). Decreasing magnesium concentrations away from original void walls support a gradual change in diagenetic environment (probably associated with increasing depth) during precipitation, stabilization, or neomorphism of the radiaxial calcite. In Upper Eocene strata of the F-1 well, echinoderm overgrowths also show a distinct decrease in magnesium concentration away from original echinoderm fragments (Fig. 24). Again this trend could reflect slow cementation in diagenetic waters whose composition is gradually changing with burial.

**STABLE ISOTOPIES**

Stable carbon and oxygen isotopes can be helpful in distinguishing between carbonate precipitated in marine, meteoric, and burial environments (Hudson, 1977; Dickson and Coleman, 1980; Moore and Druckman, 1981; Brand and Veizer, 1981; Wagner and Matthews, 1982). The $\delta^{18}O$ of calcite cements is directly related to the $\delta^{18}O$ of the diagenetic waters and inversely related to the temperature of precipitation (Craig, 1965). Hence, in burial environments with elevated temperatures, $\delta^{18}O$
values for cements may be very negative.

In tropical settings, nearsurface water temperatures will remain roughly constant. Therefore, significant variations in the oxygen isotope composition of most nearsurface Enewetak cements should be determined largely by variations in the isotopic composition of the diagenetic fluids. In general, the oxygen isotopes in marine water are heavier than fresh (meteoric) water (Gross, 1964; Hudson, 1977). In tropical latitudes (where most limestones form), the stable oxygen isotope composition of meteoric waters commonly ranges from 0 to -6 o/oo (SMOW; IAEA, 1979). Gross and Tracey (1966) report $\delta^{18}O$ values between -3.8 and -5.8 o/oo (SMOW) for meteoric waters on Enewetak. Marine waters in the vicinity of Enewetak have $\delta^{18}O$ values of approximately 0.0 o/oo (SMOW; Gross and Tracey, 1966).

Fractionation of carbon isotopes in calcite changes little relative to temperature (Emrich et al., 1970). Rather, variations of $\delta^{13}C$ in calcite cements are determined mainly by the isotopic composition of CO$_2$ in the diagenetic system. Carbon isotope fractionation varies with rate of calcite precipitation (Turner, 1982). As rate of precipitation increases, $\delta^{13}C$ of calcite approaches that of the aqueous HCO$_3^-$; whereas at very slow rates of precipitation, $\delta^{13}C$ of calcite approaches the equilibrium fractionation of approximately 2.5 o/oo relative to HCO$_3^-$ (Turner, 1982). Modern marine carbon (TDC; dissolved CO$_2$) generally has a $\delta^{13}C$ value of -0.5 to +2.5 o/oo (PDB; Anderson
and Arthur, 1983); therefore, calcite inorganically precipitated from modern marine waters should have $\delta^{13}C$ values between -0.5 and +4.5 o/oo. Variable contribution of very light soil-gas and organic carbon into meteoric systems can result in large differences in $\delta^{13}C$ (-10 to +2 o/oo, PDB) for calcites precipitated in meteoric waters (Gross, 1964; Allan and Matthews, 1977, 1982).

Gross and Tracey (1966) performed stable carbon and oxygen analyses on a number of carbonate samples from the Enewetak and Bikini wells drilled in the early 1950's. Working with whole rock samples, Gross and Tracey (1966) noted that some recrystallized limestones (usually above depths of 300 m) had stable isotope compositions in equilibrium with modern Enewetak meteoric water. However, Gross and Tracey (1966) found that more deeply buried recrystallized limestones had heavier stable carbon and oxygen isotopes which they interpreted as meteoric calcite that had re-equilibrated with seawater.

Results of Stable Isotope Analyses

Results of stable isotope analyses generated during the present study are summarized in Table 5. In the Pleistocene of Enewetak, LMC cements show a rather narrow clustering of $\delta^{18}O$ values, but a rather broad range of $\delta^{13}C$ values (Fig. 33). Lower Miocene radiaxial calcites and Upper Eocene bladed cements have stable carbon and
<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>( \delta^{13}\text{C} ) (o/oo, PDB ± 1σ)</th>
<th>( \delta^{18}\text{O} ) (o/oo, PDB ± 1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pleistocene Cements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1. Fibrous Aragonite</td>
<td>1</td>
<td>2.6</td>
<td>-2.3</td>
</tr>
<tr>
<td>2. LMC (General)</td>
<td>22</td>
<td>-5.1 ± 3.1</td>
<td>-6.5 ± 0.6</td>
</tr>
<tr>
<td>3. Bladed</td>
<td>6</td>
<td>-5.6 ± 4.2</td>
<td>-6.9 ± 0.6</td>
</tr>
<tr>
<td>4. Equant-to-bladed</td>
<td>14</td>
<td>-4.4 ± 2.5</td>
<td>-6.3 ± 0.6</td>
</tr>
<tr>
<td>5. Equant mosaic</td>
<td>1</td>
<td>-6.4</td>
<td>-6.5</td>
</tr>
<tr>
<td>6. Intergranular (LMC)</td>
<td>16</td>
<td>-5.5 ± 3.3</td>
<td>-6.5 ± 0.7</td>
</tr>
<tr>
<td>7. Intragranular (LMC)</td>
<td>5</td>
<td>-4.2 ± 1.8</td>
<td>-6.5 ± 0.6</td>
</tr>
<tr>
<td><strong>Lower Miocene Cements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8. Radial Calcite</td>
<td>7</td>
<td>2.0 ± 0.5</td>
<td>-0.4 ± 0.8</td>
</tr>
<tr>
<td><strong>Upper Eocene Cements</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9. Equant-to-bladed (Core 2, E-1 well)</td>
<td>1</td>
<td>-1.9</td>
<td>-7.2</td>
</tr>
<tr>
<td>10. Bladed cements  (Core 3, E-1 well)</td>
<td>4</td>
<td>1.7 ± 0.4</td>
<td>-0.7 ± 0.2</td>
</tr>
</tbody>
</table>

Note: "n" is the number of samples analyzed.
Figure 33.

Stable isotope composition of Pleistocene cements from Enewetak. Plus signs (+) represent analyses of sparry calcite cements. The single circle represents an analysis of a fibrous aragonite cement. Analyses are in o/oo relative to PDB.
STABLE ISOTOPE COMPOSITION OF PLEISTOCENE CALCITE CEMENTS, ENEWETAK

Pleistocene fibrous aragonite cement
oxygen isotope compositions that are quite different from the Pleistocene LMC cements (Fig. 34). The stable isotope composition of other Lower Miocene and Upper Eocene cements are also shown in Figure 34. Pleistocene calcite cements show little systematic variation in $^{13}\text{C}$ or $^{18}\text{O}$ relative to depth (Fig. 35). In contrast, the $\delta^{18}\text{O}$ values of radiaxial cements tend to increase with depth ($r=0.81$; Fig. 36). $\delta^{13}\text{C}$ values of radiaxial cements show little change with depth (Fig. 36).

**Discussion of Stable Isotopes**

In this study, stable isotopes are probably the most definitive tool available to discriminate between marine and meteoric cements. As shown on Figure 3, temperatures in deep Cenozoic limestones on Enewetak are never greater than the nearsurface waters. Therefore, elevated temperatures cannot be a source of significant variation in the oxygen isotope composition of any Enewetak cements. On Enewetak, carbonate precipitated below the thermocline might be influenced by low temperatures. The lowest temperatures observed in Enewetak wells are approximately $10^\circ\text{C}$. However, the principal factor causing oxygen isotope variability in Enewetak cements should be the isotopic composition of the diagenetic waters.
Figure 34.
Stable isotope composition of Enewetak cements. Stable carbon and oxygen isotopes are in o/oo relative to PDB standard.
STABLE ISOTOPE COMPOSITION OF ENEWETAK CEMENTS

Theoretical compositions of marine cements (10 - 27°C)

Lower Miocene, F-1 Well
- Radial calcite
□ Microcodium (top of core 3)
◆ Microspar (top of core 3)
* Fine-medium crystalline bladed cement

Upper Eocene, E-1 Well
- Equant-to-bladed cement (core 2)
+ Bladed cement (core 3)
Figure 35.
Stable oxygen and stable carbon isotope compositions of Pleistocene calcite cements versus depth. Stable carbon and oxygen isotope values are in o/oo relative to PDB standard.
STABLE OXYGEN AND CARBON ISOTOPE COMPOSITION OF
PLEISTOCENE CALCITE CEMENTS, ENEWETAK

\[ \delta^{18}O \]

\[ \delta^{13}C \]

Cement:
- XEN-1
- XRI-1
- XAR-1

Unconformity:
Figure 36.
Stable oxygen and carbon isotope compositions of calcite cements versus depth in Cenozoic strata. Stable carbon and oxygen isotope values are in o/oo relative to PDB standard.
STABLE ISOTOPE COMPOSITION OF ENEWETAK CEMENTS

- Field of Pleistocene calcite cements (XRI-1, XAR-1, XEN-1 wells)
- Pliocene (?) sparry calcite cement (K-1 & F-1 wells)
- Radial calcite (F-1 well)
- Uneven, equant-to-bladed cement (core 2, E-1 well)
- Bladed cement (core 3, E-1 well)
Quaternary cements

In Pleistocene strata of Enewetak Atoll, stable carbon and oxygen isotopes show rather clearly that bladed, equant-to-bladed, and equant mosaic cements are indeed meteoric in origin. In Pleistocene samples from Enewetak, the stable oxygen isotope compositions of sparry, non-fibrous calcite cements cluster between -5.5 and -7.5 o/oo (PDB; Fig. 33). Because these Pleistocene strata are shallow (less than 80 m deep) and near the equator (11°N. latitude), cement precipitation can be assumed to have been at approximately 27°C. At 27°C, those sparry calcite cements should have precipitated from waters with δ¹⁸O values of approximately -3 to -5 o/oo (SMOW; Friedman and O'Neil, 1977). As mentioned earlier, Gross and Tracey (1966) found modern meteoric waters on Enewetak to have δ¹⁸O values between -3.8 and -5.8 o/oo (SMOW). At 27°C, the Pleistocene fibrous aragonite cements (δ¹⁸O = -2.3 o/oo; PDB) should have precipitated from water with a δ¹⁸O of approximately 0.0 o/oo (SMOW; Grossman and Ku, 1981). This data supports previous conclusions based on petrographic and trace element data which also indicated a marine origin for fibrous aragonite cements and a meteoric origin for sparry calcite cements in Pleistocene strata. These isotope data and conclusions are similar to those of Gross and
Tracey (1966).

As a whole, the $^{18}O$ compositions of Pleistocene calcite cements from Enewetak are significantly lighter than previously reported Pleistocene rocks and cements from other geographic locations (Fig. 37; Gross, 1964; Land, 1973a; Allan and Matthews, 1977, 1982). This difference is probably due to (1) lighter oxygen isotopes in meteoric waters on Enewetak relative to other geographic locations (Gross, 1964; Land, 1973a) and (2) inclusion of original marine sediments in whole rock analyses from other geographic locations (Allan and Matthews, 1977, 1982). Meteoric groundwaters on Bermuda and Jamaica generally have $^{18}O$ values between -2.5 and -3.5 o/oo (SMOW; Gross, 1964; Land and Epstein, 1970). The lighter meteoric waters on Enewetak (-3.8 to -5.8) probably reflect the influence of isotopically light, monsoon-type precipitation (Aharon, 1983).

Stable carbon isotopes also support a marine origin for fibrous aragonite cements and a meteoric origin for sparry calcite cement in Pleistocene strata from Enewetak. The $^{13}C$ value of +2.6 o/oo (PDB) for fibrous aragonite cement is quite consistent with a marine origin. The $^{13}C$ of sparry calcite cement varies between -10 and 0.5 o/oo (PDB; Fig. 33), suggesting a mixture of carbon from marine sediments and organic material (or soil gas).

No distinct trends in $^{13}C$ and $^{18}O$ were found in Pleistocene cements relative to subaerial exposure surfaces.
Figure 37.
Comparison of stable isotopes in Pleistocene calcite cements on Enewetak with analyses of other Pleistocene limestones altered by meteoric water. Field of Gross (1964) is for diagenetic calcites ("soil bases", stalagmites, and cements) from Bermuda. Field of Land and Epstein (1970) includes bulk rock, flastone calcite, cave calcite, and neomorphosed corals in Pleistocene carbonate rocks from Jamaica. Field of Allan and Matthews (1982) is from bulk rock analyses of Pleistocene limestones from Barbados.
COMPARISON OF STABLE ISOTOPES IN QUATERNARY LIMESTONES ALTERED IN METEORIC WATER

Pleistocene calcite cements, Enewetak

Barbados (Allan and Matthews, 1982)

Jamaica (Land and Epstein, 1970)

Bermuda (Gross, 1964)
(Fig. 35). In contrast to studies by Allan and Matthews (1977, 1982), $\delta^{13}C$ values of calcite cements on Enewetak do not show steady decreases below exposure surfaces. Enewetak cements immediately below Pleistocene exposure surfaces usually do have very light carbon isotopes; however, cements significantly below exposure surfaces may also exhibit very light carbon isotopes (Fig. 35; XEN-1, 39 m; XRI-1, 48, 51, 72, and 73 m). Because whole rock samples were not systematically analyzed in this study, other $\delta^{13}C$ and $\delta^{18}O$ trends observed by Allan and Matthews (1982) relative to exposure surfaces and water tables can not be evaluated by this study.

**Lower Miocene and Upper Eocene cements**

Stable isotope analyses clearly indicate that radiaxial calcites formed in marine waters (Fig. 34). The mean $\delta^{18}O$ (-0.4 o/oo, PDB) and $\delta^{13}C$ values (2.0 o/oo, PDB) of radiaxial spars are much heavier than Pleistocene meteoric cements on Enewetak and are similar to modern marine cements (Fig. 34; Hudson, 1977). Assuming precipitation from normal seawater ($\delta^{18}O = 0.0$ o/oo; SMOW), the paleothermometry equation of Friedman and O'Neil (1977) predicts formation of radiaxial spar at temperatures between 12°C ($\delta^{18}O = 0.4$ o/oo) and 22°C ($\delta^{18}O = -1.8$ o/oo; PDB). Stable carbon isotopes of radiaxial calcites are slightly lighter than modern marine cements and might
reflect (1) precipitation of radiaxial calcites in relatively deep marine water where $\delta^{13}C$ of marine bicarbonate is 1 to 2 o/oo lighter than surface marine waters (Kroopnick et al., 1977), or (2) inheritance of light carbon from the dissolution of coralline aragonite (Land et al., 1975). The increase in $\delta^{18}O$ of radiaxial calcite with depth suggests that radiaxial cements are being precipitated in or equilibrating with progressively colder water at greater depths (Fig. 36; Friedman and O'Neil, 1977).

Finer non-radiaxial bladed cements from Lower Miocene strata of the F-l well have $\delta^{13}C$ and $\delta^{18}O$ values similar to the radiaxial calcites and are also probably marine in origin (Fig. 34). However, the Microcodium and microspar samples from the upper part of F-l core 3 (375 m) have much lighter carbon and oxygen isotopes (Fig. 34) confirming that those strata have probably been subjected to subaerial exposure and meteoric diagenesis.

The stable isotopic composition of equant-to-bladed cements in core 2 (854 - 856 m) of the E-l well clearly shows that those cements have a meteoric origin (Fig. 34; Table 5). A $\delta^{18}O$ value of -7.1 o/oo (PDB) indicates precipitation from meteoric waters with a $\delta^{18}O$ composition of approximately -4.6 o/oo (SMOW; Craig, 1965). This value also suggests that the $\delta^{18}O$ composition of meteoric water in the vicinity of Enewetak has remained fairly constant since Late Eocene or Oligocene time when those equant-to-bladed cements probably formed. The stable
isotope compositions of bladed cements in E-1 core 3 (1,243 – 1,250 m) are very similar to radially calcites and support precipitation from normal marine waters (Figs. 34).

DISCUSSION OF CEMENTS

Cementation on Enewetak Atoll is quite variable. Meteoric and marine diagenesis has resulted in intense cementation of some stratigraphic intervals; whereas, other limestone intervals have remained virtually uncemented. Cementation of Enewetak carbonates is not directly related to depth; rather, variations within marine and meteoric diagenetic environments are apparently responsible for good cementation in some intervals and poor cementation in other areas.

Meteoric Cements

In Pleistocene strata of Enewetak and core 2 (854 – 856 m) of the E-1 well, petrographic and geochemical data suggest that bladed, equant-to-bladed, and equant mosaic cements have precipitated from meteoric water. In samples from Enewetak, the repeated association of microspar with soil-related alteration and subaerial exposure suggests that microspar also has a meteoric origin. Meteoric cements are closely related to subaerial exposure surfaces. Obviously,
subaerial exposure is required to catch meteoric water and conduct it into the subsurface without dilution by marine water. The intensity and distribution of cementation is directly related to the abundance and spacing of subaerial exposure surfaces. The periodic rises and falls of Pleistocene sea level have resulted in numerous vertically stacked subaerial exposure surfaces and intense meteoric cementation in Pleistocene strata. In contrast, subaerial exposure and associated meteoric cementation in Upper Eocene and Lower Miocene strata are apparently limited to the uppermost parts of Upper Eocene and Lower Miocene strata in the F-1 and E-1 wells (Fig. 38).

**Soil zone, vadose, and meteoric-phreatic cementation**

In strata that have been subjected to subaerial exposure, meteoric cementation is quite variable and apparently related to meteoric subenvironments (vadose and phreatic) in which the strata have been altered. Therefore, discriminating between meteoric subenvironments is important relative to the intensity of cementation. Dunham (1969a, 1969b, 1971) discusses several textural features characteristic of vadose diagenesis including vadose silt, vadose pisolites, meniscus cements, and uneven distribution of cements. Studies by Moore et al. (1976), Moore and Shedd (1977), Land and Moore (1980), Esteban and Pray (1977), and others have cast doubt on the reliability of "vadose" silt and
Figure 38.
Drill rate logs for Enewetak E-1 and F-1 well. Columns to right of drill rate logs indicate cored intervals. Note that much of the Lower Miocene of the E-1 well and Upper Eocene of the F-1 well drilled very quickly indicating only minor cementation in those intervals. Modified from Ladd and Schlanger (1960).
DRILL RATE LOG

F-1 Well   E-1 Well

Depth (m) 0 5 ft/m   0 5 ft/m

Plio.-Pleist.

Lower Miocene

Upper Eocene

1400 ft/m
pisolites as indicators of vadose diagenesis. Hailey and Harris (1979) conclude that pendant as well as meniscus cement structures and uneven cement distribution are good indicators of vadose cementation; whereas, isopachous cement crusts are characteristic of phreatic cementation (Land, 1970; Hailey and Harris, 1979). Well-developed vadose silt, pisolites, pendant cements, and meniscus cements are rare in samples of Pleistocene limestone from the XRI-1, XAR-1 and XEN-1 wells. Isopachous cement crusts are present in Pleistocene strata of Enewetak; however, they are rarely uniform in distribution on a mesoscopic scale. Based on the dominance of uneven cement distribution, Goter (1979) concluded that most Pleistocene calcite cements in wells on Aranit Island have a meteoric-vadose origin.

In the Pleistocene of Enewetak and core 2 of the E-l well, three typical suites of cement morphology and distribution dominate. (1) Immediately below exposure surfaces, unevenly distributed micrite, microspar, equant-to-bladed, and sometimes equant mosaic cements are often present. These cements vary from being virtually absent to being very abundant, and probably represent soil-zone cementation.

(2) Distinctly separate from and between exposure surfaces are intervals exhibiting crusts of bladed or equant-to-bladed cement. These cement crusts are generally isopachous within individual voids and probably have a meteoric-phreatic origin. The variable thickness of these cement crusts may be due to differential phreatic fluid
flow through very heterogeneous pore systems present in Pleistocene strata. Similar patchy, circumvoid cement crusts are described by Halley and Harris (1979) in a modern phreatic system on Joulter's Cay, Bahamas.

(3) The third typical suite of cements includes equant-to-bladed and equant mosaic cements which preferentially fill intragranular and small intergranular voids. Cements in this suite are usually not volumetrically important though they do generally bind sediments. These cements are always patchy, preferentially filling small voids that have high capillary attraction and/or otherwise tend to retain water in vadose environments. This suite of patchy (uneven) intergranular and intragranular cements probably formed in meteoric-vadose environments below the soil zone but above the water table. Poor development of meniscus and pendent cement structures in this zone may be due to Enewetak grains which are irregularly shaped bioclasts with rough surfaces and abundant intraparticle porosity. Those rough grain surfaces and intraparticle voids tend to preferentially hold vadose water, so meniscus water structures may not develop. Likewise, vadose water may tend not to drain to a single low point on irregularly shaped grains, and, hence, pendent cement structures may also tend not to form.
Inclusion-rich bladed cements

Inclusion-rich bladed cements are petrographically different from most other meteoric cements described in this and other Pleistocene studies (Land, 1970; Halley and Harris, 1979; and many others). Trace element and stable isotope data strongly support a meteoric origin for the inclusion-rich bladed cements of the XRI-1 and XEN-1 wells. In three inclusion-rich bladed cements analyzed for stable isotopes, the mean $\delta^{13}C$ of -9.0 o/oo (PDB) and mean $\delta^{18}O$ of -7.1 o/oo (PDB) clearly indicate a meteoric origin. Likewise, low magnesium concentrations (mean = 0.163 wt. % Mg) suggest a meteoric origin for the inclusion-rich bladed cements. The isopachous nature of inclusion-rich bladed crusts suggest formation in a phreatic environment.

The inclusion-rich bladed cements may exist as "isolated" bladed cements which usually do not touch adjacent bladed cements (Fig. 16). Other inclusion-rich bladed cements have inclusion-rich cores with clear rims and appear to be isolated bladed cements that have been overgrown at a later time by clear bladed or equant-to-bladed cement (Fig. 16). There are at least two viable hypotheses for the origin of the inclusion-rich bladed cements.

The first hypothesis involves alteration of a fibrous precursor to produce inclusion-rich portions of bladed cements. Alteration of a fibrous precursor could result in a coarser calcite with linear inclusions. The common
occurrence of inclusion-rich bladed calcites in space formerly occupied by aragonitic coral, and slightly elevated strontium concentrations in the inclusion-rich cores, suggest that the potential fibrous precursor was aragonite. According to this hypothesis, inclusion-rich bladed cements in primary intergranular voids would probably be the result of alteration of a fibrous aragonite cement.

A second hypothesis for the origin of inclusion-rich bladed calcite involves direct void-fill precipitation of the isolated inclusion-rich bladed calcite in the form shown by SEM photomicrographs (Fig. 16). The linear inclusions could have formed along the faces of knife-like and arrow-shaped projections of the isolated inclusion-rich bladed cements. Direct precipitation of inclusion-rich bladed cements is supported by petrographic data. Parallel linear inclusions within individual bladed crystals suggest that the inclusion-rich bladed cements are not alteration products of coralline aragonite or fibrous aragonite cement. If the inclusions resulted from the alteration of coralline aragonite, linear inclusions should exhibit patterns similar to aragonite needles in coral, but they do not. Likewise, if the inclusion-rich bladed cements in primary intergranular voids formed as an alteration of fibrous cements, the linear inclusions should exhibit patterns similar to fibrous cement. In general, fibrous cements are oriented perpendicular to the original void wall or are in radiating bundles; however, linear inclusions in inclusion-rich bladed cements
usually do not show those patterns of fibrous cementation (Fig. 16). Inclusions within individual crystals would tend to be parallel to each other if inclusions developed on crystals with knife-like and arrow shaped projections similar to those in Figure 16.

As shown in Figure 23, magnesium concentrations in inclusion-rich bladed cements and clear bladed overgrowths are similar suggesting a common origin by direct precipitation for both. The relatively low magnesium concentrations (mean = 0.163 wt. % Mg) in inclusion-rich bladed cements suggest that they are not associated with the alteration of HMC. Slightly higher strontium concentrations (Fig. 23) suggest that the inclusion-rich portions of bladed cements might be associated with an aragonitic precursor. However, strontium concentrations in inclusion-rich portions of bladed cements are far below strontium levels in neomorphosed coral, casting some doubt on an aragonitic precursor. The observed magnesium and strontium concentrations might develop if a fibrous metastable precursor was converted to LMC prior to alteration into inclusion-rich bladed calcite.

While inclusion-rich bladed cements apparently formed in the meteoric-phreatic zone, reasons for the inclusion-rich nature and strange form (Fig. 16) are unclear. The isolated inclusion-rich bladed cements are petrographically similar to "flower spar" of James (1972) and "bladed spar" of Harrison (1977). James (1972) and Harrison (1977) found their "flower" and "bladed" spars in caliche profiles on Barbados. They
both imply that the precipitation of "flower" or "bladed" spar occurred rapidly in extremely supersaturated conditions perhaps due to rapid evaporation of soil water.

The widespread distribution of inclusion-rich bladed cement suggests that it is not a caliche product on Enewetak. On Enewetak, the inclusion-rich bladed cements are not associated with caliche surfaces but are found scattered between depths of 44.8 and 64.0 m in the XRI-1 well and between 25.6 and 39.0 m in the XEN-1 well. The association of some similar bladed cements with travertine suggests relatively rapid precipitation of those cements in greatly supersaturated waters. The widespread distribution of isolated inclusion-rich bladed cements might be the result of rapid cement precipitation at the top of a rising or sinking water table. Clear isopachous calcite overgrowths on inclusion-rich bladed cements probably precipitated later, also in a meteoric-phreatic environment.

**Marine Cements**

On Enewetak, evidence strongly indicates that the following cements are marine in origin: (1) fibrous calcite and aragonite cements in Quaternary, Lower Miocene, and Upper Eocene strata, (2) radiaxial calcites in Lower Miocene strata of the F-1 well, and (3) bladed cements in Upper Eocene strata. These marine cements are found in greatest abundance in near reef, reef crest and reef wall limestones.
where oceanic circulation would have forced large quantities of marine water through the limestone substrate. Because atoll growth is largely vertical, reef-related strata may be adjacent to the seaward edge of the atoll for long periods of time after deposition. Furthermore, hydrologic information suggests that marine circulation may laterally move ocean water over 3 km into the atoll subjecting reef-related strata to circulating ocean water for millions of years after deposition.

Fibrous marine cement

Marine cements in Quaternary samples of the XRI-1, XAR-1, and XEN-1 wells generally occur in minor amounts, except between 14.0 and 18.3 m in the XEN-1 well where fibrous aragonite cements comprise 5 - 10% of most samples. In this interval, marine cementation occurs in back-reef and reef-related grainstones. Islands of the Enewetak Atoll are generally in back-reef and lagoon-margin environments (Couch et al., 1975); therefore, those marine cements between 14.0 and 18.3 m in the XEN-1 well may be related to beach rock formation associated with an island. Beach rock type cementation is exceptionally common on the lagoonward margins of all islands on the Enewetak Atoll (Schmalz, 1971; C.H. Moore, 1984, pers. comm.). Most of the island of Engebi is underlain by a hard layer usually less than 30 cm thick with beach rock type cementation (Goff, 1979).
The lack of volumetrically important marine cementation in most of the XRI-1, XAR-1, and XEN-1 wells probably reflects their deposition in environments away from islands with beach rock type cementation and away from the seaward margin of the atoll. The limited marine cementation is analogous to basinward portions of the Jurassic Smackover Formation where marine cementation is also minor and is confined mainly to a few insular settings (Moore and Druckman, 1981).

The correlation between Holocene marine cementation and proximity to the atoll margin is clearly shown by cementation in Holocene strata in the vicinity of Aranit Island (Fig. 39). As core descriptions by Couch et al. (1975) illustrate, cementation in Holocene strata decreases dramatically lagoonward. Most of that cementation is probably marine because the well-cemented zones are in Holocene strata that have probably not been exposed to freshwater (Fig. 39). Goter (1979) confirms that most (if not all) of the Holocene cementation in the seaward wells is marine in origin.

Fibrous LMC cements are scattered throughout Lower Miocene and Upper Eocene strata of the F-1 well. A marine origin for those fibrous LMC cements is inferred from their (1) fibrous morphology (Folk, 1974), (2) association with radiaxial calcites having distinctly marine stable isotopes, and (3) occurrence in strata lacking distinct evidence of meteoric diagenesis. When compared to abundant radiaxial calcite in the F-1 well, the small amounts of fibrous LMC
Figure 39.
Cementation in Holocene strata of and adjacent to Aranit Island. Note that cementation in Holocene strata is largely confined to the seaward margin of the atoll (right). Data from Couch et al. (1975).
CEMENTATION IN HOLOCENE STRATA ON ARANIT ISLAND, ENEWETAK

[Diagram showing elevation (m) with labels XAR-1, XAR-3, XAR-2, PAR-15, PAR-16, Lagoon, Ocean, and symbols representing exposure surface, well cemented, and poorly or uncemented.]
marine cement suggest that it was precipitated in a relatively inefficient hydrologic system. In Lower Miocene strata of the F-1 well, the occurrence of fibrous cement in some aragonite molds indicates that at least some of the fibrous cement formed after aragonite dissolution.

**Radial Calcite**

Since Bathurst (1959) first described radial spars, their origin has been problematic. In 1975, Bathurst states "...when their [radial spars'] origin is eventually understood, the fabric will be useful as an indicator of diagenetic environment". During the last 10 - 15 years, the formation of radial spars has generally been attributed to the "neomorphic replacement" of fibrous (acicular) precursors usually inferred to be HMC or aragonite cements (Kendall and Tucker, 1973; Kendall, 1977; Bathurst, 1975; Bathurst, 1977; Davies, 1977; Lohmann and Meyers, 1977; Marshall, 1981; Videtich, 1982). Very recently, Kendall (1984) recanted some of his earlier ideas and proposed that radial spar is a direct (probably marine) precipitate. Evidence from this study supports Kendall's (1984) conclusions. There are two fundamental questions regarding Enewetak radial spars which must be answered. (1) Were radial spars a direct marine precipitate or an alteration product of a [fibrous] precursor? (2) Where and when were those radial spars precipitated?
Origin by Replacement

Kendall and Tucker (1973) present a set of arguments against direct precipitation of radiaxial calcite and for origin by replacement of pre-existing cements. Arguments of Kendall and Tucker (1973) against primary precipitation include (1) "relations to erosional surfaces" where cavities [probably bioerosion cavities] cross-cut internal sediments, but do not cross-cut radiaxial cements, (2) "presence of non-planar intercrystalline boundaries", (3) "absence of competitive growth fabrics", and (4) "lattice curvature within crystals". Evidence for replacement of a pre-existing (acicular) cement include linear inclusions, inclusion-rich bands that parallel cavity walls, and undulose extinction due to lattice deformation (Kendall and Tucker, 1973; Kendall, 1977; Lohmann and Meyers, 1977). Videtich (1982) concluded that Lower Miocene radiaxial calcite from Enewetak formed by neomorphism of a fibrous marine HMC cement in meteoric water.

The arguments against a primary cement origin are all equivocal and are challenged by Kendall (1984). (1) A late stage cement could fill cross-cutting voids present in previously cemented internal sediments and could explain Kendall and Tucker's (1973) "cross-cutting" relationships. Boring sponges commonly create cross-cutting voids through internal sediments (Moore and Shedd, 1977). (2) Dickson (1983) has clearly shown that many true cements do not
have planar intercrystalline boundaries. (3) Many bladed marine cements do not show significant crystal widening when growing away from cavity walls; however, Kendall and Tucker (1973) believe that crystal widening with growth toward the center of a void is evidence of competitive growth and is diagnostic of primary cements. (4) The origin of lattice curvature (and undulose extinction) is poorly understood and is not good evidence against radiaxial spars being a primary precipitate. Scenarios for the possible development of linear inclusions and undulose extinction during direct precipitation of a cement will be discussed later in this section.

Origin by Direct Precipitation

In the Lower Miocene of the F-1 well, four lines of evidence suggest direct precipitation of radiaxial spar as a cement. First, original HMC and aragonite bioclasts do not show alteration patterns similar to radiaxial spars. Second, some radiaxial spar (identified by its characteristic undulose extinction) is clear (inclusion-free) and appears like any other void-fill cement (Fig. 18). Third, radiaxial spars often overgrow fibrous cements which retain their own optical and crystallographic identity after they are overgrown (Fig. 18). If radiaxial spars were formed by neomorphism of a fibrous precursor, the existing fibrous cements which have been overgrown by radiaxial spar should also have been neomorphosed.
The fourth and most compelling evidence for direct precipitation of radiaxial calcite is that inclusion-rich bands within radiaxial spar show growth patterns similar to those observed on existing radiaxial terminations (Figs. 18 and 19). Mimicking of existing terminations by the inclusion-rich bands indicates that radiaxial spars have grown with essentially the same crystal form that they have today. Inclusion-rich bands that define former rhombic and scalenohedral crystal faces are especially strong evidence that these spars grew originally as larger bladed or equant-to-bladed crystals (Figs. 18 - 20). It is difficult to imagine how alteration of a fibrous cement could produce inclusion patterns that apparently define former crystal faces.

Organic coating and crystal flaws on or associated with subcrystals could easily result in roughly linear inclusions. As subcrystals tended to converge and coalesce, the master crystals would develop undulose extinction with converging optic axes which is characteristic of radiaxial spars (Bathurst, 1959; Kendall and Tucker, 1973; Kendall, 1984). Kendall (1984) concludes that formation of radiaxial spar is the result of crystal splitting followed by the convergence of coalescing subcrystals. Therefore, development of linear inclusions, lattice curvature, and undulose extinction would not require neomorphism but could develop by direct precipitation in their present form.
Diagenetic Environment of Formation

Stable carbon and oxygen isotopes strongly indicate that the Enewetak radiaxial cement formed in marine water; however, it is unclear when the radiaxial cement precipitated and whether precipitation was in shallow or deep marine water. Petrographically, two observations can be used to help decipher the approximate timing of cementation. First, most radiaxial cements formed distinctly after pelleted internal sedimentation, but in at least one case, radiaxial cementation alternates with pelleted internal sedimentation. Second, the radiaxial cements generally precipitated after dissolution of aragonite.

The single occurrence of alternating radiaxial cement and pelleted internal sediment is difficult to evaluate because it may well be an isolated occurrence and because the origin of pelleted internal sediment is uncertain. Macintyre (1977) describes similar pelleted internal sediments from Panama and concludes that they are essentially a marine cement. In contrast, Land and Moore (1980) discuss the formation of pelleted internal sediments in association with reef-related organisms, especially Clionid sponges. If the internal sediments are basically marine cements, they could theoretically form in any marine waters supersaturated with respect to calcite, provided that sufficient volumes of waters were able to circulate through the pore system. Modern Pacific Ocean water is supersaturated with respect to calcite down to approximately 1000 m. Active
modern marine circulation occurs to depths of at least 579 m in the vicinity of the F-1 well.

However, if the internal sediment was formed by marine organisms like Clionid sponges, the internal sediment must have been generated within 50 cm of the rock-water interface (Moore, 1984, pers. comm.). The lone observation of internal sediment alternating with radiaxial-type cementation occurs in core 6 of the F-1 well. Core 6 (811 - 819 m) is the deepest core in which radiaxial calcite was positively identified. Carbonate rocks in core 6 probably formed in a deep reef or shallow fore-reef environment that was significantly deeper than environments in which carbonate rocks of F-1 cores 3 - 5 (375 - 611 m) were deposited (Schlanger, 1963). Therefore, even if the internal sediments had an organic origin, the internal sediments alternating with radiaxial cements may have formed in relatively deep water (maybe 200 m) very near the rock-water interface.

Precipitation of radiaxial cement after aragonite dissolution is very significant. If radiaxial spars were precipitated in shallow marine conditions, one would expect radiaxial spars to form shortly after deposition and prior to aragonite dissolution, but this is not the case. If meteoric waters were responsible for aragonite dissolution, radiaxial cements could have formed anywhere from near sea level to their present burial depth.

Data presented here and in following sections suggest that most Lower Miocene strata have never been exposed
to any significant meteoric diagenesis. The general absence of (1) meteoric cements, (2) meteoric neomorphic spars, and (3) meteoric-type alteration of coralline algae (see Discussion of HMC) suggests that pervasive aragonite dissolution was not accomplished by meteoric waters. In this situation, the only viable alternative to meteoric dissolution of aragonite is aragonite dissolution by marine water below the aragonite saturation depth. Modern Pacific Ocean water become undersaturated with respect to aragonite at depths of approximately 300 - 350 m (Li et al., 1969; Scholle et al., 1983). It is probable that the aragonite saturation depth has been even shallower in the past, possibly reaching into the thermocline 100 - 250 m deep. Given the relatively free circulation of modern marine waters through the atoll, aragonite dissolution by deeper marine waters is quite feasible especially at the site of the F-1 well.

If aragonite dissolution did occur in marine waters below the aragonite saturation depth, most radiaxial cements would have had to precipitate between the aragonite saturation depth and their current burial depth (375 - 819 m deep). A similar sequence of deep marine aragonite dissolution and calcite precipitation has been described in the Tongue of the Ocean, Bahamas (Schlager and James, 1978). At that location, cements and other diagenetic calcites containing 3.5 - 5.0 mole % MgCO$_3$ were formed in a deep marine environment (Schlager and James, 1978). The deep marine diagenesis described in the Tongue of the Ocean by Schlager and James
(1978) seems closely analogous to the diagenetic alteration of deep marine strata in the F-1 well.

Videtich (1982) suggests that these radiaxial calcites were originally HMC and lost their magnesium during meteoric diagenesis. While data presented here suggest that these Lower Miocene strata have not been subjected to significant freshwater diagenesis, there is a distinct possibility that these radiaxial cements may have lost some magnesium after precipitation. However, stable carbon and oxygen isotopes indicate that any possible HMC to LMC transition occurred in marine waters (Land and Epstein, 1970). If the aragonite dissolution did occur in marine waters below the aragonite saturation depth, the radiaxial calcite cements must have originally been less soluble (more stable) than the previously dissolved aragonite. Therefore, radiaxial calcite probably contained less than 8 - 12 mole % MgCO$_3$ when it was initially precipitated (Chave et al., 1962; Plummer and Mackenzie, 1974; Walter, 1984).

Videtich (1982) argues that the consistently low magnesium content of inclusion-rich laminations (relative to clear laminations) is the result of greater porosity and more efficient expulsion of magnesium in inclusion-rich laminations relative to clear laminations. An alternative explanation is that the magnesium concentrations observed in the radiaxial cements are largely primary. If those cements precipitated at significant depths in the ocean, it is very possible that the 2-4 (and sometimes 2-8) mole % MgCO$_3$ calcites
were precipitated directly from seawater. The chemical conditions responsible for some cements being clear and others being inclusion-rich could also be responsible for clear cements being magnesium-rich and inclusion-rich cements being magnesium-poor.

The large magnesium variations observed within clear radiaxial cements (Fig. 24) suggest that there are significant precipitational variations in magnesium concentrations in radiaxial cements which are not related to differences in porosity or subsequent diagenesis. The tendency of magnesium to decrease with slower growth rates could correspond to slow or periodic cement growth under increasing burial depth and decreasing calcite saturation conditions. The alternation of clear (Mg-rich) and inclusion-rich (Mg-poor) radiaxial cements could reflect smaller scale oscillations in geochemical conditions which might increase and decrease calcite saturation levels and precipitation rates.

Decreasing magnesium concentration in radiaxial cements with depth can be correlated to decreases in temperature and degree of calcite saturation with depth in adjacent ocean water (Fig. 3). Fuchtbauer and Hardie (1976) have experimentally demonstrated that the amount of magnesium incorporated in calcite decreases with decreasing temperature. Chave et al. (1962) have also demonstrated that as magnesium concentration in calcite decreases, that calcite will be stable in waters with lower degrees of calcite saturation. The decrease in magnesium concentration with depth in radiaxial
cement might be due to (1) a continuous re-equilibration of radiaxial cements with interstitial marine waters resulting in loss of magnesium with increased burial or (2) precipitation of radiaxial spars with lower original magnesium contents in progressively deeper marine environments. Loss of magnesium from calcite during burial will be discussed further in a section on diagenesis of HMC.

The general trend of increasing $\delta^{18}O$ with depth (Fig. 36), probably reflects the precipitation of radiaxial spar in progressively colder and deeper marine waters. It is possible that the increasing $\delta^{18}O$ of radiaxial cements could also reflect a progressive re-equilibration of oxygen isotopes during burial. However, the presence of significant internal variations in $\delta^{18}O$ within individual cores (see isotope analyses from cores 3 and 5) and preservation of very light carbon and oxygen isotopes in E-1 core 2 (855 m), suggest that significant isotopic re-equilibration has not occurred.

Comparison to Ancient Radiaxial Calcites


Davies (1977), Lohmann and Meyers (1977), Mirsal and Zankl (1979), and Mattes and Mountjoy (1980) found dolomites associated with radiaxial calcites. Davies (1977) and Lohmann and Meyers (1977) documented microdolomites dispersed through their radiaxial cements and used the microdolomite as evidence of a fibrous HMC precursor for the radiaxial spars. Furthermore, Lohmann and Meyers (1977) proposed that microdolomite exsolved from the HMC precursor. Mirsal and Zankl (1979) found fine, idiomorphic dolomites filling pore spaces within a radiaxial cement lamination and suggested that the dolomites were a significantly later diagenetic feature. Mattes and Mountjoy (1980) found dolomite overgrowing radiaxial cements in the Devonian of Canada.

The dolomites overlying radiaxial spars in sample F-1-3-22 are most likely a direct precipitate. The close association of dolomite and the radiaxial cement in the Lower Miocene of Enewetak suggests that radiaxial cements and dolomites can be directly precipitated in similar or associated aqueous systems. This association, in turn, suggests that microdolomites in radiaxial cements might
be directly precipitated from almost the same aqueous system
that is precipitating radiaxial cements or a periodically
modified system. Therefore, it may be possible that the
microdolomites of Davies (1977) and Lohmann and Meyers
(1977) are directly precipitated or are due to replacement
rather than exsolution.

Most ancient radiaxial calcites occur within rocks
that were, or could have been, in contact with actively
circulating deep ocean water at the time of radiaxial cementa-
tion (settings roughly similar to that of Lower Miocene
strata in the Enewetak F-1 well). Radiaxial spars are
commonly found in Late Paleozoic bioherms, especially
Waulsortian mounds (Bathurst, 1959, 1975; Kendall and Tucker,
1973; Lohmann and Meyers, 1977). Late Paleozoic bioherms
are thought to have formed in moderately deep basins and
were perhaps associated with active marine circulation
(Wilson, 1975). Likewise, radiaxial spars are found in
ancient shelf margin reefs (Davies, 1977; Bebout and Loucks,
1974; Achauer, 1977; Mirsal and Zankl, 1979) where moderately
deep marine water could have been circulating through very
permeable reef-related limestones. Achauer (1977) indicates
that radiaxial cements are restricted to reefs of the Stuart
City trend at the seaward edge of the continental shelf
in Lower Cretaceous carbonates in Texas. The Devonian
reef complex described by Mattes and Mountjoy (1980) has
a geometric configuration similar to the Enewetak Atoll
with a large carbonate mound building vertically above
a deeper marine basin. That Devonian reef complex, like the Lower Miocene of Enewetak also contains abundant radiaxial cements.

It is quite possible that most ancient radiaxial cements were precipitated in an island or shelf margin environment similar to that of Miocene strata on Enewetak where moderately deep marine waters (undersaturated with respect to aragonite) flowed through very permeable carbonate rocks.

**Coarse Bladed Cements in Upper Eocene Strata**

Bladed cements of E-1 core 3 (1243 - 1250 m) are similar to bladed and fibrous cements in allochthonous clasts in Upper Eocene strata of the F-1 well. Petrographically, these bladed cements of the Upper Eocene of the E-1 and F-1 wells are often indistinguishable (Figs. 21 d & f). Strontium and magnesium concentrations in bladed and fibrous cements of allochthonous clasts are approximately the same as in autochthonous bladed cements in core 3 of the E-1 well (Table 2). Stable carbon and oxygen isotopes clearly indicate that the bladed cements in E-1 core 3 are marine in origin. The similarity of bladed cements in the allochthonous clasts and bladed cements in E-1 core 3 suggests that bladed and fibrous cements in the allochthonous clasts are also marine in origin.

In this study, the only important difference found
between the autochthonous bladed cements (Upper Eocene, E-1 well) and the bladed to fibrous cements in allochthonous clasts (Upper Eocene, E-1 well) involves timing of cementation relative to aragonite dissolution. In allochthonous clasts of the Upper Eocene strata of the F-1 well, all bladed and fibrous cements precipitated before aragonite dissolution. In core 3 of the E-1 well, a significant amount of cementation by bladed calcite occurred after aragonite dissolution. As with the massive dissolution of aragonite in the Lower Miocene of the F-1 well, aragonite in these Upper Eocene strata could have been dissolved by meteoric water or fairly deep marine water. There is no conclusive petrographic or geochemical evidence of meteoric alteration in these rocks. These Upper Eocene strata are now far below the modern aragonite saturation depth for the Pacific Ocean (Li et al., 1969). Atoll hydrology indicates that marine waters are still circulating through those Upper Eocene strata and, hence, could easily dissolve aragonite. No sediments are found in aragonite molds of the allochthonous clasts suggesting that the molds formed after the allochthonous clasts were deposited.

These bladed and fibrous cements (in Upper Eocene strata) probably precipitated from seawater near the seaward margin of the atoll. Prior to aragonite dissolution, clasts of some well-cemented reef and near-reef strata could have been broken off and transported downslope until they were deposited in deep fore-reef and slope environments similar
to those represented by Upper Eocene strata of the F-1 well. After being transported downslope, aragonitic grains in those clasts were probably dissolved by relatively deep marine waters circulating through the sediments. Other Upper Eocene reef and reef-wall strata, like core 3 of the E-1 well, remained in place. As the atoll subsided, marine cementation continued in those strata near the seaward margin of the atoll. When subsidence had lowered the strata below the aragonite saturation depth (presently about 300 m), dissolution of aragonite occurred. After dissolution of aragonite, those aragonite molds were refilled by bladed calcite cement precipitated by marine water circulating through E-1 core 3. The bladed cements now contain fairly low magnesium concentrations (less than 0.5 weight %), similar to magnesium concentrations in co-existing coralline algae. This similarity suggests that the Upper Eocene bladed cements (like the coralline algae) originally contained more magnesium.

**Echinoderm Overgrowths**

It is difficult to directly determine the environment of precipitation of echinoderm overgrowths because (1) echinoderm overgrowths grow syntaxially on echinoderm fragments and hence show almost no variation in morphology and (2) most overgrowths are too small to extract for stable isotope analysis. However the origin of echinoderm overgrowths
can often be inferred using petrographic, magnesium, and stable isotope data from clearly related cements.

The origin of echinoderm overgrowths in the Lower Miocene of the F-1 well can be inferred with a fair degree of confidence. Inclusion-rich growth laminations can be traced from radiaxial calcites into echinoderm overgrowths indicating that the overgrowths, precipitated synchronously with radiaxial calcite. Because it was concluded that radiaxial calcite has a marine origin, echinoderm overgrowths in the Lower Miocene of the F-1 well can also be inferred to have a marine origin.

Similarly, diagenetic alteration in Upper Eocene strata of the F-1 well appears to be marine. The lack of diagnostic meteoric alteration suggests that precipitation of echinoderm overgrowths in Upper Eocene strata of the F-1 well also occurred in marine waters. Precipitation in progressively deeper, less saturated marine waters might have caused the consistent decrease in magnesium concentration observed in overgrowths away from the echinoderm grain.

In Pleistocene strata on Enewetak, however, many echinoderm overgrowths probably formed in meteoric environments, as have most other Pleistocene cements. The magnesium and strontium concentrations of many echinoderm overgrowths are similar to many adjacent meteoric cements suggesting a meteoric origin for those overgrowths. The widely scattered distribution of echinoderm overgrowths in the Pleistocene suggests precipitation in both vadose and phreatic environments.
In Pleistocene samples from Enewetak, magnesium concentrations suggest that some early echinoderm overgrowths formed in marine waters or in meteoric waters with a significant marine component. Echinoderm overgrowths in the XEN-1 well at 14.3 m have approximately 1.4 weight % magnesium. Using the distribution coefficients of Katz (1973) and Winland (1969), the waters precipitating those overgrowths should have Mg\(^{2+}\)/Ca\(^{2+}\) ratios between 1.0 and 2.8 which are significantly above most meteoric waters (Mg/Ca = 0.05 - 0.20, Harris, 1971; 0.082 - 0.89, Livingstone, 1963). Equal and even higher magnesium concentrations can be found in the proximal portions of other overgrowths (Fig. 23). In both cases, overgrowths with elevated magnesium levels suggest that some marine water was mixed with meteoric water to raise the Mg\(^{2+}\)/Ca\(^{2+}\) content in the precipitating water and in the resulting echinoderm overgrowth.
DIAGENESIS OF ORIGINAL CARBONATE SEDIMENTS

Typically, shallow marine carbonate sediments consist of aragonite (40 - 100%) and high-magnesian calcite (HMC; 5 - 50%) with only minor low-magnesian calcite (LMC; 0 - 25%; Stehli and Hower, 1961; Friedman, 1964; Bathurst, 1975). During diagenesis, carbonate sediments are generally transformed into LMC and dolomite which are thermodynamically more stable under most sedimentary conditions (Garrels and Christ, 1965). Conversion of HMC and aragonite to LMC in meteoric waters has been well documented (Friedman, 1964; Schlanger, 1963; Land, 1966; Land et al., 1967; Matthews, 1967). Dissolution and conversion of HMC and aragonite to LMC by deep marine waters has also been documented by Schlager and James (1978) and Haggerty (1982); however, studies of ancient carbonates rarely propose conversion of HMC and aragonite to LMC by deep marine waters. Dissolution and conversion of HMC and aragonite to LMC may also occur in burial environments (Moore and Druckman, 1981).

In previous studies, carbonate petrologists have attempted to establish a hierarchy of carbonate grain stability and dissolution (Crickmay, 1945; Schlanger, 1964; Land et al., 1967). Observations summarized in Figures 40 - 42 show that no single grain type is always more susceptible to dissolution than any other grain type. From Figures 40 - 42, it is apparent that aragonitic fossils are generally
Figure 40.
Alteration of carbonate grains in Quaternary strata of the XRI-1 and XEN-1 wells.
ALTERATION OF QUATERNARY GRAINS

XRI-1 WELL

XEN-1 WELL

Depth (meters)

- Unaltered
- Dissolved
- Dissolved and refilled with cement
- Neomorphosed

D - partial delicate dissolution
C - coral
H - Halimeda
G - gastropods

→ exposure surface
Figure 41.
Alteration of carbonate grains in Quaternary strata of the XAR-1 well.
ALTERATION OF QUATERNARY GRAINS

XAR-1 WELL

Depth (meters)

- Unaltered
- Dissolved
- Dissolved and refilled with cement
- Neomorphosed

D - partial delicate dissolution
C - coral
H - Halimeda
G - gastropods
-> exposure surface
Figure 42.
Alteration of calcareous grains in Cenozoic carbonate strata of the E-1 and F-1 wells, Enewetak.
ALTERATION OF DEPOSITIONAL GRAINS

F-1 WELL

E-1 WELL

DEPTH (METERS)

0

200

400

600

800

1000

1200

1400

Pleistocene

Pliocene

Middle to
Upper
Miocene

Lower
Miocene

Upper
Eocene

Unaltered

Dissolved and refilled with cement

Dissolved

Neomorphosed

Dolomitezed
more susceptible to dissolution than originally high-magnesian calcite (HMC), because HMC converts (or neomorphoses) to LMC more efficiently than aragonite.

Diagenetic alteration of aragonite and HMC is quite variable in Cenozoic carbonates on Enewetak. Most Holocene grains are unaltered. Alteration of Pleistocene metastable grains is heterogeneous and incomplete. For example in a single thin section, it is common for: (1) some coral to be dissolved while other parts of the same coral remain intact, (2) some open pores to have much more cement than other pores, and (3) calcitized coral, Halimeda or gastropods to coexist with unaltered or partially dissolved coral, Halimeda or gastropods. Those features were previously recognized on Enewetak by Goter (1979). In Lower Miocene and Upper Eocene strata of the F-1 well and core 3 (1,243 - 1,250 m) of the E-1 well, all original aragonite and HMC grains have been dissolved or converted to LMC or dolomite (Fig. 42).

ARAGONITE

In most ancient rocks, the alteration of aragonite grains results in either complete dissolution of aragonite or neomorphism to more coarsely crystalline calcite (Friedman, 1964). Cores from Enewetak provide some valuable insight into the processes by which aragonite is diagenetically altered. The present distribution of aragonite in Cenozoic
Enewetak strata is shown in Figures 10 - 14. Original aragonite consisted primarily of coral, *Halimeda*, and mollusc skeletons. The diagenetic alteration of those 3 grain types is qualitatively shown for samples from the XRI-1, XAR-1, XEN-1, F-1 and E-1 wells in Figures 40 - 42. Partial delicate intrafabric dissolution is very common in Pleistocene strata (Figs. 40 and 41) and apparently represents an intermediate state of alteration between unaltered aragonite and completely dissolved or neomorphosed aragonite. Partial delicate dissolution (intrafabric dissolution of Goter, 1979) involves the delicate microscopic dissolution of a petrographically identifiable amount of a grain's original aragonite ultrastructure. Delicate dissolution is disseminated throughout a grain resulting in a residual meshwork of aragonite and organic material, preserving original fossil wall structure, but causing up to 80% intrafabric porosity (Fig. 43a-c). In a hand sample, partial delicate dissolution appears as a chalky fabric.

**Aragonite Neomorphism**

Folk (1965) defines neomorphism as a "comprehensive term of ignorance... for all transformations between one mineral and itself or a polymorph - whether inversion or recrystallization... It does *not* include simple pore-space fillings; older crystals must have gradually been consumed, and their place simultaneously occupied by new crystals
Figure 43. Partial delicate dissolution of aragonite (left) and calcite spar overgrowing partial delicately dissolved aragonite to form neomorphic spar (right) in Pleistocene strata from Enewetak.

(a) Photomicrograph of partial delicately dissolved coralline aragonite (70 m, XAR-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.

(b) SEM photograph of partially delicately dissolved coralline aragonite (70 m, XAR-1 well). Bar scale at bottom equals 100 microns.

(c) Close-up of (b). Bar scale at bottom equals 10 microns.

(d) Photomicrograph of neomorphic calcite (N) replacing a coral adjacent to partially delicately dissolved coralline aragonite (D; 45m, XRI-1 well). Bar scale at lower left equals 0.1 mm.

(e & f) Neomorphic calcite (dark) overgrowing remnants of partially delicately dissolved aragonite (light; 32 m, XRI-1 well). Bar scales at bottom equal 10 microns.
of the same mineral or a polymorph...". In ancient rocks it is virtually impossible to know how a transformation occurred. Aragonite neomorphism will be used here "as a term of ignorance" to describe the transformation of aragonite to calcite with a partial retention of original wall structure without regard to the mechanism of transformation. This usage is similar to Bathurst (1975) who used aggrading neomorphism to "describe a process, or collection of processes, about which we know with certainty only the nature of the sparry product and, in some cases, the composition of the original material".

**Petrography**

On Enewetak, neomorphosed aragonite is common in Pleistocene strata, very rare in Lower Miocene strata of the F-1 well and Upper Eocene strata (core 3) of the E-1 well, and absent in Upper Eocene strata of the F-1 well. Neomorphic calcite (after aragonite) is almost as common as, if not slightly more common than, sparry calcite cement in the Pleistocene (Figs. 10 - 12). In Quaternary strata below the first exposure surface, neomorphic calcite commonly replaces coral, *Halimeda*, and molluscs (Figs. 40 and 41). In Pleistocene strata, partial delicately dissolved aragonite is also very common, accounting for approximately 50 - 70% of the fabric selective dissolution of Pleistocene aragonite (Figs. 40 and 41). Of 57 Pleistocene samples
containing neomorphic spar, 40 samples contain neomorphic calcite within partial delicately dissolved aragonite skeletons (Figs. 43 and 44). In only 6 samples are neomorphosed parts of grains separated from intact aragonite by thin alteration zones. In Pleistocene samples, neomorphic spar is often observed passing laterally into clear void-fill cement and/or open voids (Fig. 44f).

Only two samples containing neomorphosed aragonite were found in Lower Miocene strata of the F-1 well. Both occurrences are within a meter of each other in core 5 and consist of neomorphic calcite in corals that are apparently in growth position.

Geochemistry of Neomorphosed Aragonite

Trace element concentrations and stable isotope compositions of neomorphic spar provide valuable insight into processes by which aragonite is neomorphosed to calcite on Enewetak. Using an electron microprobe, strontium and magnesium concentrations have been determined for neomorphosed coral, *Halimeda*, and molluscs (Table 6; Figs. 45 - 47). Iron and manganese concentrations in a few neomorphosed coral were determined using atomic absorption spectrophotometry (Table 7). Microprobe analyses show large point-to-point variations in strontium concentrations within neomorphic spars (Fig. 48). In addition, clear cements that fill primary intracoralline voids generally have lower strontium
Figure 44.
Photomicrograph of neomorphic spar and partial delicately dissolution of aragonite in Pleistocene strata.
(a) Neomorphic calcite (N) within a partially delicately dissolved *Halimeda* flake (D) (20 m, XAR-1 well). Bar scale at lower left equals 0.2 mm. Crossed nicols.
(b) Gastropod which has parts that have been partially dissolved (D), neomorphosed to calcite (N), and completely dissolved (V) (23 m, XAR-1 well). Bar scale at lower left equals 0.1 mm.
(c) Aragonite grain in which part has been completely dissolved, (V), part is partially delicately dissolved (D), part is unaltered (A), and part is neomorphosed to calcite (N) (30 m, XRI-1 well). Bar scale at lower left equals 0.1 mm.
(d) Partial delicately dissolved *Halimeda* (D) adjacent to a *Halimeda* flake neomorphosed to calcite (N) (45 m, XRI-1 well). Bar scale at lower left equals 0.5 mm. Crossed nicols.
(e) Same as (b) except with crossed nicols. Bar scale at lower left equals 0.1 mm. Crossed nicols.
(f) Clear calcite cement overgrowing neomorphic calcite (N) replacing a mollusc fragment (45 m, XRI-1 well). Bar scale at lower left equals 0.1 mm.
### TABLE 6: GEOCHEMISTRY OF NEOMORPHIC CALCITE AND RELATED FEATURES

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>Mean Sr (wt.% ± 1σ)</th>
<th>Mean Mg (wt.% ± 1σ)</th>
<th>n</th>
<th>Mean δ¹³C (‰, PDB ± 1σ)</th>
<th>Mean δ¹⁸O (‰, PDB ± 1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pleistocene, Enewetak</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coral</td>
<td>32</td>
<td>0.780 ± 0.078</td>
<td>0.082 ± 0.023</td>
<td>8</td>
<td>-1.5 ± 1.1</td>
<td>-3.9 ± 0.5</td>
</tr>
<tr>
<td>Halimeda</td>
<td>7</td>
<td>0.834 ± 0.152</td>
<td>0.036 ± 0.036</td>
<td>7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Neomorphosed coral</td>
<td>36</td>
<td>0.155 ± 0.045</td>
<td>0.221 ± 0.030</td>
<td>19</td>
<td>-4.3 ± 2.9</td>
<td>-7.1 ± 1.2</td>
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<tr>
<td>Neomorphosed Halimeda</td>
<td>21</td>
<td>0.192 ± 0.043</td>
<td>0.231 ± 0.070</td>
<td>5</td>
<td>-4.8 ± 1.2</td>
<td>-6.3 ± 0.3</td>
</tr>
<tr>
<td>Neomorphosed molluscs</td>
<td>18</td>
<td>0.112 ± 0.016</td>
<td>0.286 ± 0.028</td>
<td>5</td>
<td>-</td>
<td>-</td>
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<tr>
<td>Calcite cement</td>
<td>147</td>
<td>0.060 ± 0.017</td>
<td>0.236 ± 0.061</td>
<td>22</td>
<td>-5.1 ± 3.1</td>
<td>-6.5 ± 0.6</td>
</tr>
<tr>
<td><strong>Lower Miocene, F-1 Well</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neomorphosed coral</td>
<td>2</td>
<td>0.252 ± 0.026</td>
<td>0.356 ± 0.038</td>
<td>2</td>
<td>-1.8 ± 1.1</td>
<td>-3.6 ± 0.9</td>
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<tr>
<td>Radial cement</td>
<td>17</td>
<td>0.033 ± 0.009</td>
<td>0.820 ± 0.274</td>
<td>7</td>
<td>2.0 ± 0.5</td>
<td>-0.4 ± 0.8</td>
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<tr>
<td>Intracoralline cement</td>
<td>2</td>
<td>0.031</td>
<td>0.803</td>
<td>1</td>
<td>0.6</td>
<td>-1.9</td>
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<tr>
<td><strong>Barbados</strong></td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neomorphosed coral</td>
<td>43</td>
<td>0.168 ± 0.064</td>
<td>0.239 ± 0.096</td>
<td></td>
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</table>

**Notes:**
1. "n" is the number of samples analyzed.
2. Sr and Mg data from Enewetak is based on electron microprobe analyses.
3. Data from Barbados is from Pingitore (1978)
Figure 45.
Strontium and magnesium concentrations for coral neomorphosed to calcite in Pleistocene strata of the XRI-1, XAR-1, and XEN-1 wells. Note that strontium concentrations in neomorphosed coral are always between modern coral and the average strontium concentration of Pleistocene calcite cements, but generally closer to the concentration of calcite cements. Mean magnesium concentrations in neomorphosed coral are similar to LMC cements and are often higher than the modern coral. Data from electron microprobe analyses. Composition of modern coral derived from data in Milliman (1974).
STRONTIUM VERSUS MAGNESIUM FOR NEOMORPHOSED CORAL, PLEISTOCENE, ENEWETAK

Modern Coral

Average Pleistocene LMC Cement
Figure 46.
Strontium and magnesium concentrations of neomorphosed Halimeda in Pleistocene strata of the XRI-1, XAR-1, and XEN-1 wells. Note that strontium concentrations in neomorphosed Halimeda are intermediate between original concentrations and average Pleistocene calcite cement, but closer to average Pleistocene calcite cement. Average magnesium concentration of neomorphosed Halimeda is similar to Pleistocene calcite cement and significantly higher than modern Halimeda. Data from electron microprobe analyses. Field of modern Halimeda is derived from data in Milliman (1974).
STRONTIUM VERSUS MAGNESIUM FOR NEOMORPHOSED HALIMEDA, PLEISTOCENE, ENEWETAK

Modern Halimeda

Average Pleistocene LMC Cement
Figure 47.
Strontium and magnesium concentrations in neomorphosed originally, aragonitic molluscs. Data from electron microprobe analyses. Composition of modern aragonitic molluscs is derived from data in Milliman (1974).
STRONTIUM VERSUS MAGNESIUM FOR NEOMORPHOSED MOLLUSCS, PLEISTOCENE, ENEWETAK

Modern Aragonitic Molluscs

Mean Pleistocene calcite cement
# TABLE 7

## ELEMENTAL ANALYSES OF NEOMORPHOSED CORAL

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Sr</th>
<th>Fe</th>
<th>Mn</th>
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<tr>
<td>XEN-89</td>
<td>2,270</td>
<td>1,178</td>
<td>24</td>
<td>11</td>
<td>329</td>
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<tr>
<td>XRI-164</td>
<td>2,890</td>
<td>1,400</td>
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<tr>
<td>XRI-231</td>
<td>2,939</td>
<td>996</td>
<td>17</td>
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<tr>
<td>K-1-24</td>
<td>1,145</td>
<td>3,013</td>
<td>40</td>
<td>8</td>
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<td><strong>Lower Miocene, F-1 Well</strong></td>
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<tr>
<td>F-5-26</td>
<td>6,536</td>
<td>750</td>
<td>44</td>
<td>8</td>
<td>470</td>
</tr>
</tbody>
</table>

Note: Data based on atomic absorption spectrophotometry.
Figure 48.
Electron microprobe traverses of neomorphosed coral and intracoralline cements. Intracoralline cements are generally in optical continuity with neomorphic calcite. Note that strontium concentrations are generally higher in neomorphic calcite than in intracoralline cements. Also note that some points have very high strontium concentrations which might be due to the electron beam encountering small aragonitic inclusions within neomorphic calcite. Location of traverse A-A' is shown in Figure 50a.
TRAVERSES OF PLEISTOCENE NEOMORPHOSED CORAL

XRI-1
Well, 41 m

XRI-1
Well, 25 m

N = neomorphosed coral  C = intracoralline calcite cement

Sr concentration  Sr background ± S.D.

Mg concentration  Mg background ± S.D.
concentrations than adjacent and optically continuous neomorphic spar (Table 8; Fig. 48). Clear cements filling Halimeda utricles also tend to have lower strontium concentrations than optically continuous crystals in neomorphosed Halimeda.

Results of stable isotope analyses of neomorphosed coral and neomorphosed Halimeda from Enewetak are summarized in Table 6 and Figure 49. Stable carbon and oxygen isotope analyses were also performed on aragonitic coral (Fig. 49).

Discussion of neomorphism

Friedman (1964) used the term "paramorphic replacement" to describe the replacement of aragonite by calcite with partial retention of original wall structure. Friedman (1964) suggested that paramorphic replacement resulted from "solution-deposition" on a microscale (thin-film neomorphism). Kinsman (1969) then reasoned that because aragonite concentrations in neomorphic calcite are generally intermediate between a fossil's original aragonite and theoretical strontium concentrations in calcite precipitated from seawater, neomorphic spar forms in a semi-closed system. Neomorphism by a thin film of water migrating across an aragonitic fossil could theoretically precipitate calcite in such a semi-closed system and preserve relicts of the original fossil wall structure (Kinsman, 1969). "Thin-film neomorphism" has since become widely accepted as the process by which neomorphism of aragonite to calcite occurs (Sandberg et al., 1973;
TABLE 8

<table>
<thead>
<tr>
<th>XAR-1 Well</th>
<th>Mean Sr (Weight %)</th>
<th>Mean point-to-point S.D. (Weight % Sr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Neomorphosed Coral</td>
<td>Optically Continuous Intracoralline Calcite Cement</td>
</tr>
<tr>
<td>34 m</td>
<td>0.165</td>
<td>0.093</td>
</tr>
<tr>
<td>38 m</td>
<td>0.189</td>
<td>0.132</td>
</tr>
<tr>
<td>56 m</td>
<td>0.193</td>
<td>0.108</td>
</tr>
<tr>
<td>65 m</td>
<td>0.112</td>
<td>0.019</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>XRI-1 Well</th>
<th>δ¹³C (o/oo, PDB)</th>
<th>δ¹⁸O (o/oo, PDB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 m</td>
<td>-3.3</td>
<td>-3.1</td>
</tr>
<tr>
<td></td>
<td>-6.2</td>
<td>-5.9</td>
</tr>
</tbody>
</table>

Note: Sr data based on electron microprobe analyses.
Figure 49.
Stable isotope composition of aragonitic coral, neomorphosed coral, and *Halimeda* in Pleistocene strata of the XRI-1, XAR-1, and XEN-1 wells. Lines connect co-existing aragonitic coral and neomorphosed coral. Note that the fields of neomorphosed coral and *Halimeda* are distinctly different from their original aragonitic compositions; however fields of Pleistocene neomorphosed coral and *Halimeda* are quite similar to the field of Pleistocene calcite cement. Field of modern *Halimeda* is from data in Milliman (1974).
STABLE ISOTOPE COMPOSITION OF PLEISTOCENE NEOMORPHOSED CORAL AND HALIMEDA

\[ \delta^{13}C (\text{o/oo PDB}) \]
\[ \delta^{18}O (\text{o/oo PDB}) \]

- Coral
- Neomorphosed Coral
- Neomorphosed Halimeda

Modern Halimeda

Pleistocene calcite cements
Pingitore, 1976). Brand and Veizer (1980) later introduced the term "messenger film" to remove the dimensional connotation of "thin-film" and to emphasize that the reaction film was "transferring textural and chemical 'information' from the dissolving carbonate phase to the precipitating carbonate phase" during neomorphism.

Petrographic and geochemical data from Pleistocene strata on Enewetak indicate that aragonite to calcite neomorphism (in situ and other kinds) does not occur by thin or messenger films. Rather, neomorphism apparently results from a partial delicate intrafabric dissolution of aragonite followed by calcite infilling the intrafabric voids at a distinctly later time. Then, when calcite overgrows the remaining aragonite and organic material, the original wall structure is partially preserved. This process is essentially the hybrid replacement of Goter (1979) and is similar to a sequence of events described by Gvirtzman and Friedman (1977) for the alteration of aragonitic coral to calcite. This method of neomorphism is in contrast to thin or messenger film neomorphism where calcium carbonate is simultaneously being dissolved on one side of a reaction zone and precipitated as calcite on the other side with only moderate chemical and textural modifications. Goter (1979) also describes in situ neomorphism of aragonite by thin reaction films in the Pleistocene of Enewetak.
Discussion of Petrography

Of 57 Pleistocene samples from Enewetak containing neomorphosed aragonite, 53 samples contain aragonite as well as neomorphic spar suggesting that stabilization of aragonite is incomplete in most Pleistocene samples from Enewetak (Figs. 40 and 41; Goter, 1979). However, neomorphic calcite was found separated by a reaction zone from unaltered aragonite in only 6 samples suggesting that thin-film (or messenger film) neomorphism is not the main process in which aragonite is converted to neomorphic calcite. Rather, petrographic observations suggest that aragonite neomorphism occurs by partial delicate dissolution of aragonite followed by calcite infilling of intrafabrics voids. In 40 Pleistocene samples, neomorphic calcite can be observed within partially delicately dissolved Halimeda or coral fragments (Figs. 43 and 44). In those samples, neomorphic calcite spar appears to have simply been precipitated into partially dissolved intrafabrics voids (Figs. 43 and 44).

Neomorphic spar is often observed laterally changing to clear void-fill cement (Fig. 44f). In other Pleistocene rocks, partial delicately dissolved fossils can be traced laterally into areas of complete dissolution (Fig. 44c). If neomorphism is by partial delicate dissolution and calcite infilling, neomorphic spar and mold-fill cements could be juxtaposed simply by calcite infilling fossils which are partially delicately dissolved in one area and completely dissolved nearby (Fig. 44). Creating a similar texture
with thin-film neomorphism would require that: (1) a thin reaction film pass through part of the fossil, (2) the rest of the fossil be completely dissolved, and then (3) calcite cement fill the part of the fossil that was completely dissolved, a complex and unlikely scenario.

Discussion of geochemistry

In Pleistocene strata of Enewetak, magnesium and stable isotope data also indicate that neomorphism of aragonite to calcite has not occurred by thin-film neomorphism. Pleistocene neomorphic spar has generally not inherited the magnesium or stable isotope geochemistry of its aragonitic precursor (Table 6; Figs. 45 - 47 and 49). Rather, the stable isotope compositions and magnesium concentrations of neomorphic spar are quite similar to Pleistocene calcite cements. Because the CO$_2$ reservoir in water is small (Garrels and Christ, 1965), carbon from the aragonitic precursor should dominate the stable carbon isotopes of calcite produced by thin-film neomorphism, but it does not (Table 6; Fig. 49). Likewise, in thin-film neomorphism, the magnesium concentration of aragonitic precursors should largely control magnesium concentration in neomorphic spar, but it does not.

The geochemical similarity of Pleistocene neomorphic spar and Pleistocene calcite cement (Table 6; Fig. 49) suggests that the source of neomorphic calcite is essentially the same as void-fill calcite cement. Therefore, magnesium and stable isotope data clearly support neomorphism by
partial delicate dissolution and later calcite infilling. Stable carbon and oxygen isotope values also indicate that Pleistocene neomorphism occurred in meteoric waters. The mean stable oxygen isotope composition of neomorphosed coral (-6.9 o/oo, PDB) is in equilibrium with waters having a stable oxygen isotope composition of -4.4 o/oo (SMOW; at 27°C, Friedman and O'Neil, 1977).

The strontium concentrations in neomorphic calcite are intermediate between original aragonitic fossils and meteoric calcite cements. Strontium concentrations could be due to precipitation of neomorphic calcite in semi-closed systems as envisaged by thin or messenger film neomorphism (Kinsman, 1969; Brand and Veizer, 1980). On the other hand, aragonite inclusions could also elevate strontium concentrations in neomorphic calcite which has overgrown partially delicately dissolved aragonite. The large point-to-point strontium variations observed during electron microprobe analyses of neomorphosed spar (Fig. 48; Pingitore, 1976) were probably caused by the electron beam (5 - 10 microns in diameter) hitting former aragonite inclusions. Sandberg et al. (1973), Gvirtzman and Friedman (1977), and Lasemi and Sandberg (1983) have confirmed the existence of such aragonite inclusions in neomorphic calcite. Higher strontium concentrations in neomorphic spar relative to clear optically continuous cements filling intraskeletal voids (Fig. 48; Table 8), also suggest that aragonite inclusions (some of which may have inverted to calcite) are the cause
of elevated strontium levels in neomorphic spar.

**Lower Miocene Neomorphism**

Unfortunately, data regarding the two samples of neomorphosed Lower Miocene coral (F-1 well) do not conclusively point toward any single mechanism or environment of neomorphism. Petrographically, those Lower Miocene neomorphosed corals appear similar to Pleistocene corals which were neomorphosed to calcite in meteoric waters. The strontium and magnesium concentrations of the two Lower Miocene neomorphosed corals, however, are quite distinct from Pleistocene neomorphosed coral (Table 6). The two Lower Miocene neomorphosed corals contain strontium levels significantly higher than most Pleistocene neomorphosed coral suggesting (1) that much aragonite and/or strontium from the original coral were (was) trapped and incorporated in the neomorphosed coral or (2) neomorphism occurred in a fairly closed system that did not allow much original strontium to be removed.

The magnesium concentrations in the two Lower Miocene neomorphosed corals are high relative to Pleistocene neomorphosed coral but very low relative to cements in their intra-coralline voids (Table 6). These high magnesium contents suggest that (1) neomorphism did not occur in meteoric waters and (2) neomorphic spar was not precipitated from waters that were in equilibrium with the waters precipitating the intra-coralline cements.
The stable isotope composition of the two Lower Miocene neomorphosed coral also indicate neomorphism in a relatively closed system, with $\delta^{13}C$ and $\delta^{18}O$ compositions similar to those of original aragonitic coral (Table 6; Fig. 49). While the carbon isotopes in the neomorphosing system could logically be controlled by the original coral, the stable oxygen isotopes should be controlled by the water in which neomorphism was occurring. Using the paleothermometry equation of Friedman and O'Neil (1977), the $\delta^{18}O$ value of $-3.0$ o/oo (PDB) for one neomorphosed coral could be construed as being in equilibrium with ocean water. However the $\delta^{18}O$ value of $-4.3$ o/oo (PDB) for the other neomorphosed coral cannot be considered marine. The lone analysis of an Upper Eocene or Oligocene meteoric cement on Enewetak (E-1 well, core 2) suggests that meteoric water has had $\delta^{18}O$ compositions similar to Quaternary meteoric waters since the Oligocene; hence, a $\delta^{18}O$ value of $-4.3$ o/oo (PDB) is not compatible with neomorphism in meteoric waters. Geochemically, neomorphism in mixed marine and meteoric water is a possible explanation for the oxygen isotope composition of the neomorphosed coral.

The intra-coralline cements in those two neomorphosed corals have strontium, magnesium, $\delta^{13}C$, and $\delta^{18}O$ values which are similar to radiaxial spar (Table 6). Previously presented evidence indicates that radiaxial spar has a marine origin. There is no diagnostic evidence of meteoric diagenesis near the neomorphosed coral. Unfortunately,
the environment in which two Lower Miocene coral samples of core 5 were neomorphosed cannot be determined at this time.

Dissolution of Aragonite

Dissolution of aragonite grains occurs sporadically through much of the Cenozoic of Enewetak Atoll (Figs. 40 - 42). Aragonite dissolution and neomorphism are quite heterogeneous in Pleistocene strata. Complete dissolution and/or neomorphism of all aragonite was observed in only 5 out of 100 Pleistocene samples. Partial dissolution of aragonite occurs in most Pleistocene samples (Figs. 40 and 41). In some cases, certain types of aragonite (like gastropods) will be selectively leached while other types (like fibrous cement) remain intact (Fig. 50b).

In Pleistocene strata on Enewetak, complete dissolution of some or all aragonitic grains occurs most commonly in zones of intense dissolution and in zones where original aragonite is not abundant. For example, totally dissolved aragonite grains (some of which have been refilled with cement) are commonly found both immediately below subaerial exposure surfaces and in Pleistocene rocks that are composed primarily of micritic internal sediments or coralline algae.

Complete dissolution of aragonite is pervasive in Lower Miocene and Upper Eocene strata of the F-1 well (Fig. 42). Much of the aragonite dissolved in Lower Miocene
Figure 50.
Alteration of carbonate grains.
(a) Neomorphosed Pleistocene coral (25 m, XRI-1 well). See Figure 48 for electron microprobe traverse A-A'. Bar scale at lower left equals 0.5 mm.
(b) Dissolved gastropod surrounded by crusts of intact fibrous aragonite cement (18 m, XEN-1 well). Bar scale at lower left equals 0.1 mm.
(c) Dissolved Halimeda flake (H) with micritic material filling former utricles (core 10, 1,208 - 1,216 m, Upper Eocene, F-1 well). Bar scale at lower left equals 0.5 mm.
(d) Pleistocene coralline algae (CA), now LMC, with dissolved edges (41 m, XAR-1 well). Bar scale at lower left equals 0.1 mm.
(e) Dolomite rhombs partially replacing Upper Eocene coralline algae (CA), (1,243 m, E-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(f) Internal sediments (I) that would have filled primary intracoralline voids of a coral that was later dissolved (core 9, 1,114 - 1,117 m, Upper Eocene, F-1 well). Bar scale at lower left equals 0.5 mm. Crossed nicols.
strata of the F-1 well has been replaced by radiaxial calcite (Figs. 18c-d), but aragonite grains dissolved in Upper Eocene strata have generally not been refilled with cement. Dissolved coral, Halimeda, and molluscs in those Upper Eocene strata can only be identified by intra-skeletal cements and internal sediments (Figs. 50 c & f). Undoubtedly, many other aragonite grains have been dissolved without leaving any identifiable trace (mold).

In core 1 of the E-1 well (610 - 618 m), minor aragonite dissolution is limited to partial delicate dissolution of a few mollusc fragments. In cores 2 and 3 of the E-1 well, complete dissolution of aragonite grains is prevalent. In E-1 core 2 (854 - 856 m), dissolved aragonite grains have often been refilled with clear, equant-to-bladed and equant mosaic cements. In core 3 of the E-1 well (1,243 - 1,250 m), dissolved aragonitic fossils have generally been refilled with bladed, often inclusion-rich, cements (Fig. 21).

Discussion of aragonite dissolution

Because aragonite dissolution is a destructive process, its mode of occurrence must be inferred from its geologic setting and diagenetic spars associated with dissolution.
Meteoric dissolution

Aragonite dissolution by meteoric waters has been documented in numerous studies of Holocene, Pleistocene, and ancient carbonates (Friedman, 1964; Halley and Harris, 1979; and many others). In Pleistocene strata of Enewetak, meteoric cement and meteoric neomorphic spar are commonly associated with aragonite dissolution suggesting that aragonite dissolution has also occurred in meteoric water. Likewise, association with meteoric cement suggests that dissolution of aragonite grains in core 2 of the E-1 well (854 - 856 m) is also a result of meteoric diagenesis.

Dissolution of aragonite by meteoric waters is very patchy in Pleistocene samples from Enewetak and much aragonite has survived meteoric diagenesis (Figs. 40 - 41). A little aragonite has also survived meteoric diagenesis in core 2 of the E-1 well (Upper Eocene). The survival of aragonite and predominance of partial delicate dissolution in the Pleistocene of Enewetak is probably the result of several different factors including (1) thick packages (10 - 15 m) of aragonite-rich strata deposited between periods of subaerial exposure and (2) periods of subaerial exposure that were generally too short or meteoric diagenesis not intense enough to completely alter aragonite. Buffering of meteoric waters by rapid dissolution of some aragonite may have resulted in waters that were only slightly undersaturated with respect to aragonite. In turn, those slightly
undersaturated waters may have been responsible for partial delicate dissolution of aragonite.

**Marine dissolution**

Evidence suggests that relatively deep marine waters have caused pervasive dissolution of aragonite in Lower Miocene and Upper Eocene strata of the F-1 well and in core 3 (1,243 - 1,250 m) of the E-1 well. In Lower Miocene strata of the F-1 well, many aragonite molds have been infilled with radiaxial calcite. As discussed earlier, radiaxial calcite in the F-1 well is apparently a marine cement. Except for the uppermost portion of core 3 (375 m), there is no convincing evidence of meteoric diagenesis in the Lower Miocene of the F-1 well. Therefore, pervasive aragonite dissolution in these Lower Miocene strata is probably the result of marine processes. Likewise, dissolution of aragonite in Upper Eocene strata of the F-1 well was also probably marine because (1) associated cements are apparently marine (see Discussion of Cements), (2) deposition of most Upper Eocene strata in the F-1 well is in relatively deep water (at least 200 m deep; Schlanger, 1963) and (3) there is no clear evidence of meteoric diagenesis.

Likewise, evidence indicates that aragonite dissolution in core 3 (1,243 - 1,250 m) of the E-1 well probably occurred in marine water. Petrographically, aragonite dissolution follows one generation of bladed calcite cement and precedes
a second generation of bladed cement (Fig. 21e). Both generations of cement have carbon and oxygen isotope compositions in equilibrium with modern seawater (Fig. 34), suggesting cement precipitation and aragonite dissolution in marine water. While incursion of a meteoric system between precipitation of the two generations of cement is a possible mechanism to dissolve aragonite in core 3 of the E-1 well, the absence of meteoric spar suggests marine dissolution.

In the Pacific Ocean, marine waters below approximately 305 m are undersaturated with respect to aragonite (Fig. 3; Li et al., 1969; Scholle et al., 1983). Deep marine waters are currently circulating through Lower Miocene and Upper Eocene strata of the F-1 well and lowest Upper Eocene strata of the E-1 well, and probably have been for some time (Swartz, 1958). Therefore, it is quite reasonable to call on relatively deep marine water circulating through the atoll to dissolve aragonite in Lower Miocene and Upper Eocene strata of the F-1 well (375 - 1,388 m) and core 3 of the E-1 well (1,243 - 1,250 m).

HIGH-MAGNESIAN CALCITE (HMC)

High-magnesian calcite (HMC) constitutes 5 - 50% of most modern carbonate sediments (Stehli and Hower, 1961; Friedman, 1964; Land, 1967); however, HMC is virtually non-existent in ancient limestones (Bathurst, 1975, p.237). In contrast to aragonite neomorphism, HMC fossils are often
converted to LMC without any distinguishable petrographic change in wall structure (Friedman, 1964; Gross, 1964; Land, 1966; Land et al., 1967; Purdy, 1968; Gavish and Friedman, 1969; Goter, 1979; and others). The geochemical process (or processes) by which HMC is converted to LMC is (are) poorly understood. Experimentally, HMC dissolves completely in waters undersaturated with respect to calcite; however, when waters are slightly supersaturated with respect to LMC, HMC "incongruently dissolves", consuming HMC and producing LMC plus magnesium-rich water (Land, 1967; Plummer and Mackenzie, 1974; Walter and Hanor, 1979; Walter, 1984). Several hypotheses have been offered regarding this "incongruent dissolution" or magnesium loss:

(1) To explain loss of magnesium without petrographically altering HMC grains, Bathurst (1975) suggests that magnesium ions in HMC could be diffused to crystal surfaces, and there be exchanged with calcium ions in interstitial waters. Though Bathurst (1975) does not prefer this explanation, he states that "the geologically slow rate of lattice diffusion may be offset by the extremely small crystal size in the skeletons and the large resultant surface area exposed to ground water after organic matrices have decayed" (p. 337).

(2) The loss of magnesium from HMC could be the result of thin reaction films along which microscopic dissolution and reprecipitation occur (Friedman, 1964; Bathurst, 1975). In at least some cases, the conversion of HMC to LMC is
accompanied by a re-equilibration of stable carbon and oxygen isotopes with meteoric water, suggesting that the synchronous dissolution of HMC and precipitation of LMC occurred in meteoric waters (Land and Epstein, 1970).

(3) A third possible way to explain the loss of magnesium without any apparent textural change is that magnesium in HMC originally existed in lattice defects, lattice interstices, and inclusions (Schroeder, 1969; Schroeder and Siegel, 1969). If magnesium was concentrated in lattice interstices or inclusions, it could be transported away without loss of fossil texture (Schroeder and Siegel, 1969). A related option is that magnesium exists in sub-microscopic, magnesium-rich minerals (i.e. brucite) which are preferentially dissolved in fresh water; however, only minor quantities of minerals other than calcite have been found in modern HMC coralline algae (Schmalz, 1967; Milliman et al., 1971).

The geochemical and petrographic behavior of three types of HMC (coralline algae, echinoderm fragments, and micritic sediments) were systematically studied in cores from Cenozoic strata on Enewetak in an effort to understand the processes involved in HMC stabilization. Coralline algae and echinoderm fragments were selected for study for three main reasons. First, both were probably HMC when living. Second, both are scattered throughout most of the Cenozoic section. Third, both coralline algae and echinoderm fragments are easily identified in thin section. Although less dependably HMC in original composition, micritic sediments
are widespread and provide insight into the role which permeability and grain size seem to play in the HMC-LMC conversion.

Petrographically, the alteration of echinoderm fragments, coralline algae, and micrite is similar. In general, all three will either dissolve or lose magnesium without any apparent petrographic alteration. Diagenetic micritization of coralline algae may also occur. Because HMC coralline algae, echinoderm fragments, and micrite are impossible to distinguish petrographically from their LMC counterparts, all three grain types were systematically analyzed with an electron microprobe to determine their magnesium concentrations.

**Coralline Algae**

Most modern living coralline algae are composed of HMC containing over 4 weight % Mg (Milliman, 1974). In most Cenozoic samples examined from Enewetak, coralline algae have converted to LMC containing less than 1 weight % Mg and showing little or no petrographic change, except for partial dissolution of coralline algae in some Pleistocene samples. Only in Holocene samples and E-1 core 1 (610 - 618 m) were coralline algae skeletons still HMC (Figs. 51 and 52). Coralline algae in E-1 core 1 have significantly less magnesium than Holocene coralline algae and are apparently in transition between HMC and LMC (Fig. 52). Dolomite
Figure 51.
Magnesium concentrations in Quaternary coralline algae and micrite in the XAR-1, XRI-1, and XEN-1 wells. Note that all coralline algae and micrite below the first exposure surface (top of the Pleistocene) are LMC. Data from electron microprobe analyses.
MAGNESIUM CONCENTRATIONS IN QUATERNARY CORALLINE ALGAE AND MICRITE

Uppermost Exposure Surface + Coralline Algae □ Micrite
Figure 52.
Magnesium concentrations in Lower Miocene and Upper Eocene coralline algae versus depth. Note that Lower Miocene and Upper Eocene coralline algae of the F-1 well have quite consistent magnesium concentrations relative to Pleistocene coralline algae. Also note the consistent decrease of magnesium with depth in the F-1 well ($r = -0.85$) down to the intensely dolomitized zone. Data from electron microprobe analyses.
MAGNESIUM CONCENTRATIONS OF CENOZOIC CORALLINE ALGAE, ENEWETAK

Pleistocene Coralline Algae

Intense Dolomitization

+ F-1 Well

□ E-1 Well
rhombs can be observed replacing parts of coralline algae in cores 11 - 14 of the F-1 well (1,279 - 1,379 m) and in core 3 of the E-1 well (1,243 - 1,250 m; Fig. 50e).

Strontium and magnesium concentrations in Pleistocene coralline algae are erratic and show no trends relative to depth (Figs. 51 and 53). Magnesium and strontium concentrations in the Lower Miocene and Upper Eocene of the F-1 well are much more consistent and show a general decrease in magnesium and strontium with depth (Figs. 52 and 54; r (magnesium) = -0.85; r (strontium) = -0.64). However below the intensely dolomitized zone in the F-1 well (1,279 - 1,323 m), there is a slight increase in magnesium with depth (Fig. 52). Likewise, coralline algae of the E-1 well show a decrease in magnesium and strontium with depth (Figs. 52 and 54).

Plots of strontium versus magnesium in coralline algae display some very interesting patterns (Figs. 55 and 56). In Quaternary coralline algae, cluster analysis indicates three distinct strontium versus magnesium fields (Fig. 55). Field 1 (Fig. 55) consists of coralline algae with high, probably original, magnesium concentrations (4 - 7 weight % Mg; 15 - 25 mole % MgCO₃). Field 2 (Fig. 55) includes coralline algae which have lost much of their original magnesium but have apparently retained their original strontium concentrations (0.080 - 0.180 weight % Sr). Coralline algae in field 3 (Fig. 55) have lost significant amounts of original strontium and magnesium. Furthermore, Pleistocene
Figure 53.
Strontium concentrations in Quaternary coralline algae versus depth. Note that strontium concentrations are erratic relative to depth. Data from electron microprobe analyses.
STRONTIUM CONCENTRATIONS OF QUATERNARY CORALLINE ALGAE, ENEWETAK
Figure 54.
Strontium concentrations in Lower Miocene and Upper Eocene coralline algae versus depth. Note that strontium concentrations in Lower Miocene and Upper Eocene coralline algae of the F-1 well are more consistent than Quaternary coralline algae (Fig. 53) and generally decrease with depth ($r = -0.66$). Data from electron microprobe analyses.
STRONTIUM CONCENTRATION OF CENOZOIC CORALLINE ALGAE, ENEWETAK

Pleistocene coralline algae

Intense Dolomitization

+ F-1 Well

□ E-1 Well
Figure 55.
Strontium versus magnesium concentrations in Quaternary coralline algae. Cluster analysis (SAS, 1983) defines 3 distinct strontium-magnesium fields. Field 1 consists entirely of Holocene coralline algae with apparently original magnesium and strontium concentrations. Field 2 includes coralline algae which have lost much original magnesium but have apparently retained original strontium concentrations. Most coralline algae in field 2 are Pleistocene. Field 3 includes Pleistocene coralline which have apparently lost both original strontium and magnesium. Coralline algae in field 3 have a strong correlation between strontium and magnesium ($r = 0.93$). Data from electron microprobe analyses.
STRONTIUM VERSUS MAGNESIUM CONCENTRATIONS
IN QUATERNARY CORALLINE ALGAE

Field 2

Field 3

Field 1

WEIGHT % Sr

WEIGHT % Mg

0.00
0.05
0.10
0.15
0.20

0
1
2
3
4
5
6

WEIGHT % Mg

231
Figure 56.
Strontium and magnesium concentrations in Lower Miocene and Upper Eocene coralline algae of the F-1 well. Dashed line represents a linear regression for Pleistocene coralline algae in field 3 of Figure 55. In Lower Miocene and Upper Eocene strata of the F-1 well, correlation of strontium and magnesium is moderate ($r = 0.60$) but has a significant correlation probability (99% confidence interval). Data from electron microprobe analyses.
STRONTIUM VERSUS MAGNESIUM IN LOWER MIocene AND
UPPER EOCENE CORALLINE ALGAE, F-1 WELL
coralline algae in field 3 show a linear correlation between strontium and magnesium \( (r = 0.93; 99\% \text{ confidence level}) \). In Lower Miocene and Upper Eocene strata of the F-1 well, magnesium concentrations in coralline algae show a significant correlation with strontium concentration \( (r = 0.60; 99\% \text{ confidence level}) \).

**Echinoderm Fragments**

Modern echinoderm fragments are generally HMC (Milliman, 1974); whereas, echinoderm fragments in most ancient carbonate rocks are LMC or dolomite. Petrographically, most Cenozoic echinoderm fragments from Enewetak show no diagenetic alteration other than the precipitation of syntaxial calcite overgrowths; although a few Pleistocene echinoderm fragments have suffered selective dissolution (Figs. 40 and 41). Also, some echinoderm fragments in core 12 of the F-1 well \( (1,315 - 1,323 \text{ m}) \) have been dolomitized.

No echinoderm fragments from Holocene strata on Enewetak were available for analysis. Most Pleistocene echinoderm fragments have converted to LMC, but a few still contain 5 - 8 mole \% MgCO\(_3\) \( (1.2 - 2.1 \text{ wt. \% Mg;} \) Fig. 57). Core 1 of the E-1 well \( (610 - 618 \text{ m}) \) also contains echinoderm fragments that are still HMC (Figs. 57 and 58). In Lower Miocene and Upper Eocene strata of the F-1 well and in Upper Eocene strata of the E-1 well, all echinoderm fragments have converted to LMC (Figs. 57 and 58). In contrast to
Figure 57.
Strontium and magnesium concentrations in echinoderm fragments in Cenozoic carbonates on Enewetak. Strontium-magnesium fields 1 - 3 were previously identified by cluster analysis of Pleistocene coralline algae (Fig. 55). Data from electron microprobe analyses.
STRONTIUM AND MAGNESIUM CONCENTRATIONS IN ENEWETAK ECHINODERM FRAGMENTS

Field 2

Field 1

Field 3

- Pleistocene
- Lower Miocene and Upper Eocene, F-1 Well
- Lower Miocene (core 1), E-1 Well

WEIGHT % Mg

WEIGHT % Mg
Figure 58.
Magnesium concentration versus depth for echinoderm fragments and micrite in the E-1 and F-1 wells. Data from electron microprobe analyses.
MAGNESIUM CONCENTRATIONS OF ECHINODERM FRAGMENTS AND MICRITE, ENEWETAK
Pleistocene coralline algae on Enewetak, Pleistocene echinoderm fragments have very significant point-to-point variations in magnesium. For example, the mean point-to-point standard deviation in magnesium for coralline algae is 17% and for echinoderm fragments is 38%.

Magnesium concentrations in Pleistocene echinoderm fragments show no consistent trend relative to depth. In contrast, echinoderm fragments tend to decrease in magnesium concentrations with depth in Lower Miocene and Upper Eocene strata of the E-1 and F-1 wells (Fig. 58). Strontium and magnesium concentrations of Pleistocene echinoderm fragments tend to fit into the 3 fields previously identified for coralline algae (Fig. 57). Field 1 apparently represents unaltered HMC echinoderm fragments (Fig. 57). Fields 2 and 3 are LMC and correspond to fields 2 and 3 for coralline algae (Figs. 55 and 57). It should be noted that when echinoderm fragments coexist with coralline algae, often both do not fall into the same Sr-Mg field. Echinoderm fragments in Lower Miocene and Upper Eocene strata of the F-1 well fall into Sr-Mg field 3 (Fig. 57).

**Micritic Material**

Micritic material, mainly in reef-related internal sediments, was also systematically analyzed with an electron microprobe as a part of this study on Enewetak. Internal sediments were generally pelleted micrites that occasionally
contained small foraminifera. Such reef-related micrites and pelleted micrites in the Caribbean are dominantly HMC (Macintyre, 1977; Land and Moore, 1980), though minor contributions of aragonitic micrite may be present. As with coralline algae, HMC micrite is common in Holocene strata but is absent below the first exposure surface (Fig. 51). No HMC micritic sediments were found in Pleistocene strata or Lower Miocene and Upper Eocene strata of the E-l and F-l wells (Figs. 51 and 57; no micritic material was analyzed from E-l core 1).

Discussion of HMC diagenesis

The thermodynamic stability of calcite is dependent on the magnesium concentration in calcite. Plummer and Mackenzie (1974) show that the equilibrium ion activity product (K) of calcite with 3 mole % MgCO₃ is 3.0 X 10⁻⁹, while K of calcite with 12.7 mole % MgCO₃ is 15.1 X 10⁻⁹. Modern coralline algae generally contain 15 - 25 mole % MgCO₃ (Milliman, 1974). Skeletal fragments from living echinoids vary between 3.7 and 13.2 mole % MgCO₃ (Milliman, 1974). Variations in original magnesium concentration of Pleistocene echinoderm fragments have probably caused the heterogeneous alteration of echinoderm fragments. As a result, echinoderm fragments with more than 8 mole % MgCO₃ (2.1 weight % Mg) have been altered to LMC while some HMC echinoderm fragments with less than 8 mole % MgCO₃
remain intact.

It appears that calcite with over 2.1 weight % Mg (8 mole % MgCO$_3$) is significantly more prone to diagenetic alteration than calcite with less than 2.1 weight % Mg. This value of 2.1 weight % Mg (8 mole % MgCO$_3$) might represent a critical magnesium concentration above which calcite solubility is greater than aragonite and below which calcite solubility is less than aragonite. Plummer and Mackenzie (1974) determined experimentally that 7.5 mole % magnesian calcite has the same thermodynamic stability as aragonite. Using new experimental data, Walter (1984) concludes that 12 mole % magnesian calcite has approximately the same thermodynamic stability as aragonite. However, data presented here would tend to support conclusions of Plummer and Mackenzie (1974). This distinct variation in HMC alteration suggests that it is not appropriate to outline the diagenetic trends of HMC grains (or even echinoderm fragments) as a single homogeneous group (see Brand and Veizer, 1980).

**Environments of HMC alteration**

Conversion of HMC to LMC in meteoric water has been described by Friedman (1964), Land (1967) and many others. In all Quaternary strata which have been exposed to meteoric waters (below the first exposure surface), coralline algae and micrite have been converted to LMC suggesting that meteoric waters are generally responsible for the HMC to
LMC conversion in Pleistocene strata (Fig. 51). In core 2 (854 - 856 m) of the E-1 well, abundant meteoric cements (see Discussion of Cements) suggest a meteoric conversion of HMC to LMC in that stratigraphic interval.

In Pleistocene coralline algae and echinoderm fragments that have been converted to LMC, magnesium concentrations are erratically scattered between 0.15 and 0.95 weight % Mg (Fig. 51). The consistency of magnesium concentrations in coralline algae and echinoderm fragments between 375 and 1,388 m in the F-1 well suggests that meteoric diagenesis is not responsible for the conversion of coralline algae and echinoderm fragments to LMC in those strata. The association of LMC coralline algae and echinoderm fragments with LMC marine cements (see Discussion of Cements) suggests that the HMC to LMC transition occurred in marine waters below the HMC saturation depth in Lower Miocene and Upper Eocene strata of the F-1 well. The absence of meteoric cements and dominance of LMC marine cements in core 3 (1,243 - 1,250 m) of the E-1 well also suggest that conversion of coralline algae in E-1 core 3 occurred in marine waters.

In coralline algae and echinoderm fragments of the F-1 well, the gradual decrease in magnesium with burial depth suggests that calcite in coralline algae and echinoderm fragments is continuously or periodically losing magnesium in order to re-equilibrate with interstitial seawater. Decreasing calcite saturation with depth is probably the fundamental cause of decreasing magnesium concentration
in coralline algae with depth in the F-1 well. Calcite saturation in the Pacific Ocean decreases steadily with depth (Li et al., 1969; Scholle et al., 1983). Chave et al. (1962) showed experimentally that the stability of magnesian calcite is directly related to the degree of calcite saturation in the surrounding waters. In the F-1 well, the magnesium concentration in LMC coralline algae decreases downward until interstitial waters become undersaturated with respect to calcite and coralline algae begin to dissolve in zones of intense dolomitization.

Mechanisms of Conversion from HMC to LMC

The dominance of LMC coralline algae in Pleistocene strata suggests that the conversion of fine crystalline HMC to LMC can be very rapid. In all strata showing aragonite alteration, and in many Pleistocene strata that show little aragonite diagenesis, coralline algae and HMC micrite have converted to LMC. In Quaternary samples from Enewetak, magnesium versus strontium plots for coralline algae suggest that coralline algae and echinoderm fragments have lost magnesium by two distinctly different processes (Figs. 55 and 57). In one process (Figs. 55 and 57) HMC coralline algae and echinoderm fragments lose magnesium but retain their original strontium concentration. In the other process (Figs. 55 and 57), both strontium and magnesium are lost
from the original HMC fossils. In the magnesium-strontium plots for Quaternary coralline algae (Fig. 55), the lack of transitional grains between the three fields suggests that HMC coralline algae converted directly to either field 2 or 3.

Coralline algae and echinoderm fragments in field 2 (Figs. 55 and 57) have lost magnesium while apparently retaining original strontium. Because strontium should also partially re-equilibrate with interstitial waters in a dissolution-reprecipitation process, magnesium was probably lost without dissolution and reprecipitation. Magnesium loss (Ca/Mg exchange) by diffusion could produce LMC without altering the strontium concentration (Bathurst, 1975). This might correspond to Towe and Hemleben's (1976) stage 1 of HMC alteration where magnesium is lost but fossil ultra-structure (as viewed by SEM) remains unchanged. Towe and Hemleben (1976) also suggest that their stage 1 of HMC alteration involves a Ca/Mg exchange with ambient waters, but without any micro-dissolution or reprecipitation. Stable carbon and oxygen isotope analyses of coralline algae and echinoderm fragments in field 2 might clarify the process by which HMC is altered to field 2.

Strontium and magnesium concentrations in Pleistocene coralline algae in field 3 (Fig. 55) fall into a linear pattern in which strontium and magnesium concentrations are directly proportional to each other ($r = 0.85$). Coralline algae in field 3 have lost significant amounts of original
strontium as well as magnesium, suggesting conversion to LMC by a dissolution/reprecipitation process (Friedman, 1964; Land, 1967; Land and Epstein, 1970) in which both strontium and magnesium have partially re-equilibrated with interstitial waters.

The slope of the magnesium-strontium linear regression for deep F-1 coralline algae is similar to but slightly less than the magnesium-strontium slope for coralline algae in field 3 of the Pleistocene coralline algae of Enewetak (Fig. 56). The similarity of slopes suggests that similar processes controlled the magnesium and strontium composition of coralline algae in the two systems. Because diagenetic alteration of the two systems occurred in very different chemical systems, any explanation for the similarity of their magnesium-strontium trends must not be dependent on the calcium, magnesium, and strontium concentrations of the interstitial waters.

The roughly linear correlation of strontium and magnesium in field 3 (Fig. 55) might reflect the rate at which the dissolution/reprecipitation process occurred and the rate at which the excess magnesium and strontium were removed from the dissolution/reprecipitation system. Lower calcite saturation states might cause slower reprecipitation rates allowing more effective removal of both magnesium and strontium ions from the diagenetic system (effectively lowering the distribution coefficients of magnesium and strontium). In Lower Miocene and Upper Eocene coralline algae of the
F-1 well, coincidental decreases in magnesium and strontium concentration can be correlated with decreasing depth and calcite saturation. The slightly lower slope (Sr/Mg ratio) of the deep F-1 coralline algae relative to Pleistocene coralline algae (Fig. 56), may reflect the much higher Mg$^{2+}$/Ca$^{2+}$ ratio in ocean water relative to meteoric water.

It is unclear why some Pleistocene coralline algae and echinoderm fragments convert to field 2 and others to field 3. Petrographically there is no difference between fields 1, 2 or 3. Often an echinoderm fragment in field 3 will coexist with coralline algae in field 3 and vice versa. Coralline algae with the lowest strontium and magnesium concentrations in field 3 usually come from intervals believed to have been in paleo-meteoric phreatic zones. However, coralline algae from adjacent samples which also should have been in meteoric phreatic zones are often in field 2. It is not readily apparent why some coralline algae invert to field 2 and others to field 3. Systematic stable carbon and oxygen isotope analyses of coralline algae in the three strontium-magnesium fields might provide the answer.
Compaction is an important process in the reduction of porosity in ancient carbonate rocks (Brock and Moore, 1981; Halley and Schmoker, 1982; and others). Enewetak Atoll provides a natural laboratory for the study of compaction in carbonate grainstones and packstones. All carbonate strata on Enewetak are currently at their maximum burial depth (Schlanger, 1963). Therefore, if a rock from the E-1 or F-1 wells shows compaction features, those features must have developed at their current burial depth or shallower. Likewise, if a rock shows no significant compaction effects, it indicates that lithostatic pressures at the current rock depth are not great enough to initiate formation of compaction features. In this study, compaction features were only observed in uncemented and poorly-cemented grainstones and packstones. Grains in mud-rich or well-cemented rocks do not show compaction features as readily as uncemented grainstones (Bhattacharyya and Friedman, 1979); therefore, this discussion will be confined to compaction in uncemented and poorly-cemented grainstones and packstones.

Several factors seriously constrain a detailed assessment of carbonate compaction on Enewetak. First, only a few short cores were taken around 610 m where compaction effects in grainstones are first noticed. Second, between 375 and 1,000 m in the F-1 well, uncemented and poorly-cemented
grainstones and packstones are quite rare. Significant compaction features were found in bioclastic grainstones and packstones between 1,114 and 1,379 m in the F-1 well and in core 1 (610 - 618 m) of the E-1 well. No distinct compaction features were observed in any other samples examined from Enewetak.

**Upper Eocene of the F-1 Well**

Rotaline foraminifera and coralline algae fragments are commonly fractured in Upper Eocene cores between 1,114 and 1,379 m in the F-1 well (Figs. 3 and 59a). Frequency and intensity of fracturing increases with depth from grainstones at 1,114 m to grainstones at 1,287 m. Compaction in cores between 1,315 and 1,379 m is not noticeably more intense than at 1,287 m. However, strata between 1,315 and 1,379 m are often packstones containing mud, which Bhattacharyya and Friedman (1979) show suppresses compaction fracturing. Pressure solution of foraminifera coralline algae, and other grains is found in rocks between 1,114 and 1,379 m in the F-1 well (Figs. 13 and 14). Like fracturing, pressure solution increases in intensity from 1,114 to 1,287 m and then remains relatively constant between 1,315 and 1,379 m.

Sparse fibrous cements and echinoderm overgrowths are present in cores between 1,114 and 1,379 m. Fibrous cements are never observed growing in compaction fractures;
Figure 59.
Photomicrographs of compaction features in Upper Eocene and Lower Miocene strata. Bar scales at lower left equal 0.1 mm.
(a) Compaction fracturing and minor pressure solution of Upper Eocene coralline algae (1,282 m, F-1 well).
(b) Pressure-solution contact of a euhedral echinoderm overgrowth (O) and an adjacent echinoderm fragment (E) (1,284 m, F-1 well). Crossed nicols.
(c) Pressure-solution compaction of a large rotaline foraminifera (F) into a coralline algae fragment (CA) (1,285 m, F-1 well). Crossed nicols.
(d) Echinoderm overgrowth with stress twinning (1,282 m, F-1 well).
(e) Dolomite rhomb (center) overgrowing a compaction fracture in a coralline algae fragment (1,284 m, F-1 well). Crossed nicols. Dolomite rhomb (center) at extinction.
(f) Minor, incipient compaction fracturing (F) of a thin-walled rotaline foraminifera (core 1, 610 - 618 m, E-1 well).
however, fibrous cements are observed at pressure solution contacts (Fig. 21a). In only a few rare cases do echinoderm overgrowths fill fractures. Much more commonly, echinoderm overgrowths (often euhedral) are compacted into each other or into other grains (Fig. 59b). These petrographic relationships indicate that most compaction followed calcite cementation. Between 1,114 and 1,287 m, stress twinning is common in echinoderm overgrowths which have been pressed into adjacent grains (Fig. 59d); however stress twinning was never observed in echinoderm overgrowths in shallower strata. In cores 11 and 12, dolomite rhombs sometimes overgrow compaction fractures, but are never involved in compaction (Fig. 59e). Therefore, compaction appears to have been completed prior to dolomitization.

**E-l Well: Core 1 (610 - 618 m)**

Core 1 of the E-l well (610 - 618 m) is an uncemented bioclastic grainstone which has suffered minor dissolution and very minor compaction (Fig. 14). Between 610 and 618 m in the E-l well, only a few thin-walled foraminifera have been fractured due to compaction (Fig. 59f). Though coralline algal fragments are abundant in core 1 of the E-l well, none were observed with compaction fractures in contrast to strata 1,114 - 1,379 m deep in the F-l well where coralline algae fragments and thick-walled rotaline foraminifera are commonly fractured. Very minor pressure
solution is also observed in grainstones of E-1 core 1.

Discussion of compaction

Significant compaction-related fracturing and pressure solution of rigid grains in poorly cemented grainstones apparently starts at approximately 610 m on Enewetak and gradually intensifies down to a depth of 1,280 m. Assuming an average porosity of 30% for overlying Cenozoic Enewetak carbonate, lithostatic pressure would be approximately 100 bars more than hydrostatic pressure at 610 m and approximately 215 bars more than hydrostatic pressure at 1,280 m. Between 900 m and 1,100 m, Pacific Ocean waters become undersaturated with respect to calcite (Li et al., 1969; Scholle et al., 1983). At approximately 300 m, Pacific Ocean water becomes undersaturated with respect to aragonite (Li et al., 1969). This suggests that pressure solution may be connected to or aided by subsurface waters which are undersaturated with respect to the grains involved in pressure solution.

Admittedly the data base for these conclusions is minimal, and the conclusions of this study must be used with knowledge of the data base. However, the unique setting of Enewetak, where the onset of compaction fracturing can be directly observed, is fortuitous. Other studies regarding the compaction of carbonates have been based largely on (1) experimental work or (2) ancient rocks where the timing,
and hence the burial depth, of compaction must be inferred, often from equivocal data.

Experimental studies on the compaction of carbonate sands (grainstones) are relatively rare. Rather, experimental studies have concentrated on the compaction of carbonate muds and mud-sand mixtures (Terzaghi, 1940; Fruth et al., 1966; Ebhardt, 1968; Shinn et al., 1977; Bhattacharyya and Friedman, 1979; Shinn and Robbin, 1983). Fruth et al. (1966) ran a series of experiments in which they measured the porosity change in carbonate sands with increasing pressure. Experiments showed intense fracturing and interpenetration of grains (in sands) with confining pressures of 1,000 bars. Unfortunately, they did not check compaction features at intermediate pressures to see when grain fracturing started. Likewise, Bhattacharyya and Friedman (1979) do not report at what pressure ooid fracturing started, but they do describe abundant fracturing at the end of experiments with maximum confining pressures of 555 bars.

In recent years, petrographic studies describing the compaction of ancient carbonates have been numerous (Pray, 1960; Rahle, 1966; Zankl, 1969; Coogan, 1970; Conley, 1977; Shinn et al., 1977; Wanless, 1979; Meyer, 1980; Brock and Moore, 1981; Moore and Druckman, 1981; Meyer and Hill, 1983). Two studies of ancient limestones have attempted to establish absolute depths at which compaction features (pressure solution) began. Dunnington (1967, p.340) estimates that overburden pressures can begin to cause significant
vertical interpenetration (pressure solution, stylolitization) at burial depths of 610 - 900 m in the Persian Gulf area. Sellier (1979) reasons that pressure solution began at a burial depth of 300 m in Mesozoic strata of the Aquitaine Basin.

Diagenetic fracturing and fabrics mimicking pressure solution have been described in Pleistocene carbonate strata that have been buried less than 15 m and altered primarily by meteoric waters (Matthews, 1967). In Quaternary strata on Enewetak (0 - 80 m), fractured grains are rare and fabrics resembling pressure-solution contacts were not observed at all. At 610 m, diagenetic fracturing in uncemented grainstones is rare, affecting only the most fragile grains and suggesting that compaction-related fracturing is just starting at 610 m. Therefore, observations from Enewetak suggest that nearsurface (meteoric) fabrics mimicking pressure solution and compaction-fracturing of carbonate grains (Matthews, 1967) are the exception rather than the rule.
DOLOMITIZATION

Several origins have been previously suggested for Enewetak and other Pacific atoll dolomites. Schlanger (1957) noted that coralline algae are preferentially dolomitized in Eocene strata of Enewetak and concluded that dolomitization was the result of a crystallographic re-ordering of high-magnesian algal calcite. Using stable carbon and oxygen isotope data, Berner (1965) and Gross and Tracey (1966) concluded that hypersaline waters dolomitized parts of the Funafunti, Kita-daito-jima, and Enewetak atolls. Schlanger (1963) argues that Funafuti and Enewetak dolomites are petrographically different and therefore probably have different origins. More recently, it has been suggested that dolomites in the Colette and Niue atolls formed in subsurface mixing zones where fresh-water lenses meet marine water (Repellin, 1977; Rodgers et al., 1982; respectively). These previously published models for atoll dolomitization are not compatible with the petrographic and geochemical characteristics of the deep Enewetak dolomites. Evidence consistently indicates that the deep Enewetak dolomites precipitated from cold, normal marine waters percolating through the atoll at burial depths of over 900 m.

Dolomite has been identified in samples from Lower Miocene strata (cores 3 and 6) and Upper Eocene strata
(cores 11 - 15) of the F-1 well and core 3 (1,243 - 1,250 m) in the E-1 well (Fig. 4; Schlanger, 1963; Videtich, 1982). In cores 3 (375 - 380 m) and 6 (811 - 819 m) of the F-1 well, dolomite is present in such small quantities that it is extremely difficult to find. The dolomite in Lower Miocene strata of the F-1 well is generally associated with radiaxial cements. Because it is volumetrically insignificant and petrographically quite distinct from the deeper dolomite, the dolomite in Lower Miocene strata will be discussed in a separate section. In cores 13 - 15 of the F-1 well (1,343 - 1,388 m), dolomite can be found in most samples, but point counts consistently indicate that the dolomite comprises less than 1% of any given sample. Volumetrically significant quantities of dolomite are present in cores 11 and 12 of the F-1 well (1,279 - 1,323 m) and core 3 of the E-1 well (1,243 - 1,250 m). Bulk samples from core 11 of the F-1 well (1,279 - 1,287) contain up to 10% dolomite (Schlanger, 1963). Core 12 of the F-1 well (1,315 - 1,323 m) contains samples with up to 99% dolomites. Bulk samples from core 3 of the E-1 well (1,243 - 1,250 m) contain up to 15% dolomite (Schlanger, 1963).

**Petrology of the Deep Enewetak Dolomite**

Enewetak dolomite in the Upper Eocene strata at 1,243 - 1,250 m in the E-1 well is very similar to dolomite at 1,279 - 1,388 m in the F-1 well. Those deep Enewetak dolomites
consist of 0.1 - 0.2 mm rhombs with cloudy centers and clear rims (Fig. 60a). Dolomite concentration varies from almost 100% between 1,316 and 1,318 m in core 12 of the F-1 well to approximately 5% in core 11 (above), and less than 1% in core 13 (below). When sparse and scattered, the dolomite rhombs are generally euhedral, preferentially nucleating on coralline algae (Fig. 56e; Schlanger, 1957, 1963). When dolomite is more abundant, it completely replaces other originally calcitic fossils as well as coralline algae (Figs. 60 e & f). Concentrated dolomite crystals are often subhedral to anhedral with interfering boundaries. Dolomite rhombs always nucleate on grains or in mud, but they often grow out into open pore space. Partial delicate dissolution of calcite bioclasts is observed in more intensely dolomitized intervals (1,315 - 1,323 m in the F-1 well; 1,243 - 1,250 m in the E-1 well; Fig. 60d). The most dolomite-rich interval of the F-1 well (1,316-1,318 m) is at the base of a porous and permeable coralline algae/rotacline foram grainstone. In the F-1 well, strata below 1318 m tend to be muddier and less permeable (Swartz, 1962; Schlanger, 1963).

In E-1 core 3 (1,243 - 1,250 m), rhombic dolomite crystals commonly replace original depositional grains and grow in open voids at the terminations of bladed cements (Fig. 60). Many of the bladed cements in core 3 of the E-1 well precipitated after aragonite dissolution. Therefore, the dolomite in E-1 core 3 (1,243 - 1,250 m) must have
Figure 60.
Dolomite in Upper Eocene strata of Enewetak Atoll.
(a) Almost 100% dolomite. Note interfering growth of dolomite crystals with cloudy centers and clear rims (core 12, 1,318 m, F-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(b) Dolomite rhomb (D) overgrowing compaction fracturing (F) in rotaline foraminifera (R) (core 11, 1,284 m, F-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(c) Dolomite rhomb (D) at terminus of coarse bladed calcite cements (C) (core 3, 1,243 m, E-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(d) Partially dissolved rotaline foraminifera (R) (core 3, 1,244 m, E-1 well). Bar scale at lower left equals 0.1 mm. Crossed nicols.
(e) Clear dolomite selectively replacing the outer portions of calcitic mollusc (M) (core 3, 1,245 m, E-1 well). Bar scale at lower left equals 0.1 mm.
(f) Fabric selective dolomitization (D) of molluscs (core 3, 1,244 m, E-1 well). Bar scale at lower left equals 0.5 mm. Crossed nicols. Slide stained with Alizarin-Red-S, darker material is calcite.
formed late, after aragonite dissolution and precipitation of bladed cements.

In cores 11 and 12 of the F-1 well (1,279 - 1,323 m), dolomite rhombs are observed overgrowing compaction fractures in grains; however, dolomite rhombs are never observed being compacted themselves, indicating that the deep dolomite formed after compaction of rigid grains in the F-1 well (Fig. 60b). Significant compaction begins at approximately 610 m in the E-1 and F-1 wells (see Compaction section). The dolomitic Eocene strata would not have been buried by 610 m of sediment until Early Miocene time (Fig. 4). Therefore, petrographic relationships suggest deep Enewetak dolomitization started sometime between Early Miocene and the present at burial depths of more than 600 m.

**Elemental Geochemistry**

Because the origin of dolomite in most sedimentary rocks is poorly understood, geochemical analyses are often used to provide additional constraints on possible origins of dolomite. Geochemical analyses of dolomite commonly characterize the calcium-magnesium stoichiometry, calcium-magnesium ordering, trace element concentrations (including strontium, sodium, manganese, and iron), and stable carbon and oxygen isotope compositions. In addition, this study examines the composition of strontium isotopes in Enewetak dolomites.
Dolomites in cores 11 - 15 (1,279 - 1,388 m) of the F-1 well (1,243 - 1,250 m) and in core 3 of the E-1 well were analyzed with the electron microprobe for calcium, magnesium, and strontium. Three samples were taken from the most dolomite-rich interval of core 12 in the F-1 well (1,316 - 1,318 m) for detailed geochemical analyses. Splits of all three samples were leached with 0.2 N HCl to remove calcite. Samples were X-rayed before and after leaching but no peak shifts were discernable indicating that leaching has not changed the composition of the dolomite minerals (Fig. 61). The three leached samples (F-12-5A, F-12-7, F-12-10) were analyzed for stable carbon and oxygen isotopes, strontium isotopes, and selected trace elements. Similar analyses were performed on one unleached dolomite sample (F-12-5B) which contained less than 2% calcite. Results of geochemical analyses are tabulated in Table 9. Previous elemental studies of these dolomites are summarized in Schlanger (1963), Graf and Goldsmith (1963), and Goldsmith and Graf (1958). Microprobe data for dolomites in cores 11 - 15 (1,279 - 1,388 m) of the F-1 well and core 3 of the E-1 well (1,243 - 1,250 m) are summarized in Table 10. Microprobe concentrations for calcium, magnesium and strontium are similar to values obtained from atomic absorption spectrophotometry.
Figure 61.
X-ray diffraction of dolomites. Note that leaching of calcite with 0.5 N HCl caused no identifiable peak shift. (321) and (333) peaks of Enewetak dolomite (core 12 of the F-1 well) are relatively sharp indicating relatively good ordering. GFS-400 (Woodville, Ohio) is a commercial reference dolomite, obtained from G. Federick Smith Chemical Company.
X-RAY DIFFRACTION OF ENEWETAK DOLOMITE

Enewetak Dolomite
(leached)

Enewetak Dolomite
(unleached)

Standard Dolomite
GFS-400
TABLE 9 GEOCHEMISTRY OF ENEWETAK DOLOMITE

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* Atomic absorption spectrophotometry performed on a Varian 475 AA.
† Weight % CO$_3$ calculated by stoichiometry.
$^5$ Mole % CaCO$_3$ and MgCO$_3$ are calculated so that mole % CaCO$_3$ + MgCO$_3$ = 100 %.
** Analyses performed on an ARL-EMX electron microprobe.
$^{++}$ Stable isotopic analyses by Coastal Science Laboratories, Austin, Texas. Results are in parts per mil (‰) relative to the PDB standard. Error (2σ) is estimated at ± 0.2 ‰. Oxygen values have been corrected by -0.8 ‰ to account for the difference in fractionation between calcite and dolomite reacting with phosphoric acid at 25°C.
$^{55}$ Strontium separations by Paul Pushkar, Wright State University and mass spectrometry by Mobil Research and Development Corp., Dallas Research Division. Values are based on a ratio of 0.71014 for standard SrCO$_3$ (NBS SRM 987). Error (2σ) is ± 0.00004-0.00006.
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<td>1</td>
<td>11.02 ± 0.021</td>
<td>0.021 ± 0.004</td>
</tr>
<tr>
<td>Core 11</td>
<td>6</td>
<td>10.93 ± 0.22</td>
<td>0.016 ± 0.004</td>
</tr>
<tr>
<td>Core 12</td>
<td>9</td>
<td>11.34 ± 0.22</td>
<td>0.018 ± 0.006</td>
</tr>
<tr>
<td>Core 15</td>
<td>1</td>
<td>11.58 ± 0.017</td>
<td>0.017 ± 0.004</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>E-1 Well</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Core 3</td>
<td>6</td>
<td>11.01 ± 0.20</td>
<td>0.020 ± 0.004</td>
</tr>
</tbody>
</table>
Calcium and Magnesium

Calcium and magnesium data indicate that the Enewetak dolomites are calcium-rich (Tables 9 and 10). Microprobe analyses of dolomites consistently yield 42 - 43 mole % MgCO$_3$ and 57 - 58 mole % CaCO$_3$ (Table 10). Atomic absorption analyses show 43 - 44 mole % MgCO$_3$ in these dolomites (Table 9). Graf and Goldsmith (1963) analyzed these same dolomites with X-ray diffraction and concluded that they have 44 - 45 mole % MgCO$_3$ (55 - 56 mole % CaCO$_3$). Excess calcium is typical of low-temperature dolomites found in Cenozoic sedimentary rocks and is common in many ancient dolomites (Goldsmith and Graf, 1958; Lumsden and Chimahusky, 1980; Land, 1973a). These Enewetak dolomites show moderate to good ordering peaks with X-ray diffraction (Fig. 61; Goldsmith and Graf, 1958). Microprobe analyses show that calcite inclusions are common in most Enewetak dolomites, especially in cloudy cores of dolomite crystals.

Strontium

The mean strontium values obtained from atomic absorption are essentially the same as the mean microprobe values. The deep Enewetak dolomite samples analyzed by atomic absorption contain between 165 and 184 ppm strontium (Table 9) which is similar to strontium concentrations of many other late Cenozoic dolomites (Table 11).
<table>
<thead>
<tr>
<th>Location</th>
<th>Mole % MgCO₃</th>
<th>Mean Sr (ppm)</th>
<th>Mean $\delta^{13}$C (‰, PDB)</th>
<th>Mean $\delta^{18}$O (‰, PDB)</th>
<th>Proposed Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enewetak (This study)</td>
<td>43</td>
<td>170</td>
<td>2.3</td>
<td>2.5°C</td>
<td>Cold Marine</td>
</tr>
<tr>
<td>Enewetak (Gross &amp; Tracey, 1966)</td>
<td>-</td>
<td>-</td>
<td>1.7</td>
<td>2.0°C</td>
<td>Hypersaline</td>
</tr>
<tr>
<td>Pacific Atolls (Berner, 1965)</td>
<td>-</td>
<td>-</td>
<td>3.1</td>
<td>4.3°C</td>
<td>Hypersaline</td>
</tr>
<tr>
<td>Plantagenet Bank (Gross, 1965)</td>
<td>43</td>
<td>-</td>
<td>2.6</td>
<td>4.2 u</td>
<td>Hypersaline</td>
</tr>
<tr>
<td>Jamaica-Falmouth (Land, 1973b)</td>
<td>44</td>
<td>3000</td>
<td>-8.4</td>
<td>-1.0 u</td>
<td>Mixed Water</td>
</tr>
<tr>
<td>Jamaica-Hope Gate (Land, 1973a)</td>
<td>42</td>
<td>220</td>
<td>1.2</td>
<td>2.2 u</td>
<td>Mixed Water</td>
</tr>
<tr>
<td>Mediterranean (Fontes and Desforges, 1975)</td>
<td>46</td>
<td>-</td>
<td>3.6</td>
<td>5.2</td>
<td>Cold Marine</td>
</tr>
<tr>
<td>San Salvador (Supko, 1977)</td>
<td>46</td>
<td>170</td>
<td>1.8</td>
<td>2.1°C</td>
<td>Unknown</td>
</tr>
<tr>
<td>Colette Atoll (Reppelin, 1977)</td>
<td>45</td>
<td>170</td>
<td>4.0</td>
<td>4.0 u</td>
<td>Mixed Water</td>
</tr>
<tr>
<td>Bonaire (Sibley, 1980; Land, 1973a)</td>
<td>-</td>
<td>210</td>
<td>2.4</td>
<td>3.1 u</td>
<td>Mixed Water</td>
</tr>
<tr>
<td>Israel (Magaritz et al., 1980)</td>
<td>-</td>
<td>-</td>
<td>-9.6</td>
<td>-1.3°C</td>
<td>Mixed Water</td>
</tr>
<tr>
<td>Yucatan (Ward, 1982)</td>
<td>42</td>
<td>-</td>
<td>2.0</td>
<td>1.7 u</td>
<td>Mixed Water</td>
</tr>
</tbody>
</table>

$c$ = Corrected by -0.8 ‰ for difference in fractionation between dolomite and calcite (Sharma and Clayton, 1965)

$u$ = Uncorrected for difference in fractionation between dolomite and calcite reacting with phosphoric acid

Note: Where true mean values were not available, above values represent mid-points of reported ranges.
The distribution coefficient for strontium in dolomite is still being debated (Land, 1980). Behrens and Land (1972) reasoned that the strontium distribution coefficient for dolomite should be approximately one-half the strontium distribution for calcite. Experiments by Jacobson and Usdowski (1976) also indicate a 2:1 ratio for the strontium distribution coefficient in calcite relative to co-precipitated dolomite. Unfortunately, the distribution coefficient for strontium in calcite is variable (Kinsman, 1969; Katz et al., 1972; Jacobson and Usdowski, 1976; Lorens, 1981). It is probably not coincidental that strontium concentrations in Enewetak dolomites (mean = 170 ppm) are approximately one-half of the mean strontium concentration of radiaxial cements (330 ppm). If radiaxial cements are indeed marine in origin, the strontium concentration in Enewetak dolomites suggests that they are also marine in origin. Katz and Matthew's (1977) distribution coefficient for strontium in dolomite (0.025) predicts a strontium concentration of 220 ppm for dolomite precipitated from seawater. That strontium concentration is roughly similar to the Enewetak dolomites. The Enewetak dolomites might be slightly lower in strontium than theoretical marine dolomite because they may have been precipitated slowly in cold marine waters. Experiments by Jacobson and Usdowski (1976) suggest that the distribution coefficient of strontium in dolomite decreases with rate of dolomite precipitation.
Iron, Manganese, and Sodium

Iron concentrations in the deep Enewetak dolomites (16 - 57 ppm) are low relative to most Cenozoic and older dolomites (Table 9; Weber 1964). However, they are similar to iron values predicted by Veizer (1983) for marine dolomites. The low iron concentrations in Enewetak dolomites probably reflect precipitation from well-oxygenated, iron-poor waters.

Manganese concentrations in Enewetak dolomites are also low relative to ancient dolomites (19 - 22 ppm; Table 9; Mattes and Mountjoy, 1980). These values are significantly higher than manganese concentrations predicted by Veizer (1983) for marine dolomite. However, manganese concentrations in Enewetak dolomites are well within the range of modern (marine) carbonate sediments (Stehli and Hower, 1961), suggesting that marine sediments are partly the source of manganese in Enewetak dolomites. These dolomites have roughly twice as much manganese as radial cements from the Lower Miocene of the F-1 well (Tables 4 and 9), suggesting that manganese is preferentially incorporated into the magnesium lattice sites of dolomites. Similarly, Mattes and Mountjoy (1980) found twice as much manganese in dolomite as in coexisting calcites in the Devonian Miette buildup. The low manganese concentrations of Enewetak dolomites indicate dolomite formation in well-oxygenated, manganese-poor environments.

Brand and Veizer (1980) and Veizer (1983) correlate
manganese concentration with intensity of diagenetic alteration and openness of the carbonate diagenetic system and inversely correlate manganese with strontium concentration. In contrast, the deep Enewetak dolomites have low manganese concentrations yet display intense diagenetic alteration in what is, and probably was, a relatively open system. The occurrence of low strontium concentrations along with low manganese concentrations is also in contrast with the systems studied by Brand and Veizer (1980). In short, the Enewetak system suggests that relationships between diagenetic alteration, manganese concentrations, and strontium concentrations are more complex than asserted by Brand and Veizer (1980).

Sodium concentrations in the deep Enewetak dolomites (290 - 375 ppm) are much lower than reported in Holocene marine dolomites (1,010 - 3,050 ppm; Land and Hoops, 1973), but similar to ancient dolomites analyzed by Weber (1964; 109 - 573 ppm Na). The use of sodium in dolomites as a paleosalinity indicator has been discussed by Fritz and Katz (1972), Land and Hoops (1973), and Veizer et al. (1978). The sodium concentration of Enewetak dolomites are similar to sodium concentrations predicted by Veizer et al. (1978) for dolomite precipitated from waters with normal marine salinities.

**Stable Carbon and Oxygen Isotopes**

Because dolomite has not been experimentally synthesized
at surface temperatures, the isotopic fractionation of oxygen between dolomite and nearsurface waters is not precisely known. Extrapolation of high temperature experimental data (300 - 600°C) suggests that dolomite formed at 25°C should be enriched in $\delta^{18}O$ by 3 - 7 o/oo relative to calcite (O'Neil and Epstein, 1966; Northrop and Clayton, 1966; Sheppard and Schwarz, 1970; Hazma and Broecker, 1974). Several studies of co-existing calcites and dolomites in nature suggest an enrichment of $\delta^{18}O$ in dolomite of 3 - 5 o/oo relative to calcite (Degens and Epstein, 1964; Clayton et al., 1968; Fritz and Smith, 1970; Aharon et al., 1977).

Results of stable isotope analyses on Enewetak dolomite samples are shown in Table 9. In this study, the stable carbon and oxygen isotope compositions of deep Enewetak dolomites show a close and consistent clustering (Fig. 62; Table 9). The mean $\delta^{13}C$ value of 2.3 o/oo (PDB) is typical of marine calcite cements (Hudson, 1977). These carbon isotopes suggest that carbonate of a marine origin was dominant and that isotopically light carbon associated with soil-gas and organic matter was not involved in dolomitization (Gross, 1964). The carbon isotope values for these dolomites are slightly higher than those of radiaxial cements in Lower Miocene strata of the F-1 well and Upper Eocene bladed cements of the E-1 well (1,243 - 1,250 m).

The mean $\delta^{18}O$ value for the deep Enewetak dolomites is 2.5 o/oo (PDB; corrected by -0.8 o/oo for the difference in fractionation between calcite and dolomite in phosphoric
Figure 62.
Stable isotope composition of 4 dolomite samples from core 12 (1,315 - 1,323 m) of the F-1 well. Analyses by Coastal Science Laboratories (Austin, Texas). $\delta^{13}C$ and $\delta^{18}O$ values are in parts per mil relative to PDB. $\delta^{18}O$ values have been corrected by -0.8 o/oo for differences in fractionation of phosphoric acid with calcite and dolomite (Sharma and Clayton, 1965).
STABLE ISOTOPIC COMPOSITION OF DOLOMITES IN EOCENE STRATA, ENEWETAK ATOLL
A \( \delta^{18}O \) value of 2.5 o/oo in dolomite could be produced either by (1) precipitation from hypersaline waters at tropical temperatures of 28°C (Berner, 1965; Gross and Tracey, 1966), or (2) precipitation from normal marine water at temperatures substantially below 28°C. If we assume that the dolomite precipitated from normal marine water (0.0 o/oo; SMOW), oxygen paleothermometry equations predict dolomitization at temperatures of 15°C (Fritz and Smith, 1970), 16°C (Matthews and Katz, 1977), and 20°C (Land, 1983). During Pleistocene glacial advances and retreats, the \( \delta^{18}O \) composition of seawater has varied by approximately 1 o/oo from the modern ocean (Savin, 1977). If the \( \delta^{18}O \) value of the water precipitating dolomite is 1.0 o/oo heavier, the calculated temperature of dolomitization should be adjusted by +4°C. Enewetak dolomite is enriched by approximately 3 o/oo relative to Lower Miocene radiaxial cement.

**Strontium Isotopes**

The physical and stratigraphic location of the deep Enewetak dolomite simplifies the interpretation of their strontium isotopes. The deep Enewetak dolomites are in Upper Eocene strata and the \( ^{87}Sr/^{86}Sr \) ratio of seawater has been steadily rising since the Eocene (Fig. 63; Burke et al., 1982). Also there is a lack of terrigenous clays,
Figure 63.
Strontium isotope ratios of 4 samples (dots) of Enewetak dolomite are plotted on the $^{87}\text{Sr}/^{86}\text{Sr}$ curve of Burke et al. (1982) for seawater through time. See Table 9 for actual isotope compositions and further explanation of strontium data.
STRONTIUM ISOTOPE RATIOS
OF ENEWETAK DOLOMITES

[Graph showing strontium isotope ratios over geologic time]

- CRETACEOUS
- JURASSIC
- TERTIARY

Geologic Periods: MIocene, Eocene, Paleocene
feldspars, and other radiogenic ($^{87}$Sr-rich) materials in or around the Enewetak Atoll (Schlanger, 1963). Almost all igneous rocks in oceanic island provences have $^{87}$Sr/$^{86}$Sr ratios of less than 0.707 (Faure, 1977). Radiogenic continental dust could conceivably settle on Enewetak; however, the closest potential exposure surface in the F-1 well is approximately 400 m above the deep dolomitic interval (Schlanger, 1963), making strontium contamination by continental dust unlikely.

Strontium isotope determinations of the four deep Enewetak dolomite samples give $^{87}$Sr/$^{88}$Sr ratios between 0.70865 and 0.70901 (Table 9). Those values correspond to the strontium isotopic composition of seawater between latest Early Miocene and Pleistocene time (Fig. 63; Burke et al., 1982). If all strontium in the dolomites came from marine water at the time of dolomite formation, the dolomites would be latest Early Miocene to Pleistocene in age. Deep in the Enewetak Atoll, the only apparent source of strontium with a $^{87}$Sr/$^{86}$Sr ratio greater that the dolomites is (1) seawater younger than ocean water with the dolomite's $^{87}$Sr/$^{86}$Sr ratio or (2) carbonate precipitated from that same ocean water. If any strontium in the dolomite came from the host Eocene sediments or trapped Eocene ocean water ($^{87}$Sr/$^{86}$Sr = 0.7077), a compensating amount of strontium from younger ocean water would be required to give the observed $^{87}$Sr/$^{86}$Sr ratios. For these reasons, strontium isotope ratios plotted on the strontium seawater
curve of Burke et al. (1982; Fig. 63) should indicate maximum
ages of formation for the deep Enewetak dolomites. Therefore,
$^{87}\text{Sr}/^{86}\text{Sr}$ ratios suggest dolomite formation between latest
Early Miocene and the present.

The spread in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the deep dolomites
may be due to (1) dolomite precipitation at several different
times between latest Early Miocene and the Holocene and/or
(2) incorporation of different amounts of "older" strontium,
possibly from the surrounding Eocene calcite, into the
dolomites. If all of the strontium came from normal seawater
at the time of dolomitization, dolomitization must have
started by latest Early Miocene and finished during or
after the latest Miocene. If the $^{87}\text{Sr}/^{86}\text{Sr}$ variability
in the four dolomite samples is due solely to mixing "older"
possibly Eocene strontium ($^{87}\text{Sr}/^{86}\text{Sr} = 0.7077$) with seawater
during a short period of time, all dolomitization must
have occurred sometime between latest Miocene and the present.
Dolomite sample F-12-5A is merely sample F-12-5B after
the calcite (less than 2% of the bulk rock) was leached
(Table 9). The difference in $^{87}\text{Sr}/^{86}\text{Sr}$ ratios between
F-12-5A (0.70892) and F-12-5B (0.70883) suggests that "older"
strontium inherited from calcite was responsible for at
least part of the $^{87}\text{Sr}/^{86}\text{Sr}$ scatter. In either case, at
least some dolomitization occurred in or after latest Miocene,
and most of the dolomite formed sometime (probably at several
times) between Middle Miocene and the present.
Nature of Deep Dolomitization

Strontium isotopes indicate that deep dolomitization occurred between Middle Miocene and the present. A minimum depth of dolomitization can be determined using Enewetak stratigraphy. The top of the Lower Miocene section is now more than 900 m above the deep dolomitic interval (Fig. 64; Schlanger, 1963). Since the dolomites are mostly Middle Miocene or younger in age, they must have formed at burial depths of over 900 m. Petrologic evidence suggests dolomitization occurred after burial by at least 610 m. In the F-1 well, coralline algae have lost 80% of their original magnesium by the time they are 400 m deep (Fig. 52). Therefore, dolomitization apparently occurs distinctly after loss of magnesium from originally HMC grains; therefore, magnesium for dolomitization probably does not come from coralline algae as Schlanger (1957) proposes.

Because Upper Eocene and Lower Miocene strata in the deep Enewetak wells are apparently in open communication with modern ocean water, it is probable that water has flowed through those Eocene and Lower Miocene strata since deposition. At depths of over 900 m the only fluid which could have reasonably been flowing through those strata is seawater. Meteoric-phreatic zones on carbonate islands and peninsulas are generally thin and water tables are near sea level. For example, the maximum elevation of the modern northern Yucatan water table is less than 2
Figure 64.
Model for dolomitization of Upper Eocene carbonate strata on Enewetak Atoll by deep marine waters undersaturated with respect to calcite.
ENEWETAK ATOLL

NW

F-1

E-1

PLIO-PLEISTOCENE

COLD DOLOMITIZING OCEAN WATER

MIOCENE

TOP OF LOWER MIocene

UPPER EOCENE

VOLCANIC BASEMENT

CASED INTERVAL

0  5

KILOMETERS

0m

500m

KILOMETERS
m above sea level on a peninsula 350 km wide (Back and Hanshaw, 1978). A freshwater lens or mixing zone could not have penetrated 900 m through extremely permeable Lower Miocene strata on an atoll which is only 42 km wide. In addition, no features characteristic of freshwater diagenesis are observed in the vicinity of the deep dolomites, making mixed-water dolomitization very unlikely.

Likewise, it is difficult to imagine a hypersaline water mass (Berner, 1965) moving intact from the surface through 900 m of very permeable strata which have actively circulating marine waters. Because no petrologic evidence of hypersaline brines is present, an alternative theory for dolomitization is necessary. The heavy oxygen isotopes of Berner (1965) and Gross and Tracey (1966) could be the result of dolomitization by cold marine water instead of hypersaline water. If the temperature profile for the Enewetak E-1 well is extrapolated to 1,320 m (Fig. 3), the modern temperature of the deep dolomitic intervals in Upper Eocene strata (E-1 and F-1 wells) would be between 10° and 20°C. In normal seawater, these temperatures are compatible with temperatures of dolomite formation (15° - 20°C) as previously determined by oxygen isotope paleothermometry equations. Hence, oxygen isotopes suggest dolomite formation under roughly the same oxygen isotope and temperature conditions that currently prevail in deep dolomitic strata.

Marine waters undersaturated with respect to calcite,
but still supersaturated with respect to dolomite were probably responsible for deep Enewetak dolomitization (Fig. 64). The modern calcite saturation depth in the Pacific Ocean is at approximately 1000 m (Fig. 3; Scholle et al., 1983; Li et al., 1969). According to thermodynamic calculations, ocean water is still greatly supersaturated with respect to dolomite at that depth. Although it is likely that the calcite saturation depth has shifted between Middle Miocene and the present, there has probably been ample opportunity for marine waters undersaturated with respect to calcite to percolate through Upper Eocene strata and cause dolomitization. The passage of undersaturated waters through Upper Eocene strata is verified by the partial dissolution of calcitic rotaline foraminifera and coralline algae in some partially dolomitized strata. Unaltered foraminifera and coralline algae present in undolomitized overlying strata consist entirely of low-magnesian calcite (less than 5 mole % MgCO₃). Therefore, it is reasonable to assume that foraminifera and coralline algae in the dolomitized zone were low-magnesian calcite prior to their partial delicate dissolution.

Theoretically, dolomitization requires a great many pore volumes of fluid moving through a rock to supply magnesium and remove calcium (Land, 1983). The temperature profile of the Enewetak E-1 well (Fig. 3), suggests that significant quantities of heat are being removed from the atoll by marine waters circulating through Eocene strata. It is
very possible that thermal convection is the force driving large quantities of deep dolomitizing ocean water through Eocene strata on Enewetak (Swartz, 1958). The dolomite-rich interval is at the base of a very porous and permeable grainstone unit (Table 1) which could serve as a conduit for convecting marine waters. Strata in cores 13 - 15 (1,343 - 1,388 m) are significantly less permeable than cores 9 - 11 (1,114 - 1,287). The deepest marine waters flowing through the grainstones are probably the most undersaturated with respect to calcite and therefore the most capable of dolomitization. This permeability variation and increasing calcite undersaturation could explain the stratigraphic distribution of the dolomite.

Alternatively, the distribution of dolomite in the Upper Eocene of the F-1 well and core 3 of the E-1 well may be a function of dolomite nucleii. Sediments in the vicinity of 1,317 m in the F-1 well may have either had more original dolomite nucleii or had grains which preferentially developed dolomite nucleii. Unfortunately our core control is not sufficient to conclusively determine the reason for the observed dolomite distribution, although stratigraphic variation in permeability is the most likely cause of patchy dolomitization.

**Dolomite in Lower Miocene strata**

The preceding discussion has focussed on the formation
of dolomite in Upper Eocene strata of the F-1 and E-1 wells under prevailing geochemical conditions. However, the extremely minor amounts of dolomite found in Lower Miocene strata of the F-1 well are (1) petrographically different from the deeper dolomites and (2) currently in waters not undersaturated with respect to calcite.

Dolomite is present in cores 3 and 6 (Lower Miocene) of the F-1 well (Schlanger, 1963); however, Schlanger could find dolomite in only one sample from each of those cores (F-1-3-20 and F-1-6-9). In both cases, Schlanger (1963, p. 1,024 - 1,028) describes the dolomites as lining open voids. I took samples of those same pieces (F-1-3-20 and F-1-6-9), but could not find dolomite in my samples. The only sample from cores 3 - 6 in which I could find dolomite was sample F-1-3-22.

In sample F-1-3-22 (375 - 383 m), dolomite also lines an open void and overgrows radiaxial calcite (Fig. 20c). The dolomite is apparently in optical continuity with the underlying radiaxial cement and has undulose extinction. Dolomite terminations are euhedral though slightly curved (Fig. 20f). There is also a thin lamination of dolomite within the radiaxial calcite which lacks a rhombic outer outline and cross-cuts some radiaxial laminations (Fig. 20c), suggesting that the dolomite is replacing a more soluble radiaxial lamination. Microprobe analyses indicate that the Ca, Mg, and Sr concentrations of dolomites in Lower Miocene strata are similar to those of the deep Enewetak
dolomite (Table 10).

Petrographic position and euhedral terminations indicate that the Lower Miocene dolomite is a late stage, void-fill cement precipitating after radiaxial calcite. In non-dolomitic samples adjacent to the dolomites, distal portions of some radiaxial cements have been dissolved indicating that subsurface waters in the Lower Miocene strata may have become undersaturated with respect to calcite at approximately the same time as dolomitization. Hence, the calcite saturation depth in the Pacific Ocean has probably been much shallower in the past than it is today. It is very possible that dolomitization was associated with that shallower calcite saturation depth. Hence, dolomite in Lower Miocene strata was also probably precipitated from marine waters undersaturated with respect to calcite.

Comparison to Other Cenozoic Dolomites

The $\delta^{13}$C, $\delta^{18}$O and strontium values for dolomites reported in other Miocene and Plio-Pleistocene carbonates are strikingly similar to the values found in the deep Enewetak dolomites (Table 11). Many of the young (Cenozoic) dolomites have $\delta^{13}$C and $\delta^{18}$O values which are approximately in equilibrium with modern seawater, yet their origins are often ascribed to mixed-water (Dorag) dolomitization (Land, 1973a; Supko, 1970, 1977; Repellin, 1977; Sibley, 1980; Ward, 1982). The consistency and absolute values
of stable carbon and oxygen isotopes in Plio-Pleistocene dolomites do not favor meteoric or mixed-water origins.

Most Cenozoic dolomites do not show any tendencies toward lighter carbon and oxygen isotopes, which would be expected if meteoric water was a significant part of the dolomitizing fluid (Table 11). Rather, the stable oxygen isotopes in many reported Cenozoic dolomites are in approximate equilibrium with normal seawater (Friedman and O'Neil, 1977). Sibley (1980) reconciles the heavy [marine] oxygen isotopes with a "mixed-water" origin by calling on "evaporation-concentrated fresh water" to be mixed with marine water to form the dolomitizing fluid. While such "evaporation-concentrated" meteoric water is possible, it is not likely to be widespread. Only the Jamaican Falmouth dolomite of Land (1973b) and Holocene dolomite in Israel studied by Magaritz et al. (1980) have light carbon and oxygen isotopes clearly indicating the influence of meteoric water.

Geochemical similarities between the deep Enewetak dolomites and many other Cenozoic dolomites suggest that other Cenozoic dolomites might have formed from marine waters. However, further study will be required to see which, if any, of those dolomites have spent significant amounts of time in environments with actively circulating marine water undersaturated with respect to calcite.
DIAGENETIC MODELS

Excellent examples of meteoric and marine diagenesis are present on Enewetak Atoll. In Pleistocene strata, meteoric diagenetic processes have dominated, resulting in calcite cementation, dissolution, neomorphism of aragonite, and conversion of HMC to LMC. In Lower Miocene and Upper Eocene strata of the F-1 well, marine diagenesis has also resulted in calcite cementation, aragonite dissolution, conversion of HMC to LMC, and sometimes dolomitization. While the products of marine and meteoric diagenesis are often similar, there are important differences (though sometimes subtle) in their petrography, geochemistry and distribution.

METEORIC DIAGENESIS

Patterns of meteoric diagenesis in the Pleistocene of Enewetak can usually be related to nearby, overlying exposure surfaces. Figure 65 shows generalized patterns of dissolution, cementation, and neomorphism in Pleistocene strata on Enewetak relative to each exposure surface. The generalized profile in Figure 65 was developed from diagenetic patterns shown in Figures 10 - 12. The position of zone 1 (Fig. 65), immediately below subaerial exposure
Figure 65.
Generalized pattern of diagenetic alteration of Pleistocene strata in XRI-1, XAR-1, and XEN-1 wells. Figures 10 - 12 show diagenetic profiles on which this generalized profile is based.
GENERAL PATTERN OF PLEISTOCENE DIAGENESIS, ENEWETAK

Zone 1. Dissolution (irregular & fabric selective) dominates. Cements range from rare to common with an uneven (patchy) distribution. Cements may include equant-to-bladed calcite, micrite, and microspar. Fine to coarsely crystalline neomorphic calcite may replace aragonite.

Zone 2. Minor dissolution and cementation. Minor dissolution is usually fabric selective and incomplete. Minor calcite cements are often equant-to-bladed and equant mosaics that preferentially fill intragranular and small intergranular voids. Medium to coarsely crystalline neomorphic calcite sometimes replaces aragonite.

Zone 3. Abundant cementation and minor fabric selective dissolution. Cements are generally circumvoid, equant-to-bladed crusts of calcite that show a slight preference to fill smaller voids.

Zone 4. Abundant dissolution and cementation. Dissolution is fabric selective. Cements are generally isopachous crusts of bladed or equant-to-bladed calcite. Neomorphism of aragonite to coarsely crystalline calcite is abundant at the top of zone 4 and decreases downward.

Zone 5. Fabric selective dissolution is dominant but generally decreases with depth. Cementation is very minor or non-existent.

Zone 6. Dissolution (fabric selective) is minor and decreases until it is virtually absent. Cementation is very minor or non-existent.
surfaces, suggests that the relatively intense diagenetic alteration occurred in a soil zone. Isopachous crusts of bladed and equant-to-bladed cement in zones 3 and 4 (Fig. 65) suggest that the intense diagenetic alteration in those zones occurred in or immediately above a meteoric-phreatic environment. Zone 2 (Fig. 65) with its minor dissolution and rare, uneven cementation apparently represents diagenetic alteration in the "middle vadose zone" above the capillary fringe zone (zone 3) and below soil-related alteration (zone 1). Diagenesis of zones 5 and 6 (Fig. 65) might represent alteration in deeper meteoric-phreatic or mixed meteoric-marine environments. In contrast, Goter (1979) concluded that most meteoric cementation (and other meteoric diagenesis) in the Pleistocene of Aranit Island (Ennewetak) occurred in the vadose zone.

Soil Zone Alteration

Dissolution, rather than cementation, is dominant in most Pleistocene Ennewetak soil zones (zone 1). The dominance of dissolution and scarcity of caliche suggest that rainfall, throughout much of the Pleistocene, was as abundant as it is in modern times (150 cm/year). Irregular dissolution in zone 1 was probably associated with plants and other soil processes. Decay of terrestrial organic material may have increased the acidity of soil waters, promoting irregular and fabric-selective dissolution.
The scarcity of cement in many Pleistocene soil zones may be due, in part, to permeable depositional textures (packstones, grainstones, boundstones), through which rainwater could move quickly. Cements present in the soil zone were probably precipitated by meteoric waters which remained in the soil zone long enough to become supersaturated with respect to calcite. Cement precipitation in zone 1 might be in response to CO$_2$-degassing or evapotranspiration of water in the soil zone. The lack of distinct root structures is probably also a result, in part, of original depositional textures. Because roots penetrated packstones, grainstones, and porous boundstones on Enewetak, they usually did not leave easily identifiable impressions like roots penetrating wackestones and mudstones.

Middle Vadose Alteration

Diagenesis in the middle vadose zone (zone 2; Fig 65) is minimal primarily because water does not reside in this zone very long. Because Enewetak strata cored by Pleistocene wells are quite permeable, most water would tend to move quickly through the middle vadose zone. Cements in zone 2 preferentially fill intragranular voids, small molds, and very small intergranular voids which should have preferentially retained water in a vadose environment. Substantial irregularities in grain size and shape among Enewetak bioclasts probably prevented vadose waters and
cements from forming meniscus structures between grains and pendent structures on the bottom of grains.

Capillary forces in partial delicately dissolved bioclasts should have been strong and quite effective in retaining vadose water. This might be the reason why neomorphic spars (calcite precipitated into partially delicately dissolved fossils) are often more abundant than intergranular cements in the middle vadose zone (Figs. 10 - 12). The thickness of the middle vadose zone can be quite variable, from less than a meter to more than 10 m.

Water Table Alteration

The intense diagenetic alteration observed in zones 3 - 5 (Fig. 65) is apparently related to cementation and dissolution associated with Pleistocene water tables. Intense diagenetic alteration associated with water tables and meteoric-phreatic zones has been previously documented on Bermuda (Land, 1970), Barbados (Matthews, 1974; Steinen, 1974), Joulter's Cay (Halley and Harris, 1979), St. Croix (Moore, 1977), and Enewetak (Goff, 1979). Well-cemented zones are common at the top of, and slightly above, water tables in Holocene sediments on Joulter's Cay, Bahamas (Halley and Harris, 1979), St. Croix (Moore, 1977), Grassey Key, Florida (Russell, 1970), and the Schooners Cays, Bahamas (Budd, 1984). While intergranular cements in zone 3 (Fig. 65) are generally isopachous crusts within individual voids,
these cements are frequently patchy on a mesoscopic scale showing a slight tendency to fill smaller voids. The distribution of cement in zone 3 and its position at the top of the water-table alteration zone (zones 3–5) suggest that zone 3 represents alteration in a capillary fringe zone immediately above the water table (Fig. 65). Zone 4 with its massive dissolution and more uniform cementation is probably the result of diagenesis in the upper part of the meteoric-phreatic zone.

Studies of modern meteoric systems on Enewetak, St. Croix, and Joulter's Cay indicate that CO₂-degassing is the main process causing cementation at the top of most water tables (Hanor, 1978; Goff, 1979; Hailey and Harris, 1979). Hanor (1978) observed rapid CO₂-degassing in the top 120 cm of the modern meteoric-phreatic zone on St. Croix. Hailey and Harris (1979) indicate that greatest cementation on Joulter's Cay is immediately above and in the top meter of the modern meteoric-phreatic zone and is probably associated with CO₂-degassing. CO₂-degassing is proposed as the primary mechanism responsible for cementation at the top of Pleistocene water tables (zone 4) and capillary fringe zones (zone 3) on Enewetak.

The intense dissolution in upper parts of zone 4 (which also exhibits substantial cementation) probably occurred in the CO₂-degassing zone at the top of the meteoric-phreatic lense prior to calcite saturation. In zone 5 and the lower part of zone 4 (Fig. 65), dissolution (without much associated
cementation) probably occurred in CO\textsubscript{2}-rich meteoric-phreatic waters below the degassing zone (Hanor, 1978). Pleistocene Enewetak, like the modern back-barrier zone on St. Croix (Hanor, 1978), probably had large quantities of organic material periodically washed into shallow meteoric-phreatic systems. That organic material would then undergo bacterial decay increasing the CO\textsubscript{2} concentration of the groundwater. Repeated influxes of rainwater carrying organic material would have periodically elevated CO\textsubscript{2} levels causing periodic dissolution, and later CO\textsubscript{2} degassing would have lowered the CO\textsubscript{2} level causing periodic cementation in zone 4 (Fig. 66). The presence of organic material undergoing [bacterial] decay in Pleistocene meteoric-phreatic zones on Enewetak is confirmed by light stable carbon isotopes in some meteoric-phreatic cements. For example, in a probable Pleistocene meteoric-phreatic zone (48 - 51 m in the XRI-1 well; Fig. 10), intergranular crusts of bladed cement have $\delta^{13}\text{C}$ values of -8.9 o/oo and -8.6 o/oo (PDB; Fig. 35).

\textbf{Alteration near base of the meteoric-phreatic zone}

In diagenetic zones 5 and 6 (Fig. 65), cementation is virtually absent and dissolution decreases steadily with depth. Zone 6 and the lower part of zone 5 may represent a transition between actively circulating meteoric-phreatic waters in zone 4 and more stagnant waters which might be meteoric, marine, or mixed meteoric and marine. Decreasing
Figure 66.

Model for meteoric alteration of Pleistocene carbonate strata on Enewetak Atoll. Meteoric diagenesis in Pleistocene strata on Enewetak is dominated by vertical rather than lateral variations.
MODEL FOR METEORIC DIAGENESIS,
ENEWETAK ATOLL

Depth (meters)

Zone 1
Soil Zone

Zone 2
Middle Vadose Zone

Zone 3
Capillary Fringe

Zone 4
Upper Meteoric-Phreatic

Zone 5
Lower Meteoric-Phreatic and/or Mixing Zone

Zone 6
Marine Water

Water Table
CO₂-degassing
water circulation might cause decreased dissolution while not inducing cementation.

An alternative explanation is that zone 6 and perhaps the lower part of zone 5, represent diagenesis in a mixing zone which grades downward into more marine waters (Fig. 66). In a mixing zone, dissolution should be dominant and should decrease with depth as subsurface waters become more marine (Runnells, 1969; Hanshaw et al., 1971). No dolomite was observed in this zone or in any other Pleistocene samples. Unaltered and slightly altered sediments below zone 6 were probably in stagnant marine waters during alteration of overlying strata in an active meteoric system.

**Distribution of Meteoric Alteration**

Meteoric alteration should only affect the upper part of the atoll during periods of subaerial exposure, therefore zones of intense meteoric alteration will probably be thin but laterally extensive. Intense soil zone alteration may only be 1 - 2 m thick but should extend over the whole subaerially exposed surface. Likewise, meteoric-phreatic zones and associated alteration in pure carbonate provences will generally be thin. In the northern Yucatan, the meteoric-phreatic zone is approximately 30 m thick in a peninsula 350 km wide (Back and Hanshaw, 1978). Fresh-water lenses under many carbonate islands are only a few meters thick (Engebi, Buddemeier and Holladay, 1977; Joulter's
While most Plio-Pleistocene strata on Enewetak show some evidence of meteoric diagenesis, most Lower Miocene and Upper Eocene strata show no evidence of meteoric diagenesis. Only strata within 30 - 50 m of major unconformities at the top of the Upper Eocene and top of the Lower Miocene show diagnostic evidence of meteoric alteration. Therefore, meteoric diagenesis is closely related to subaerial exposure, and diagenetically altered intervals should tend to be thin, though laterally extensive, depending on the size of the subaerially exposed land.

Comparison with other meteoric systems and models

The model for meteoric diagenesis shown in Figure 66 emphasizes vertical variations in diagenetic alteration and neglects horizontal variations in the meteoric system. Such a model may be applicable on Enewetak and other small island settings where subsurface carbonates are very permeable and movement of meteoric water is mainly vertical. While rainwater percolating through the vadose zone will be mainly vertical in most carbonate provences, some meteoric-phreatic systems (especially large systems) include substantial lateral water movement. A dominantly vertical meteoric system requires very permeable substrate, moderate tidal fluctuations, and a small landmass on which only a small freshwater lens is present. In such a situation, fresh
water will mix vertically with marine water due to tidal fluctuations, rather than flowing laterally to the ocean. In this vertical-meteoric system, water in the meteoric-phreatic zone is supplied primarily by rainwater percolating through the overlying meteoric-vadose zone rather than water flowing laterally through the phreatic zone from an area of meteoric recharge.

**Joulter's Cay, Bahamas**

The meteoric system on Joulter's Cay, Bahamas (Halley and Harris, 1979) fits this vertical (Enewetak) meteoric model very well. Like Enewetak islands, the water table on Joulter's Cay is approximately at sea level indicating that there is no significant head to move meteoric-phreatic waters horizontally. Qualitatively, the distribution of cement on Joulter's Cay is very similar to that predicted by the Enewetak meteoric model, with maximum cementation at the top of and immediately above the water table (Halley and Harris, 1979, Fig. 11). Porosity curves (Halley and Harris, 1979, Fig. 12) suggest dissolution is greatest just below the water table and then decreases downward on Joulter's Cay, as on Enewetak.

**Barbados**

Meteoric alteration of subsurface Pleistocene limestones
on Barbados has been described by Matthews (1967, 1974), Harris (1971), Steinen (1974), Pingitore (1976), and others. In contrast to Enewetak and Joultet's Cay, the meteoric-phreatic systems described by Harris (1971) and Matthews (1974) are dominated by the lateral movement of meteoric water. In the western part of Barbados, Harris (1971) estimates that only 1% of the meteoric-phreatic water has passed through the overlying vadose zone. As a consequence many of the vertical variations present in the meteoric-phreatic zone on Enewetak are absent in Barbados. Rather, diagenetic alteration in the meteoric-phreatic zone on Barbados appears fairly homogenous (Steinen, 1974). Steinen (1974) reports no distinct vertical variations in cementation, dissolution or neomorphism within the meteoric-phreatic zone. As in the Enewetak model, diagenetic alteration is most intense in the meteoric-phreatic zone on Barbados and decreases into the underlying mixing zone (Matthews, 1974; Steinen, 1974).

Matthews (1974) separates the vadose zone into "upper" and "deep" parts. The "upper vadose" zone of Matthews (1974) corresponds to the soil zone on Enewetak, and the "deep vadose" zone of Matthews (1974) corresponds to the middle vadose zone on Enewetak. As on Enewetak, the "deep" or middle vadose zone is an interval of less intense alteration between the more intensely altered soil zone ("upper vadose") and the meteoric-phreatic zone. Steinen (1974) and Matthews (1974) did not distinguish diagenetic alteration in the
capillary fringe zone.

Differences between stable isotope profiles in Pleistocene strata of Enewetak and Barbados may reflect differences between meteoric-phreatic zones on Enewetak and Barbados. On Barbados, δ¹³C values of soil zone rocks are quite light but become heavier with depth especially into the meteoric-phreatic zone (Allan and Matthews, 1977, 1982). On Enewetak, both soil zone cements and some meteoric-phreatic cements have very light δ¹³C values. Those light δ¹³C values for Enewetak meteoric-phreatic cements probably reflect rainwater seepage into meteoric-phreatic waters on Enewetak through the overlying, organic-rich vadose zone. In contrast, most meteoric-phreatic waters in the Barbados carbonate system flowed laterally and were probably not transporting much decaying organic material. In both the Enewetak and Barbados systems, stable oxygen isotopes are fairly consistent with depth, while stable carbon isotopes are quite variable (Allan and Matthews, 1982).

Longman model for meteoric diagenesis

Longman (1980) presents a model for diagenetic alteration in meteoric-vadose and meteoric-phreatic environments. While Longman's reasoning appears sound, diagenetic patterns observed in the Holocene of Joulter's Cay (Halley and Harris, 1979), the Pleistocene of Barbados (Matthews, 1974; Steinen, 1974), the Pleistocene of the Bahamas (Beach, 1982), and
the Pleistocene of Enewetak suggest that Longman's model rarely occurs in nature.

In the vadose zone, Longman (1980) basically predicts that dissolution should decrease with depth down to the water table while cementation should be virtually non-existent at the surface and increase downward to the water table. As Beach (1982) demonstrated in the Pleistocene of the Bahamas, cementation is frequently greatest immediately below exposure surfaces whether caliche is present or not. Away from soil-zones and capillary fringe zones, diagenetic profiles from the Pleistocene of Enewetak (Figs. 65 and 66) and the Holocene of Joulter's Cay (Halley and Harris, 1979) indicate that there is no general decrease in dissolution coinciding with an increase in cementation in the vadose zone. Rather, cementation in the middle vadose zone is generally related to nearby dissolution resulting in no significant net transport of CaCO₃ downward through the vadose zone (Halley and Harris, 1979).

Longman's (1980) model for meteoric-phreatic diagenesis includes dissolution decreasing downward with maximum dissolution at the water table, and cementation increasing downward with virtually no cementation at the water table. These ideas are contrary to diagenetic patterns observed on Joulter's Cay, Barbados, Enewetak, and many other locations. On Joulter's Cay, data of Halley and Harris (1979) clearly show maximum cementation at the water table. Water-table cementation is also common in other Holocene strata (Russell,
1970; Moore, 1977; Goff, 1979; Budd, 1984) and is probably the result of CO₂-degassing at the top of the water table (Hanor, 1978). Likewise, the model developed for meteoric diagenesis on Enewetak suggests maximum cementation at the top of the meteoric-phreatic zone and in the capillary fringe zone. Within the meteoric-phreatic zone on Barbados, dissolution and cementation are relatively uniform, showing no significant increase or decrease with depth until marine water begins to mix with the freshwater aquifer (Steinen, 1974; Matthews, 1974).

MARINE DIAGENESIS

In contrast to meteoric diagenesis, intense marine diagenesis on Enewetak pervasively alters very thick packages of limestone. Marine diagenesis is closely related to the hydrologic proximity of strata to the seaward margin of an atoll. Near the edge of an atoll, large amounts of marine water will circulate through permeable strata causing extensive diagenetic alteration. The distance which ocean water can circulate into the atoll is quite variable. As tidal fluctuations in the F-1 well show, marine waters can, in places, circulate laterally over 3 km into an atoll (Swartz, 1958).

The striking scarcity of marine diagenesis in back-reef and lagoon-margin sediments in the Pleistocene probably reflects a lack of active marine circulation through those
strata. When present, marine diagenesis in back-reef and lagoon-margin sediments is often associated with beach rock cementation. The minor, scattered occurrence of marine (beach rock) cement in back-reef and lagoon margin environments is similar to the minor, scattered marine (beach rock) cements present in basinward portions of Jurassic Smackover grainstones (Moore and Druckman, 1981).

In the Enewetak Atoll, marine diagenesis shows distinct vertical zonations. Changes in marine alteration of Enewetak strata at the seaward margin of the atoll are apparently related to zones of HMC, aragonite, LMC, and dolomite stability in the open ocean (Fig. 67).

Zone of HMC and Aragonite Stability

In shallow marine waters above the aragonite and HMC saturation depths, diagenesis consists primarily of HMC and aragonite cementation and alteration by marine organisms. Dissolution does not appear to be significant. If rocks are in a location where shallow marine water is actively circulating, HMC and aragonite cementation can effectively occlude porosity, thus impeding circulation and preventing more ocean water from penetrating deeply into the atoll.
Figure 67.
Model for Enewetak diagenesis. Note isotopic differences between marine and meteoric cements. Also note the vertical zonation of marine diagenesis.
MODEL FOR ENEWETAK DIAGENESIS

**Dissolution**

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Cement Geochemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minor; LMC; micrite, microspar, equant-to-bladed, equant mosaic, uneven</td>
<td>Sr 0.02 - 0.30, Mg 0.10 - 0.30, ( \delta^{13}C ) -10 - 1, ( \delta^{18}O ) -7.5</td>
</tr>
<tr>
<td>Intense; mainly fabric selective dissolution of aragonite</td>
<td>Sr 0.01 - 0.03, Mg 0.10 - 0.30, ( \delta^{13}C ) -8 - 1, ( \delta^{18}O ) -7.5</td>
</tr>
<tr>
<td>None</td>
<td>Sr 0.10, Mg 1.00, ( \delta^{13}C ) 2 - 5, ( \delta^{18}O ) 2.2</td>
</tr>
<tr>
<td>Intense; fabric selective diss. of aragonite</td>
<td>Sr 0.02, Mg 0.50, ( \delta^{13}C ) 0 - 3, ( \delta^{18}O ) 1.0</td>
</tr>
<tr>
<td>Variable; dissolution of calcite</td>
<td>Sr 0.02, Mg 43 - 7.0, ( \delta^{13}C ) 2 - 3, ( \delta^{18}O ) 2.0</td>
</tr>
</tbody>
</table>

**Cementation**

- Minor: LMC; micrite, microspar, equant-to-bladed, equant mosaic, uneven
- Intense near water table; LMC; bladed & equant-to-bladed crusts
- Minor: Abundant; HMC & aragonite; micrite, fibrous, bladed
- Abundant calcite; fibrous radiaxial, and bladed
- Variable: Dolomite 0.02, 45 - 45, \( \delta^{13}C \) 2 - 3, \( \delta^{18}O \) 4.0
Zone of LMC Stability

At a depth of approximately 300 m, the modern Pacific Ocean becomes undersaturated with respect to aragonite (Li et al., 1969; Scholle et al., 1983). At a depth of approximately 1,000 m, the modern Pacific Ocean becomes undersaturated with respect to calcite (Li et al., 1969; Scholle et al., 1983). Between 300 m and 1,000 m, modern Pacific ocean waters are in a zone of LMC stability where aragonite should dissolve and calcite should precipitate. In the F-1 well between 375 and 820 m, aragonite has been dissolved, HMC has been converted to LMC, and LMC cements are abundant. Much of the LMC (marine) cement is radiaxial calcite which precipitated about the same time as, or shortly after aragonite dissolution. Dissolution of aragonite would create new voids allowing marine waters to circulate more deeply into the atoll. Dissolved aragonite might also act as a source of calcium carbonate for LMC cements.

Zone of Dolomite Stability

Below approximately 1,000 m in the modern Pacific Ocean, marine waters are undersaturated with respect to calcite but supersaturated with respect to dolomite (Li et al., 1969; Scholle et al., 1983). Theoretically, when marine waters from below the calcite saturation depth flow...
through deep limestones, calcite (LMC) should dissolve and dolomite should precipitate. Dissolution of LMC and dolomitization are observed between 1,219 and 1,372 m deep in the F-1 well and at approximately 1,250 m in the E-1 well. Active circulation of deep marine waters (below the calcite saturation depth) is probably vital to effective deep marine dissolution of calcite and formation of dolomite. Formation of dolomite in deep marine waters has been previously described near Bermuda by Friedman (1964) and in the Mediterranean Sea by Fontes and Desforges (1975).

Distribution of Marine Diagenesis

Marine diagenesis is primarily dependent on the active circulation of marine waters through carbonate strata. Active marine circulation should occur in permeable limestones at continental margins, at the seaward edge of atolls, in submarine mounds and in other similar settings. The saturation state of the circulating ocean water will determine the type of marine alteration that will occur. Aragonite and calcite saturation depths show substantial variations in modern oceans (Li et al., 1969; Scholle et al., 1983). If aragonite and calcite saturation levels in ancient oceans were shallower than present day, then dissolution of aragonite, precipitation of LMC, and dolomitization could theoretically occur in shallower marine environments than observed on Enewetak.
COMPARISON OF ENEWETAK MODEL WITH ANCIENT CARBONATES

Many limestones have formed in mounds, atolls, and shelf-margin settings in which diagenetic alteration might be analogous to Enewetak. The Upper Devonian Miette buildup (Mattes and Mountjoy, 1980) and the Cretaceous Stuart City trend of Texas (Bebout and Loucks, 1974) are two such units that superficially appear to be similar to the Cenozoic of Enewetak. Cenozoic carbonates of Enewetak, the Miette buildup, and the Stuart City trend accumulated in reef complexes immediately adjacent to deep marine basins. Diagenetically, all three apparently have some meteoric and probably much marine diagenesis, including radiaxial cementation (Mattes and Mountjoy, 1980; Bebout and Loucks, 1974). Northwest of the Stuart City trend, Lower Cretaceous shelf carbonates of the Glen Rose Formation accumulated and were periodically exposed to meteoric diagenesis (Petta, 1977).

**Miette Buildup, Alberta**

Like Enewetak, the Upper Devonian Miette buildup was basically a carbonate pinnacle projecting up from a deep marine basin (Mattes and Mountjoy, 1980). As on Enewetak, meteoric cements in the buildup are generally associated with exposure surfaces. Mattes and Mountjoy (1980) found
no meteoric cementation along the margin of the Miette buildup. Widespread radially calcite generally postdates aragonite dissolution, but precedes calcite dissolution and dolomitization (Mattes and Mountjoy, 1980). The Miette's basic diagenetic sequence of (1) aragonite dissolution, (2) calcite cementation, (3) calcite dissolution, and (4) dolomitization could be produced by marine diagenesis during subsidence of the buildup through the calcite and dolomite stability zones (Fig. 67). Dolomite abundance increases with depth and toward the margins of the buildup (Mattes and Mountjoy, 1980, Figs. 4 & 10). Such a distribution of dolomite would be expected if dolomitization was caused by deep marine waters circulating through the buildup. Relative $\delta^{13}C$ and $\delta^{18}O$ values for early (meteoric) calcites, radially calcites, and mosaic dolomites in the Miette buildup are similar to Enewetak (Fig. 68; Mattes and Mountjoy, 1980).

It is possible that much of the calcite cementation and dolomitization in the Miette buildup is not marine, but is associated with basinal fluids expelled from nearby shales. Calcites and dolomites associated with brines expelled from basinal shales should be greatly enriched in iron and manganese and have more radiogenic strontium isotopes than calcites and dolomites formed in normal marine waters (Moore and Druckman, 1981; Moore, 1984). Marine calcites and dolomites should incorporate the $^{87}Sr/^{86}Sr$ ratio characteristic of seawater at the time of their formation.
Figure 68. Stable isotope composition of diagenetic cements and dolomite in the Miette buildup (data from Mattes and Mountjoy, 1980) compared with fields for Enewetak calcite cements and dolomite. Note that the relative $\delta^{13}C - \delta^{18}O$ positions of early sparry cements, radiaxial calcites and mosaic dolomite in the Miette buildup are similar to meteoric cements, radiaxial cements, and dolomites on Enewetak.
STABLE ISOTOPIC COMPOSITION OF DIAGENETIC ELEMENTS ON ENEWETAK

Average Values
- Mosaic Dolomite
- Radial Calcite
- Early Sparry Calcite

MIE TTE BUILDUP
The Enewetak diagenetic model might also fit diagenetic alteration in the Lower Cretaceous Glen Rose Formation and Stuart City trend (Achauer, 1977). As on Enewetak, meteoric alteration can frequently be associated with nearby caliches and subaerial exposure surfaces in the Glen Rose Formation (Achauer, 1977; Allan and Matthews, 1982). In the Glen Rose, meteoric diagenetic products are similar to those on Enewetak and commonly include dissolution of aragonite and formation of equant-to-bladed cements (Achauer, 1977; Petta, 1977; Allan and Matthews, 1982). Fibrous and micritic marine cements are present only in primary intergranular voids of the Glen Rose suggesting that marine cementation occurred prior to aragonite dissolution (Petta, 1977). No radiaxial calcite has been reported in the Glen Rose Formation (Achauer, 1977).

Diagenetic alteration in the Stuart City trend is quite similar to marine diagenetic alteration observed in the zone of calcite stability on Enewetak (300 - 1,000 m deep). In parts of the Stuart City trend described by Bebout and Loucks (1974) and Achauer (1977), distinctively meteoric cements are present, but rare, and radiaxial cements are common. As on Enewetak, radiaxial calcites of the Stuart City trend frequently fill voids created by aragonite
dissolution (Bebout and Loucks, 1974). Achauer (1977) notes that radiaxial cements "postdate the few occurrences of authentic vadose calcite in Sligo reefs". Bebout and Loucks (1974) and Achauer (1977) decided that meteoric waters were probably responsible for aragonite dissolution in the Stuart City trend. Bebout and Loucks (1974) also suggested a meteoric-phreatic origin for radiaxial spar because of the radiaxial cement's association with aragonite dissolution. However, Achauer (1977) supported an origin of radiaxial calcite by replacement of a synsedimentary marine cement in the Stuart City trend.

Different research groups have studied stable isotopes of the Glen Rose Formation and Stuart City trend. In parts of the Glen Rose altered by meteoric waters, whole rocks samples have $\delta^{13}C$ values of -3.4 to +0.6 and $\delta^{18}O$ values of -4.7 to -3.3 (Allan and Matthews, 1982). Inclusion-rich radiaxial cements from the Stuart City trend have a mean $\delta^{18}O$ value of -2.6 o/oo (PDB) and $\delta^{13}C$ values of -29.1 to +3.2 o/oo (PDB). The tremendous scatter in $\delta^{13}C$ of the Stuart City radiaxial spars suggests the influence of basinal, methanogenic carbon. Isotopic analyses of whole rock samples altered in meteoric waters are difficult to compare with meteoric cements from Enewetak and radiaxial spars of the Stuart City trend. Radiaxial calcites of the Stuart City trend appear to have heavier stable oxygen isotopes than meteoric calcites suggesting a marine origin for the radiaxial cement; however, the difference is not
substantial. A single, integrated study of Lower Cretaceous cements might reveal more distinct isotopic differences between Glen Rose meteoric cements and radiaxial calcites of the Stuart City trend.

It is possible that some aragonite dissolution and all radiaxial cementation in the Stuart City trend occurred in actively circulating marine waters below the aragonite saturation depth. However, many other alternatives are possible including diagenesis in fresh water and in brines expelled from basinal evaporites and shales. As discussed in the previous section on the Miette buildup, tools such as strontium isotopes and trace elements (especially manganese and iron) may be used to distinguish diagenesis in subsurface brines from diagenesis in marine water. Further stable isotope studies might allow fresh water diagenetic calcites to be confidently distinguished from marine diagenetic calcites in the Lower Cretaceous of Texas.
CONCLUSIONS

Many different types of diagenetic alteration are observed in Cenozoic carbonates of Enewetak. In Pleistocene strata, meteoric diagenesis is dominant but variable. Intervals of intense cementation, dissolution, and neomorphism alternate with poorly-cemented, slightly altered Pleistocene strata. Intense diagenetic alteration is generally related to subaerial exposure surfaces and Pleistocene water tables. While CaCO$_3$ is redistributed by meteoric processes, there is little net reduction in porosity by meteoric processes in Pleistocene limestones as a whole.

In Lower Miocene and Upper Eocene strata on Enewetak, diagenetic alteration occurs primarily in marine waters near the margin of the atoll. In Lower Miocene strata of the F-1 well, radiaxial calcite commonly fills primary voids and secondary voids created by aragonite dissolution. The stable isotope composition of Enewetak radiaxial spar clearly indicates it is marine in origin. A lack of meteoric calcite in most of the Lower Miocene suggests that the pervasive dissolution of aragonite occurred in marine waters below the aragonite saturation depth. Therefore, radiaxial cementation also probably occurred below the aragonite saturation depth. In most samples, abundant marine cements (radiaxial calcites) are very effective in reducing original porosity. In Upper Eocene strata of the F-1 well, diagenesis is often minor. While aragonite has been pervasively dissolved,
calcite cementation (probably marine) is minor. More extensive calcite cementation in Lower Miocene strata of the F-1 well probably reflects Lower Miocene strata having more active marine circulation than Upper Eocene strata. Dolomitization is common in deeper parts of the Upper Eocene of Enewetak. Deep Enewetak dolomite apparently formed in deep marine waters circulating through the atoll. Where not extensively dolomitized, Upper Eocene strata of the F-1 well have retained much of their original porosity.

The distribution of meteoric diagenesis is closely related to subaerial exposure surfaces. For example, most Lower Miocene and Upper Eocene strata are well below unconformities and have not suffered noticeable meteoric alteration. The seaward margins of the Enewetak Atoll have significant marine diagenetic alteration extending to depths of over 1,300 m because of actively circulating ocean water associated with tidal pumping or thermal convection (Swartz, 1958). Marine diagenetic alteration tends to decrease into less permeable back-reef and lagoon-margin strata away from the seaward margin of the atoll. Atoll carbonates that have never been exposed to meteoric water or actively circulating marine water show little diagenetic alteration except compaction. In grainstones that are well below subaerial exposure surfaces and away from the atoll margin, cementation is minor and primary porosity can remain large (often more than 30%).

In summary, Cenozoic carbonates on Enewetak illustrate
that both marine and meteoric diagenesis can be very effective in transforming original HMC and aragonite sediments into more stable LMC and dolomite. Using petrography, stable isotopes, strontium isotopes, and trace elements, the products of marine and meteoric diagenesis can generally be distinguished. Because the distribution of diagenetic alteration in meteoric systems is much different than in marine systems, recognition and separation of the two are important to the prediction of porosity in ancient carbonate rocks.
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APPENDIX
ANALYTICAL METHODS

Sample Separation

In this study, geochemical analyses were performed exclusively on individual diagenetic components. Individual diagenetic components were separated from the bulk rock by scraping that component off a polished slab or a thick thin-section using a needle or microknife. In order to remove calcite from dolomite samples, calcite was selectively leached from the dolomite using a 0.5 N HCl solution and a process described by Stamatedes (1982). X-ray diffraction analyses before and after calcite leaching confirmed that leaching did not systematically alter the composition of the dolomite. Furthermore, geochemical analyses were performed on one unleached sample (F-12-5B) to confirm that leaching did not cause any significant change in the geochemical composition of dolomite (Table 9).

Atomic Absorption Spectrophotometry (AA)

Preparation

Prior to atomic absorption spectrophotometry (AA), samples were (1) powdered, (2) rinsed three times in distilled, deionized water, (3) dried, and (4) weighed. Calcite samples were then digested in 0.5 N HCl acid until completely dissolved. Dolomite samples were digested in warm (70°C), 2 N HCl acid. After digestion these dissolved carbonate
samples were passed through 0.45 micron Millipore filter paper to remove insoluble residues. Subsequent dilutions were made with 0.5 N HCl prior to AA analysis. All preparatory work was performed in the L.S.U. Geochemistry Laboratory using glass pipettes and volumetric flasks.

Analyses

After dilutions were completed, concentrations of Ca, Mg, Sr, Na, Fe, and Mn were determined using a Varian AA-475 atomic absorption spectrophotometer at L.S.U. An air-acetylene flame was utilized for Ca, Mg, Na, Fe, and Mn determinations, and a nitrous oxide-acetylene flame was used for Sr determinations. To determine contamination during the analytical procedure a blank was processed and analyzed in parallel with all standards and samples.

A lanthanum solution was added to samples analyzed for Ca and Mg to eliminate molecular interference effects. Solutions analyzed for Ca and Mg contained a 5% lanthanum solution. Cesium was added to final solutions analyzed for Sr and Na to reduce ionization effects. Final solutions analyzed for Sr and Na contained a 1% cesium solution.

Precision and Accuracy

Results of replicate AA analyses of NBS standard 88a (dolomite limestone) are shown in Figure A-1. Ca, Mg, and Mn determinations have relative standard deviations (1σ/mean) of less than 3%. Sr concentrations were reproduced
### TABLE A-1

**REPLICATE ATOMIC ABSORPTION ANALYSES OF NBS STANDARD 88a**

<table>
<thead>
<tr>
<th></th>
<th>CA</th>
<th>MG</th>
<th>SR</th>
<th>NA</th>
<th>FE</th>
<th>MN</th>
<th>I.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study (wt.%)</td>
<td>21.5</td>
<td>13.1</td>
<td>0.0041</td>
<td>0.0044</td>
<td>0.172</td>
<td>0.0020</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>21.3</td>
<td>13.0</td>
<td>0.0037</td>
<td>0.0043</td>
<td>0.179</td>
<td>0.0020</td>
<td>1.5</td>
</tr>
<tr>
<td>Mean (wt.%)</td>
<td>21.4</td>
<td>13.0</td>
<td>0.0039</td>
<td>0.0044</td>
<td>0.175</td>
<td>0.0021</td>
<td>1.4</td>
</tr>
<tr>
<td>S.D. (wt.%)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.0002</td>
<td>0.0002</td>
<td>0.004</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>Relative S.D. (wt.%)</td>
<td>0.5</td>
<td>0.5</td>
<td>5.3</td>
<td>3.5</td>
<td>2.2</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>CA</th>
<th>MG</th>
<th>SR</th>
<th>NA</th>
<th>FE</th>
<th>MN</th>
<th>I.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NBS (1967) Analysis (wt.% )</td>
<td>21.5</td>
<td>12.9</td>
<td>0.004</td>
<td>0.01</td>
<td>0.20</td>
<td>0.002</td>
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</tbody>
</table>

**Cunningham (1981), 3 separate analyses at L.S.U.**

<table>
<thead>
<tr>
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<th>CA</th>
<th>MG</th>
<th>SR</th>
<th>NA</th>
<th>FE</th>
<th>MN</th>
<th>I.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (wt.%)</td>
<td>21.6</td>
<td>12.9</td>
<td>0.0039</td>
<td>0.139</td>
<td>0.159</td>
<td>0.002</td>
<td></td>
</tr>
<tr>
<td>S.D. (wt.%)</td>
<td>0.5</td>
<td>0.3</td>
<td>0.0004</td>
<td>0.004</td>
<td>0.018</td>
<td>0.000</td>
<td></td>
</tr>
<tr>
<td>Relative S.D. (wt.%)</td>
<td>2.5</td>
<td>2.4</td>
<td>9.0</td>
<td>26.6</td>
<td>11.3</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>

**Stamatedes (1982), 10 separate analyses at L.S.U.**

<table>
<thead>
<tr>
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<th>CA</th>
<th>MG</th>
<th>SR</th>
<th>NA</th>
<th>FE</th>
<th>MN</th>
<th>I.R.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean (wt.%)</td>
<td>21.8</td>
<td>13.1</td>
<td>0.0040</td>
<td>0.0080</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>S.D. (wt.%)</td>
<td>0.1</td>
<td>0.1</td>
<td>0.001</td>
<td>0.0014</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Relative S.D. (wt.%)</td>
<td>0.3</td>
<td>0.5</td>
<td>1.8</td>
<td>17.8</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
</tbody>
</table>

\[
S.D. = \sqrt{\frac{\sum_{i=1}^{n} (Y_i - \bar{Y})^2}{n-1}}
\]

Relative S.D. (%) = (S.D./Mean) \times 100
to ± 0.0002 wt. % Sr (1σ) with a relative standard deviation of approximately 5%. Ca, Mg, Sr, and Mn showed little or no systematic variation through time or between operators (Table A-1). Mean values of Ca, Mg, Sr, and Mn concentrations were within 1 % of the reported NBS values (Table A-1).

In this study, Na and Fe analyses had relative standard deviations of less than 5% (Table A-1). However, Na and Fe values obtained by AA for NBS-88a showed variations according to operators at L.S.U. and are significantly different than officially reported NBS values (Table A-1). Much of the Na and Fe variability may be related to insoluble silicates in NBS-88a. Official NBS determinations are made for the bulk sample including insoluble residue; in analyses at L.S.U., the insoluble residue was separated from NBS-88a after digestion but prior to elemental analysis. Silicate clay in insoluble residues probably contain significant amounts of Fe and Na. Variations in Na and Fe values between L.S.U. operators may reflect different reactions between silicate clays in NBS-88a and the digesting acids. Cunningham (1981) dissolved the carbonate fraction in 0.5 N acetic acid. Stamatedes (1982) dissolved dolomite with 6 N HCl acid. In this study, dolomite was dissolved in a 2 N HCL solution at approximately 70°C. Contamination from glassware and laboratories reagents may also have caused some Na variability.

In order to check accuracy and precision of AA determinations further, basalt standard JB-1 was also analyzed.
After digestion of JB-1, dilutions and elemental analyses were performed with techniques similar to those used in this study for carbonate analyses (Table A-2). In analyses of JB-1, relative standard deviations for CaO, MgO, Na$_2$O, Fe and Mn were all less than 5% (Table A-2). A comparison of mean values from L.S.U. analyses and those published in Ando et al. (1971) suggest that (1) Na analyses in this study are within 10% of the true value, (2) Fe analyses are within 2% of the true value, and (3) much of the Na and Fe variability in replicate analyses of NBS-88a is probably due to variable reactions of insoluble residues with acids dissolving the carbonate fraction.

**Electron Microprobe Analyses**

Components of Enewetak carbonates were systematically analyzed for Ca, Mg, and Sr using an ARL-EMX electron microprobe at L.S.U.. All standards and sample thin sections were polished with a 0.05 micron Al$_2$O$_3$ powder and coated with carbon prior to analysis.

**Machine operation**

Electron microprobe analyses were performed using a 5 - 10 micron wide beam and a 30 - 40 nannoamperes specimen current. Each reported result is an average of nine separate point analyses, each point being analyzed for 10 seconds. A coral fragment containing 0.81 weight % Sr (AA analysis)
### TABLE A-2

**ATOMIC ABSORPTION ANALYSES OF STANDARD JB-1**

<table>
<thead>
<tr>
<th></th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>This study</strong></td>
<td>9.30</td>
<td>7.71</td>
<td>2.97</td>
<td>6.21</td>
<td>0.12</td>
</tr>
<tr>
<td><strong>Five AA analyses at L.S.U. (1981)</strong></td>
<td>9.09</td>
<td>7.61</td>
<td>3.02</td>
<td>6.15</td>
<td>0.12</td>
</tr>
<tr>
<td>Mean (wt.%)</td>
<td>0.11</td>
<td>0.10</td>
<td>0.10</td>
<td>0.06</td>
<td>0.00</td>
</tr>
<tr>
<td>S.D. (wt.%)</td>
<td>1.2 %</td>
<td>1.3 %</td>
<td>3.4 %</td>
<td>1.0 %</td>
<td>1.9 %</td>
</tr>
<tr>
<td>Ando et al. (1971)</td>
<td>9.21</td>
<td>7.67</td>
<td>2.80</td>
<td>6.32</td>
<td>0.12</td>
</tr>
<tr>
<td>Mean (wt.%)</td>
<td>0.15</td>
<td>0.15</td>
<td>0.09</td>
<td>0.13</td>
<td>0.01</td>
</tr>
<tr>
<td>% Error</td>
<td>-1.3</td>
<td>-0.8</td>
<td>+7.9</td>
<td>+2.7</td>
<td>+5.7</td>
</tr>
</tbody>
</table>

\[
\text{% Error} = \frac{\text{Mean L.S.U.} - \text{Mean (Ando et al., 1971)}}{\text{Mean (Ando et al., 1971)}} \times 100
\]
was used as a standard for strontium determinations. The standard for magnesium analyses was a dolomite containing 12.63 wt. % Mg (AA analysis). Iceland spar was used as a Ca standard for analyses of calcites; whereas Ca determinations for dolomites were based on calcium concentrations in a dolomite standard. Final Ca, Sr, and Mg concentrations were calculated using microprobe data and a modified ACREW program with a Bence-Albee matrix correction (Tracor Northern).

**Precision and Accuracy**

Ca, Mg, and Sr were calibrated at the beginning of each day's analyses. Before and after each sample was analyzed, standards were re-analyzed to verify calibration. Results of analyses of standards are shown in Table A-3.

Replicate analyses of the coral standard suggest that below 1.0 wt. % Sr, Sr precision (2σ) is approximately ±10%. Below 0.10 wt. % Sr, reproducibility (2σ) is approximately ±0.01 wt. % Sr (Table A-3). Background variability (1σ) is approximately 0.01 wt. % Sr for each 10 second counting period.

Replicate analyses of the Mg standard have a relative standard deviation (2σ) of approximately 2 %. At low Mg concentrations (less than 0.10 wt. %), Mg reproducibility is approximately 0.01 wt. % (Table A-3). Background variation (1σ) in 10 second analyses is ±0.010 wt. % Mg.

To evaluate the accuracy of electron microprobe analyses, several microprobed samples were also analyzed by AA.
### TABLE A-3

**REPLICATE ELECTRON MICROPROBE ANALYSES**

<table>
<thead>
<tr>
<th></th>
<th>n</th>
<th>Mean Sr ± la (wt.%)</th>
<th>Mean Mg ± lo (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coral Standard</td>
<td>63</td>
<td>0.805 ± 0.041</td>
<td>-</td>
</tr>
<tr>
<td>Dolomite Standard</td>
<td>62</td>
<td>-</td>
<td>12.63 ± 0.23</td>
</tr>
<tr>
<td>Iceland Spar</td>
<td>52</td>
<td>0.019 ± 0.006</td>
<td>0.023 ± 0.006</td>
</tr>
</tbody>
</table>

*Note: n = the number of days for which mean Sr and Mg values were averaged*

Programmed Sr value for coral standard is 0.810 wt. % Sr.

Programmed Mg value for dolomite standard is 12.63 wt. % Mg.
Results are shown in Table A-4. As demonstrated in the previous section on atomic absorption spectrophotometry, AA analyses for Sr and Mg were accurate to better than \( \pm 5\% \). In comparing AA and electron microprobe analyses, there are no systematic differences (Table A-4). In most cases, the AA values are within one standard deviation (1\( \sigma \)) of the microprobe values (Table A-4). Mean Sr values determined by electron microprobe are generally within 10 \% of the AA value. Most mean Mg concentrations determined by electron microprobe are within 15\% of the AA value (Table A-4). Spatial variation of Sr and Mg concentrations in most carbonates is quite large; hence, there is a significant probability that the true Mg and Sr composition of samples analyzed by AA is different from the sample analyzed by electron microprobe. Given the heterogeneity of trace elements in carbonates, the Sr and Mg values obtained by electron microprobe are in remarkably close agreement with AA values. When analyzing trace amounts of Sr and Mg in calcite by microprobe, our results are generally accurate to \( \pm 10\% \) or \( \pm 0.010 \) wt. \% (whichever is greater) of Sr and Mg values determined by AA analyses.

**Stable Isotopes**

Carbonate samples analyzed for stable carbon and oxygen isotopes were dried for one hour at 70\( ^\circ \)C and then sent to Coastal Science Laboratories (CSL) in Austin, Texas.
### TABLE A-4
COMPARISON OF ELECTRON MICROPROBE AND ATOMIC ABSORPTION ANALYSES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sr (ppm)</th>
<th>Mg (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Probe Value ± 1σ</td>
<td>Percent* Difference</td>
</tr>
<tr>
<td>XRI-164</td>
<td>1400</td>
<td>1470 ± 580</td>
</tr>
<tr>
<td>XRI-231</td>
<td>996</td>
<td>1000 ± 250</td>
</tr>
<tr>
<td>XRI-239</td>
<td>540</td>
<td>570 ± 20</td>
</tr>
<tr>
<td>XAR-234</td>
<td>1042</td>
<td>1210 ± 200</td>
</tr>
<tr>
<td>XEN-89</td>
<td>1178</td>
<td>1180 ± 1200</td>
</tr>
<tr>
<td>KI-24</td>
<td>3013</td>
<td>3240 ± 1200</td>
</tr>
<tr>
<td>F-5-20</td>
<td>347</td>
<td>310 ± 100</td>
</tr>
<tr>
<td>F-6-16</td>
<td>257</td>
<td>300 ± 70</td>
</tr>
<tr>
<td>F-6-30</td>
<td>236</td>
<td>220 ± 70</td>
</tr>
<tr>
<td>CI-4; 54</td>
<td>1264</td>
<td>1290 ± 120</td>
</tr>
<tr>
<td>CI-4; 90</td>
<td>773</td>
<td>710 ± 100</td>
</tr>
<tr>
<td>K-239; 37.5</td>
<td>1520</td>
<td>1600 ± 240</td>
</tr>
<tr>
<td>Core 12**</td>
<td>173</td>
<td>180 ± 60</td>
</tr>
</tbody>
</table>

* (% Difference) = ((Mean Probe - AA) / AA) X 100
** (AA) = average of 4 analyses
*** = weight % Mg
for extraction and mass spectrometry. At CSL, calcite samples were reacted with phosphoric acid for 18 - 24 hours at 25°C. CSL uses TCH as an internal standard and reports all values relative to PDB. CSL claims precision and accuracy to ± 0.2 o/oo for both δ¹³C and δ¹⁸O.

A disguised internal standard (L.S.U. Solenhofen or NBS-20) was included along with each set of samples sent to CSL. Results of analyses of those internal standards are shown in Table A-5. Analyses of those internal standards have standard deviations (1σ) for both carbon and oxygen isotopes of 0.1 - 0.2 o/oo (Table A-5).

To check the accuracy of CSL analyses, splits of internal standards and splits of some samples were sent to CSL, the University of Texas at Austin (UT), and the Marathon Research Laboratory (Littleton, Colorado) for analysis. Results of interlab comparisons are shown in Table A-6. Oxygen analyses by CSL are always within 0.3 o/oo of the mean with an average difference of 0.2 o/oo. Carbon analyses by CSL are always within 0.2 o/oo of the mean with an average difference of 0.1 o/oo. All three labs show similar variations relative to the mean δ¹³C and δ¹⁸O values. CSL oxygen isotope determinations are consistently lighter (0.4 - 0.6 o/oo) than UT determinations. Oxygen isotope determinations from the Marathon Research Lab are not consistent relative to the other two labs.

Stable carbon isotope determinations show only minor and apparently random interlab variations with a maximum
### TABLE A-5

**REPLICATE ANALYSES OF LIMESTONE STANDARDS FOR STABLE CARBON AND OXYGEN ISOTOPES**

Coastal Science Laboratories (CSL)

<table>
<thead>
<tr>
<th></th>
<th>NBS-20</th>
<th>LSU Solenhofen</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$\delta^{13}$C</td>
<td>$\delta^{18}$O</td>
</tr>
<tr>
<td>7-82</td>
<td>-1.3</td>
<td>-4.1</td>
</tr>
<tr>
<td>8-82</td>
<td>-0.9</td>
<td>-4.2</td>
</tr>
<tr>
<td>11-82</td>
<td>-1.1</td>
<td>-4.3</td>
</tr>
<tr>
<td>9-83</td>
<td>-1.0</td>
<td>-4.3</td>
</tr>
<tr>
<td>Mean ± S.D.</td>
<td>-1.1 ± 4.2 ±</td>
<td>3.0 ± 2.9 ±</td>
</tr>
</tbody>
</table>

Marathon Oil Laboratory

<table>
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<tr>
<th></th>
<th></th>
<th>12-82</th>
</tr>
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<tbody>
<tr>
<td></td>
<td></td>
<td>+3.0</td>
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University of Texas (UT)

<p>| | | | | | | |</p>
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<tbody>
<tr>
<td></td>
<td>L.S. Land</td>
<td></td>
<td>8-80</td>
<td>+2.78</td>
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</tr>
<tr>
<td>&quot;</td>
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<td>+2.77</td>
<td>-2.54</td>
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<tr>
<td>&quot;</td>
<td></td>
<td>2-81</td>
<td>+2.70</td>
<td>-2.72</td>
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<tr>
<td>&quot;</td>
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<td>+2.69</td>
<td>-2.74</td>
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<td></td>
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<tr>
<td>D.A. Budd</td>
<td></td>
<td>7-82</td>
<td>+2.79</td>
<td>-2.50</td>
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<tr>
<td>Mean ± S.D.</td>
<td></td>
<td>2.75 ± 2.65 ±</td>
<td>0.05</td>
<td>0.12</td>
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</tr>
</tbody>
</table>

Note: All analyses in o/oo relative to PDB
## TABLE A-6

<table>
<thead>
<tr>
<th>Sample</th>
<th>CSL</th>
<th>UT</th>
<th>Marathon</th>
<th>Mean</th>
<th>CSL</th>
<th>UT</th>
<th>Marathon</th>
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</thead>
<tbody>
<tr>
<td>F-9-2</td>
<td>1.2</td>
<td>1.8</td>
<td>1.15</td>
<td>1.38</td>
<td>-0.2</td>
<td>0.4</td>
<td>-0.23</td>
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<tr>
<td>XRI-239</td>
<td>-7.1</td>
<td>-6.5</td>
<td>-6.85</td>
<td>-6.82</td>
<td>-0.3</td>
<td>0.3</td>
<td>-0.03</td>
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<tr>
<td>LSU Sol. Std.</td>
<td>-2.9</td>
<td>-2.5</td>
<td>-3.2</td>
<td>-2.9</td>
<td>0.0</td>
<td>0.3</td>
<td>-0.3</td>
</tr>
<tr>
<td>F-12-5A</td>
<td>3.5</td>
<td>3.9</td>
<td>3.98</td>
<td>3.79</td>
<td>-0.3</td>
<td>0.1</td>
<td>0.18</td>
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<tr>
<td>F-12-5B</td>
<td>3.4</td>
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<td>3.97</td>
<td>3.69</td>
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<td>0.28</td>
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<td></td>
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<td>0.22</td>
<td>0.27</td>
<td>-0.02*</td>
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<table>
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<th>δ13C</th>
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<td>F-9-2</td>
<td>1.9</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
<td>0.1</td>
<td>0.0</td>
<td>0.0</td>
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<tr>
<td>XRI-239</td>
<td>-9.8</td>
<td>-9.6</td>
<td>-9.9</td>
<td>-9.8</td>
<td>0.0</td>
<td>0.2</td>
<td>-0.1</td>
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<tr>
<td>LSU Sol. Std.</td>
<td>3.1</td>
<td>2.8</td>
<td>3.0</td>
<td>2.9</td>
<td>0.2</td>
<td>-0.1</td>
<td>0.1</td>
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<tr>
<td>F-12-5A</td>
<td>2.3</td>
<td>2.1</td>
<td>2.09</td>
<td>2.16</td>
<td>0.1</td>
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<td>-0.07</td>
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<tr>
<td>F-12-5B</td>
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<td>2.08</td>
<td>2.19</td>
<td>0.1</td>
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<td>-0.11</td>
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<tr>
<td>Mean deviation</td>
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<td>0.10</td>
<td>0.0</td>
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</table>

Note: All analyses in o/oo relative to PDB
* Mean absolute difference = 0.20

Samples F-9-2, XRI-239, and LSU Sol. Std. are calcite.
Samples F-12-5A and F-12-5B are dolomite.
interlab difference of 0.3 o/oo (Table A-6). Therefore, the accuracy of CSL stable carbon and oxygen isotope analyses is apparently similar to stable isotope laboratories at the University of Texas (Austin) and Marathon Oil Company.
VITA

Arthur Henry Sailer was born March 30, 1956 in Kansas City, Missouri, where he spent the largest portion of his childhood. After graduating from Shawnee Mission South High School (Overland Park, Kansas), he attended the University of Kansas, where he received a B.S. degree in geology (1977). Arthur then moved to Palo Alto, California where he attended Stanford University and received a M.S. degree in geology (1980). His masters thesis involved a study of Pennsylvanian sedimentary rocks in north-central Nevada. Portions of that study are published in the Journal of Sedimentary Petrology (Sailer, A.H., and Dickinson, W.R., v.42, p.925-940). In December 1979, Arthur married Julia Ann Gray, and in August, 1980 the Sallers moved to Baton Rouge, Louisiana where Arthur began work on a Ph.D. in geology. Upon completion of his Ph.D. the Sallers will move to Tulsa, Oklahoma where Arthur will join the Cities Service Research Laboratory.
Candidate:       Arthur Henry Sailer

Major Field:     Geology (Petrology)

Title of Thesis:   Diagenesis of Cenozoic Limestones on Enewetak Atoll

Approved:

[Signature]
Major Professor and Chairman
[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:
April 27, 1984