48. GEOCHEMISTRY OF MIT AND TAKUYO-DAISAN CARBONATE PLATFORMS COMPARED WITH OTHER NORTHWEST PACIFIC GUYOTS DRILLED DURING LEG 144: IMPLICATIONS FOR THEIR DIAGENETIC HISTORY¹

Janet A. Haggerty² and Robert J. van Waasbergen²

ABSTRACT

Petrographic analysis, electron microprobe analysis, stable isotope geochemistry, and gas analysis of volatile components in fluid inclusions of platform limestones from MIT and Takuyo-Daisan guyots in the northwest Pacific show very little evidence of subaerial exposure. Thus, based on geochemical evidence, meteoric influences associated with subaerial exposure are unlikely to account for the 100- to 200-m-deep karstlike depressions observed in SeaBeam bathymetry of the summits of these two guyots.

The stable isotope geochemistry of the MIT and Takuyo-Daisan platform limestones is predominantly a marine signature. Electron microprobe analysis of the MIT lower platform limestones reveals early depositional and some early diagenetic environments characterized by high concentrations of sodium, potassium, sulfur, and strontium in the carbonates; these are interpreted as oxidizing marine or saline fluids. Late-stage cements in the lower platform are characterized by sodium, sulfur, iron, and manganese; these are interpreted as saline-reducing fluids. The bulk gas extracted from MIT and Takuyo-Daisan limestone samples included several generations of paleo-pore fluids from different diagenetic environments. Only two samples from MIT Guyot and one from Takuyo-Daisan Guyot contained air inclusions as evidence of intervals of vadose diagenesis. The majority of the samples contained H₂S as evidence for the migration of reducing fluids through these limestones during part of their diagenetic history; this concurs with interpretations taken from electron microprobe data. We speculate that generation of the 100- to 200-m-deep depressions on the surface of MIT and Takuyo-Daisan guyots could involve two forms of marine dissolution: dissolution of aragonitic components associated with the aragonite compensation depth, and dissolution associated with sulfate reduction deep within the platform.

The upper sections of limestone from Limalok and Wodejebato guyots in the Marshall Islands chain differ geochemically from those at MIT and Takuyo-Daisan guyots. In addition, the morphology of the Marshall Islands guyots is also different from MIT and Takuyo-Daisan guyots because of the presence of a well-developed pelagic cap and the absence of deep depressions within the platforms. At Site 873 on Wodejebato Guyot, there is evidence for two emersion events. A 5-m.y. hiatus between platform and pelagic sedimentation on Wodejebato Guyot supports the interpretation of platform exposure before final submersion. Typically, a 1- to 2-m.y. hiatus is associated with Marshall Islands guyots, which display no geochemical evidence of subaerial exposure. The 1.5-m.y. hiatus on MIT Guyot sheds doubt on significant subaerial exposure there.

INTRODUCTION

Leg 144 drilled five northwest Pacific guyots: Limalok (Site 871), Lo-En (Site 872), and Wodejebato (Sites 873-877) guyots in the Marshall Islands chain; MIT Guyot (Site 878) as an isolated feature midway between the Marshall Islands and Japan; and Takuyo-Daisan Guyot (Sites 879-880) in the Seiko cluster of the Japanese Seamount Province (Fig. 1). All five of the drilled guyots have either a cap or a sparse layer of pelagic sediment, but only four of these guyots have pelagic sediment immediately overlying a carbonate platform. The carbonate platform is underlain by a basal clay deposit resting atop the volcanic substrate (Premoli Silva, Haggerty, Rack, et al., 1993; Haggerty and Premoli Silva, this volume; Holmes, this volume).

The primary focus of this chapter is to compare the diagenesis of the older carbonate platforms on MIT and Takuyo-Daisan guyots with the younger platforms drilled in the Marshall Islands. To attain this goal, other objectives of Leg 144 pertaining to the diagenesis of the carbonate platforms must be examined: (1) determine the origin of the rough surface topography of MIT Guyot and Takuyo-Daisan Guyot in relation to the hypothesis of emergence and karsting of the shallowwater limestone cap before the final submersion; and (2) investigate the nature and variability of the perimeter ridges on Wodejebato and Takuyo-Daisan guyots.

In this chapter, we document the geochemical characteristics of platform limestones from the two northern mid-Cretaceous guyots: MIT and Takuyo-Daisan. Specifically, we present new petrographic analyses, cathodoluminescence results and electron microprobe analyses of the MIT platform limestones. These are additional analyses beyond those presented in van Waasbergen and Haggerty (this volume).

Other new geochemical data presented are carbon and oxygen stable isotope analyses from MIT and Takuyo-Daisan platform limestones, and analyses of fluid-inclusion volatiles that represent samples of paleo-pore fluids from these platform limestones. These data were evaluated with respect to the interpretation of the irregular topography of the platform summits, and were compared with the results from the Eocene platform limestones from Limalok Guyot and the Upper Cretaceous platform limestones from Wodejebato Guyot. Details of the geochemistry from these southern guyots are found in Camoin et al., Enos et al., Lincoln et al., and Opdyke et al. (all this volume) for Wodejebato Guyot, and Wyatt et al. (this volume) for Limalok Guyot.

BACKGROUND

Geology of Western Pacific Guyots

Many Pacific seamounts are flat-topped features that lie at depths between 1000 and 2000 m below sea level (mbsl). Hess (1946) documented 160 of these features in the Pacific when he defined the term guyot and speculated that guyots were Precambrian volcanic islands truncated by erosion. The presence of Cretaceous shallow-water carbonate deposits on the summits of some flat-topped seamounts or guyots was discovered by Hamilton (1956) during a 1950 surveying and dredging expedition of guyots in the Mid-Pacific Mountains. Since Hamilton's discovery, many other oceanographic expeditions (Heezen et al., 1973; Ladd et al., 1974; Premoli Silva and Brusa,

¹ Haggerty, J.A., Premoli Silva, I., Rack, F., and McNutt, M.K. (Eds.), 1995. Proc. ODP, Sci. Results, 144: College Station, TX (Ocean Drilling Program).

² Department of Geosciences, University of Tulsa, 600 S. College Ave., Tulsa, OK 74104, U.S.A.



Figure 1. Bathymetry of western Pacific seafloor showing the locations of Leg 144 drill sites and major seamount provinces.

1981; Schlanger and Premoli Silva, 1981; Haggerty et al., 1982; Haggerty and Premoli Silva, 1986; Lincoln and Schlanger, 1991; Laurs et al., 1992; Winterer et al., 1993) have documented the existence of Pacific Cretaceous shallow-water, limestone-bearing guyots and seamounts beyond the Mid-Pacific Mountains to include features to the east in the northern and southern Line Islands, the Emperor Seamounts to the north, and the Magellan Seamounts, Marshall Islands, and Japanese Seamounts to the west (Fig. 1). These structures, nowsubmerged Cretaceous carbonate platforms, are preserved largely undisturbed by tectonic processes that deform similar deposits found on the margins of the ancient Tethys ocean.

Menard (1958) suggested that a mid-Pacific region associated with atolls and guyots more than 10,000 km long and 4000 km wide was previously a rise on the basis of subsidence and its mid-basin location. In today's tectonic terminology, this would be called a mid-plate swell rather than a mid-ocean ridge (Menard, 1984). Using the heights of the platform summits above the seafloor, Menard (1964) developed a Pacific paleobathymetric map and named this feature the Darwin Rise, which encompasses the anomalously shallow basinal region from the Tuamotus to the Marshall Islands.

McNutt and Fisher (1987) described a region of seafloor in the south Pacific that is also too shallow for its age. They attributed this to the presence of thermally anomalous lithosphere in this region, which they called the South Pacific Superswell. McNutt and Fisher (1987) also commented on the similarity between the morphologic and petrologic characteristics of the South Pacific Superswell and the Cretaceous Darwin Rise; they proposed that the South Pacific Superswell is the modern equivalent of the Darwin Rise. McNutt et al. (1990) concluded from bathymetric and gravity data that Cretaceous guyots in the Darwin Rise region were likewise underlain by anomalous lithosphere.

Previous Investigations

Drilling and dredging of many of these guyots showed that deposition of platform carbonates in the western Pacific began in the late Barremian to early Aptian in the Mid-Pacific Mountains (Heezen, et al., 1973; Shipboard Scientific Party, 1973; Ladd et al., 1974; Matthews et al., 1974; Winterer et al., 1993; van Waasbergen et al., 1990) and in the Japanese Seamounts Province (Konishi, 1985, 1989; Grötsch, 1991; Grötsch and Flügel, 1992; Sager, Winterer, Firth, et al., 1993), and lasted until late Albian to Cenomanian time. In the Marshall Islands group, Albian carbonate platforms developed after a mid-Cretaceous pulse of volcanism, and then again during the Campanian-Maastrichtian and Eocene after a second pulse of Late Cretaceous volcanism (Schlanger and Premoli Silva, 1981; Lincoln, 1990; Lincoln et al., 1993; Bergersen, 1993; Premoli Silva, Haggerty, Rack, et al., 1993; Haggerty and Premoli Silva, this volume).

Sedimentologic and paleontologic evidence from the Marshall and Line islands suggests that many of the now-submerged Cretaceous islands of those regions underwent sedimentation, interrupted by periods of either subaerial exposure or marine hardground formation (Schlanger and Premoli Silva, 1981; Schlanger et al., 1981; Haggerty et al., 1982; Lincoln et al., 1993).

Dredged Cenozoic limestones from seamounts in the Line Islands, submersible retrieved Cenozoic limestones from Johnston Atoll, and Cretaceous limestones dredged from the Magellan Seamounts were investigated for their diagenetic history (Haggerty, 1983, 1985; Aydemir and Haggerty, 1985; Orban and Haggerty, 1987). Although some of the samples had petrographic characteristics, textures, and mineralogy compatible with meteoric phreatic diagenesis, all geochemical evidence displayed a marine signature (Haggerty, 1983, 1985). Haggerty (1984) compared the biostratigraphic, depositional, and diagenetic histories of seamounts in the southern Line Islands interpreted from sedimentary rocks with geophysical models for vertical tectonism. Although rejuvenescent Eocene volcanism and uplift occurred in that area, only marine diagenesis took place; hence, there was insufficient uplift for emergence.

Previous geophysical studies of Mid-Pacific Mountain guyots, Wake Seamounts, and guyots in the Japanese Seamount Province (Winterer and Metzler, 1984; van Waasbergen et al., 1989; Winterer et al., 1989; Winterer and van Waasbergen, 1989; van Waasbergen et al., 1990; van Waasbergen and Winterer, 1993) suggest that some of their carbonate-capped summits were deeply eroded by subaerial processes during a period of lower relative sea level. This evidence takes the form of deep (100-200 m) depressions visible in multibeam bathymetric data (Fig. 2) and acoustic profiles (Winterer and Metzler, 1984; van Waasbergen and Winterer, 1993), as well as the occurrence of terraces and apparent drainage channels on and around the summit regions of many of these guyots. Perimeter ridges that occur on some of these guyots (Fig. 3) were interpreted as relict features from subaerial erosion (van Waasbergen and Winterer, 1993). The scale of this erosional relief suggests exposure of the summits on the order of 200 m above sea level for a significant period of time before final drowning,

Previous geochemical work on dredged Cretaceous limestone from the Mid-Pacific Mountains and from guyots in the Wake and Japanese Seamount Province (Heezen, et al., 1973; Winterer and Metzler, 1984; van Waasbergen, 1993; Winterer et al., 1993) used stable isotope geochemistry and X-ray diffraction analysis to determine whether geochemical evidence for subaerial exposure of summit limestone exists. The results of these studies showed that most of the diagenetic elements in these samples could be attributed to precipitation in the marine environment, although highly negative (light) oxygen isotopic values in some of the earliest diagenetic material suggested the influence of freshwater (van Waasbergen, 1993).

MIT and Takuyo-Daisan guyots in the northwest Pacific, drilled during Leg 144, have irregular topography characterized by pronounced vertical relief. Bathymetric maps of the guyot summits (Figs. 2 and 3) display features that closely resemble the surface topography of many present-day karst terrains. Depressions, as deep as 200 m, occur on the summit plateau of MIT Guyot (Fig. 2). Site 878 is located on a topographic high on the summit plateau of MIT Guvot. The summit of Takuyo-Daisan Guyot (Fig. 3) is characterized by depressions as deep as 75 m and a perimeter ridge. This ridge is composed of discontinuous segments 600 to 1000 m wide and up to 110 m high. These perimeter features are best developed along the northeast and south sides of the summit platform. Site 879 is located on the southern perimeter ridge of the summit of Takuyo-Daisan Guyot. A primary objective of this paper is to characterize geochemically the carbonate diagenesis of these guyots and to evaluate the origin of the irregular topography on MIT and Takuyo-Daisan guyots.

METHODOLOGY

Microscopy

The upper and lower platform units, as well as the polymictic breccia, from MIT Guyot and the platform limestone from Takuyo-Daisan Guyot were surveyed, and representative samples were selected aboard ship. Cathodoluminescence and blue-violet fluorescence microscopy applied to polished thin sections revealed cement stratigraphy and other geochemically based microstructures. The blue-violet fluorescence microscopy is especially useful for revealing the relict microstructure of altered bioclasts.

Minerals with a suitable electron configuration produce cathodoluminescence from the emission of light during electron bombardment (Smith and Stenstrom, 1966), or fluorescence from the emission of a longer wavelength of light than the excitation wavelength (van Gijzel, 1979). Chemical inhomogeneities in grains or cements from crystal zonation, the presence and abundance of fluid or solid inclusions, or differences in mineralogy can produce different colors or variations in the intensity of the luminescence. The color and hue of cements are used by some investigators (Barnaby and Rimstidt, 1989) to suggest the Eh-pH conditions at the time of cement formation. Work by Machel (1985) has noted that other factors must be considered, such as the availability of various activators, sensitizers, and quenchers.

The operating conditions for the Nuclide Luminoscope ELM-2B mounted on a Nikon Optiphot-pol petrographic microscope were as follows: 10- to 12-kV accelerating voltage, 0.8- to 1.0-mA beam current, and 5- to 10-mm-diameter beam.

Electron Microprobe Analysis

Elemental analyses in carbonate minerals are commonly used as a means of determining chemical variations in diagenetic fluids and inference is therefore made about the diagenetic environment. Other factors that may affect the elemental composition of a mineral are (1) the presence of solid and fluid inclusions incorporated into the crystal lattice, (2) the concentration of elements in the precursor mineral before neomorphic replacement, (3) the rate of ion diffusion across an intercrystalline diffusion gradient, and (4) the rate of crystallization. These additional factors are considered with the interpretations offered for each of the samples presented. Details of the electron microprobe analysis and the methodology for analysis of silver-coated carbonate thin sections are given in van Waasbergen and Haggerty (this volume). Only a brief description of the technique is listed below.

Polished thin sections were coated with silver following the method of Smith (1986). Results produced with this coating differ from those produced with traditional carbon coating; detection limits are lowered and spatial resolution enhanced. The operating conditions for the Cameca 3-spectrometer electron microprobe were an accelerating potential of 20 kV, a sample current of 20 nA for dolomite and 12 nA for calcite, employing a 4-µm-diameter focused beam. Counting times on the peak and background for each calcite analysis were 60 seconds for Ca and Mg and 360 for Fe, Mn, Sr, Na, K, and S. Counting times for Ca and Mg in dolomite were 10 and 300 for Fe, Mn, Sr, Na, and S. With the exception of Sr, elemental analysis employed the Ka peak. The $Sr-L_{\alpha}$ peak analyzed using the thallium acid phthalate crystal (TAP), rather than with the traditional pentaerythritol crystal (PET), provided greater intensity of X-rays and lower detection limits. The only drawback to analysis of Sr using this crystal is if interference occurs from the Si-KB peak. If silicates are present, and are excited by the beam or secondary fluorescence, then the $Si-K_{\beta}$ peak will interfere with the Sr-L_a peak, producing high background counts for Sr, and difficulty with Sr detection.

Detection limits for each element in calcite were Ca: 180 ppm, Mg: 110 ppm, Fe: 110 ppm, Mn: 100 ppm, Na: 60 ppm, Sr: 93 ppm, K: 80 ppm, and S: 128 ppm. Detection limits for each element in dolomite were Ca: 290 ppm, Mg: 225 ppm, Fe: 86 ppm, Mn: 81 ppm, Na: 55 ppm, Sr: 92 ppm, and S: 86 ppm. Sulfur was analyzed during most, but not all, microprobe analyses.

Stable Isotope Geochemistry

Carbon and oxygen stable isotopic compositions of 76 samples from Hole 878A in MIT Guyot and 11 samples from Hole 879A in Takuyo-Daisan Guyot were determined. Powdered samples were removed from sample billets by a small diameter bit in a hand-held drill assembly under a binocular microscope. Most of the Site 878 samples were taken from micritic matrix material in wackestones and packstones, and from micritic limestone clasts in the volcanic breccia portion of the section. In a few places, samples were taken from replaced mollusk shells and secondary spar cement. For samples from



Figure 2. SeaBeam bathymetry and *JOIDES Resolution* ship tracks across the summit of MIT Guyot. Bathymetric data were collected during Roundabout Cruise 10. On the enlarged map, depths shallower than 1450 m are contoured as thin dotted lines with a 25-m contour interval. Tick marks show downhill directions on the innermost closed contours. The inset map shows the location of the enlarged area on the overall guyot bathymetry.

Site 879, bulk rock samples and secondary spar cements were analyzed for carbon and oxygen stable isotopes.

Roasting of samples at 380°C for 1 hr removed volatile contaminants. Carbon dioxide evolved from the samples reacted with 100% anhydrous phosphoric acid at 75°C in individual reaction vessels. The carbon dioxide gas was analyzed on a Finnigan MAT 251 mass spectrometer; analyses are reported relative to the PeeDee belemnite (PDB) standard. Analytical error was no greater than $\pm 0.055\%$ for $\delta^{18}O$ and $\pm 0.04\%$ for $\delta^{13}C$. All the carbon and oxygen isotopic analyses presented in this volume were produced at the University of Michigan Stable Isotope Laboratory, thereby removing potential variation caused by analysis on different instruments and decreasing variation associated with sample preparation.

Fluid-inclusion Mass Spectrometry

To assess the nature of the diagenetic fluids involved with postdepositional history of these platforms, gas analysis of the volatile



Figure 3. SeaBeam bathymetry and *JOIDES Resolution* ship tracks across the summit of Takuyo-Daisan Guyot. Bathymetric data were collected during Roundabout Cruise 10. On the enlarged map, depths shallower than 1600 m are contoured as thin dotted lines with a 25-m contour interval. Tick marks show downhill directions on the innermost closed contours. The inset map shows the location of the enlarged area on the overall guyot bathymetry.

components in the fluid inclusions was undertaken. Fluid-inclusion mass-spectrometric analysis was conducted using a UTI100C quadrupole mass spectrometer. Roasting of samples at 200°C overnight removed any superficial volatile contaminants that were acquired by handling or previous sampling preparation. The loaded sample chamber was open to the mass-spectrometer, turbo-molecular pump for at least 15 min before sample analysis. This procedure removed all air in open pores, including that trapped in micropores. Crushing samples under vacuum released volatile components from the fluid inclusions; the bulk composition of the evolved gas is then analyzed by mass spectrometry. The analysis of the bulk gas composition is similar to the method of Barker and Smith (1986) used for analysis of gases from individual fluid inclusions. We analyzed 66 bulk rock samples from Hole 878A in MIT Guyot and 11 bulk rock samples from Hole 879A in Takuyo-Daisan Guyot. The bulk gas evolved from the sample may contain numerous generations of paleo-pore fluids from many different diagenetic environments to which the sample was exposed. Therefore, it is possible to have marine water, meteoric water, reducing pore water, and/or air trapped in different inclusions within the same carbonate rock. During the process of neomorphism, bioclasts may trap paleo-pore fluids, but they may also contain seawater or biologic fluids trapped in the skeleton during formation by the organism.

Fluid inclusions are commonly dominated by water, with the second greatest contributor being carbon dioxide (Roedder, 1984; Shepard et al., 1985). When fluid inclusions containing seawater are

volatilized, they will produce a response at mass/charge ratios (atomic mass unit = AMU) that are characteristic of water. In addition, these seawater inclusions typically have a response at AMU of 48, which is attributed to the presence of SO⁺ derived from dissolved sulfate in seawater (Haggerty and Smith, 1988). Because seawater inclusions would invariably be present (as documented by the ecologic environment of the organisms contributing their skeletal remains to these sediments, the initial depositional environment of the sediment, and the prevalent marine stable isotopic signature of these limestones), no attempt was made during analysis of the mass spectra to differentiate between marine and meteoric fluids. If meteoric fluids were present, the seawater mass spectra would overwrite the meteoric water response in a bulk gas analysis. This method can therefore not be used to detect or rule out the presence of meteoric fluids. Small amounts of air trapped along with fluids can be detected, and can be used as an indication of a vadose environment.

RESULTS

Petrography of Limestones from MIT Guyot

Drilling operations at Site 878 (Premoli Silva, Haggerty, Rack, et al., 1993) penetrated 910 m into the top of MIT Guyot. Beneath a 3.2-m veneer of pelagic sediments, a 720-m-thick section of Cretaceous platform carbonates was drilled, which rests on the underlying volcanic edifice. This section can be stratigraphically divided into a 395-m-thick upper and a 120-m-thick lower platform, separated by a 205-m-thick interval of polymictic breccia composed of volcanic and carbonate clasts (Premoli Silva, Haggerty, Rack, et al., 1993). We examined new thin sections of available sample material from the three intervals to determine compositions, diagenetic elements and luminescence properties of the materials.

Upper Platform Limestones, Interval 144-878A-1R-CC, 0 cm, to -43M-1, 44 cm (3.2–399.74 mbsf)

Limestones in the upper platform consist of skeletal packstone, mudstone, and wackestone with intervals of grainstone. Allochems consist mainly of peloids and mollusk skeletal grains (fragments of gastropods and rudist bivalves). Minor constituents include benthic foraminifers, fragments of sponges, and fragments of green and bluegreen algae. In intervals of grainstone, large agglutinated benthic foraminifers occur. In the finer grained intervals, the matrix consists of lime mud (micrite) which has neomorphosed to a very fine crystalline spar with a porous, chalky texture. Most of the skeletal grains in these intervals are strongly micritized and in many places are replaced by fine crystalline calcite. Moldic porosity is very abundant in most samples. Fenestral porosity occurs in Sample 144-878A-13R-1, 16-22 cm, at 115.26 meters below seafloor (mbsf). Primary intragranular pores, such as the cellular structures of algal and sponge grains, are generally occluded with fine equant spar. Molds and fenestrae remain largely uncemented, except for a fringe of finely crystalline equant spar. Fenestrae have a geopetal infilling composed of thin micritic laminae that are partly cemented by very fine equant spar.

Intervals of grainstone tend to be much better cemented, commonly by an early generation of bladed fringing spar, which was followed by a pore-filling finely crystalline equant spar. The fringing spar is rich in inclusions, which suggests it may be neomorphosed from aragonitic isopachous acicular cement. Around rare echinoid grains, patches of syntaxial cement occur that often enclose several grains in a single crystal. Large mollusk and rare sponge fragments in both grainstone and packstone intervals are commonly replaced by a very coarse, blocky crystalline spar cement that forms a tightly interlocking crystal mosaic. In Sample 144-878A-3R-1, 66–67 cm, coarse columnar spar cement rich in inclusions fills a sponge fragment and replaces part of the original sponge structure.

Polymictic Volcanogenic Breccia, Interval 144-878A-44M-1, 0 cm, to 65R-6, 22 cm (406.1–604.3 mbsf)

This breccia contains both basalt and limestone clasts, which can be divided into two visually distinct sections. These sections grade from carbonate rich at the base to basalt rich at the top. Each section probably corresponds to a short-lived phreatomagmatic eruption from a single vent. Initially the eruptions explosively tore through pre-existing basalt and limestone platform, then, as activity continued, newly derived lavas (highly vesicular scoriaceous basalt) were incorporated into the eruptive products. In parts of the sections, the steep dip of the bedding as well as curved or overturned beds indicate deposition on a steep slope with some slumping (Premoli Silva, Haggerty, Rack, et al., 1993; Christie et al., this volume).

Samples from the brecciated zone contain abundant well-rounded clasts of fine-grained limestone in a matrix of altered volcanic glass fragments and lime mud. Carbonate clasts range in size from finesand to tens of centimeters in diameter. Most of the carbonate clasts consist of mudstone and wackestone that contain rare to common miliolid foraminifers and algal fragments, as well as fragments of bivalves and gastropods that are completely replaced by clear, equant spar. In some intervals, clasts of grainstone occur in the breccia that include well-cemented ooids and coated grains as well as fragments of coral and mollusks.

The carbonate clasts commonly contain small fractures and vugs filled with clear, fine equant spar cement that terminate at grain boundaries, indicating that the material was well indurated before the eruption. Stylolites are common in fine-grained carbonate clasts in Sample 144-878A-63R-3, 133–138 cm (579.42 mbsf), and deeper samples. Many of the micritic clasts have a thin (a few tens of μ m) rind or a rim of discolored fine-grained material that contains noncarbonate minerals as shown in the microprobe results. In Sample 144-878A-44M-2, 0–5 cm (407.6 mbsf), clusters of pyrite, identified by reflected light petrography, occur in the larger fine-grained carbonate clasts. No pyrite was seen in the matrix of this sample, indicating that the pyrite probably predates the eruption and was associated with deposition in an anoxic environment.

One grainstone interval, Sample 144-878A-51R-06, 137–139 cm (472.74 mbsf), is cemented with pre-eruption fringing bladed spar, and fine equant pore-filling spar cements. Large mollusk fragments in this sample are replaced by very coarse, clear blocky spar in association with chalcedony. In other grainstone clasts, for example in Sample 144-878A-60R-5, 100–103 cm (556.04 mbsf), primary porosity is also occluded by a cryptocrystalline siliceous material. In these samples, chalcedony partially occludes intergranular pore space in the limestone portions of the rocks and fills vesicles of volcaniclastic particles.

The matrix of the breccia consists of fine lime mud that becomes increasingly clay rich toward the bottom of the section. In several intervals, the matrix was neomorphosed to microspar and includes very small (about 10 μ m in width) rhombohedral crystal molds, possibly indicative of an episode of dolomitization. Such molds occur in Samples 144-878A-55R-2, 130–135 cm (505.07 mbsf), -62R-2, 134–139 cm (571.15 mbsf), and -63R-2, 13–18 cm (579.72 mbsf). Alteration of volcanic fragments can also cause the matrix around grains to become stained bright red (e.g., in Sample 144-878A-65R-5, 135–138 cm [603.93 mbsf]).

Lower Platform Limestones, Interval 144-878A-65R-6, 22 cm, to 78R-1, 44 cm (604.3–722.54 mbsf)

Two rock types dominate in the lower platform: grainstone of peloids and skeletal debris, and packstone-wackestone of sand-sized micritic grains, ooids, rock fragments, and a variety of bioclasts, including mollusk fragments, coral, echinoid debris, and benthic foraminifers. The grainstone intervals vary in degree of diagenetic alteration from barely cemented, highly porous sand to well-cemented calcarenite. Sample 144-878A-71R-1, 48-55 cm (655.38 mbsf), contains a well-sorted assemblage of sand-sized peloids, rock fragments, and skeletal debris, including poorly preserved mollusk fragments and echinoid debris. Grains are tightly interlocking, even sutured at point contacts, but almost no crystalline cement occurs. Primary porosity remains high, and most mollusk fragments retain original shell microstructures. In contrast, Sample 144-878A-71R-1, 119-123 cm (656.09 mbsf), which consists of a similar grain assemblage, has undergone more diagenetic change: coarse sand-sized skeletal particles, peloids, and limestone rock fragments are cemented with coarse bladed fringing spar; and the remainder of the pore spaces are filled with coarse equant blocky spar. Echinoid grains in this sample are enclosed in optically continuous syntaxial cement. Mollusk shell fragments are completely replaced with equant crystalline spar cement. Most of the grainstone samples studied were intermediate between these extremes.

Samples of packstone generally contain abundant moldic porosity and only minor crystalline cement. Grains are tightly compacted with interstitial lime mud, and stylolites are common. Isolated dolomite crystals 50- to 100- μ m in size commonly occur in the wackestone matrix and in greater concentrations in the stylolites. The dolomite grains are described in the data report by van Waasbergen and Haggerty (this volume).

Moldic porosity is abundant in these samples, with minor amounts of fine equant spar lining the insides of the molds. The most common form of cementation is a fine, equant, inclusion-rich spar. Mollusk shell fragments are commonly replaced with a similar equant spar; grains in which relict microstructures are preserved are common, however.

Cathodoluminescence Studies

None of the material from the upper platform showed significant cathodoluminescence. Only rare, and very small, luminescent spots occur, generally in the equant spar cement closest to the edges of grains in grainstone intervals.

In the polymictic volcanogenic breccia interval, cathodoluminescence shows that most of the pre-eruption cements are dully to nonluminescent. Posteruption cements that fill pore spaces in the sheltered portions of some samples, as well as the vesicles of the glassy volcanic fragments, are brightly luminescent. The coarse blocky spar that replaces mollusk shells in carbonate clasts in many samples is also brightly luminescent.

Lower platform samples show only minor amounts of luminescence, mostly in the late-stage, coarsest crystalline cements. Sample 144-878A-71R-1, 119–123 cm (656.09 mbsf), shows tightly banded, alternately bright and nonluminescent zones in the coarse void-filling cement (Fig. 4A), indicative of rapidly fluctuating redox conditions and/or pore fluid compositions during formation of this cement.

Microprobe Analyses

Limestones from the upper platform interval rarely have much cementation and show little to no luminescent cements; therefore, these were not a priority for electron microprobe analysis. These observations, coupled with data obtained from the microprobe analyses of nonluminescent intervals in the lower platform, may indicate that diagenetic conditions above the breccia zone remained normal marine, or that an insufficient supply of activators, sensitizers, and quenchers were incorporated into the cements during precipitation under reducing conditions to generate luminescence.

In addition to the analyses presented in van Waasbergen and Haggerty (this volume) for limestones from the lower carbonate platform on MIT Guyot, additional samples from the polymictic breccia and the lower platform intervals of MIT Guyot were analyzed. Tabulated analytical results from the electron microprobe analyses are given in the Appendix.

Polymictic Volcanogenic Breccia Zone

In samples from the top of the breccia zone, all the analyzed limestones consist of low-magnesium calcite, with magnesium values rarely exceeding 2 wt%. Luminescent cements contain elevated concentrations of manganese (up to 5000 ppm), and lower concentrations of iron (up to 1200 ppm). Strontium concentrations were uniformly low, rarely exceeding the detection limit of 93 ppm; interference from adjacent silicates, if present, during microprobe analysis cannot be discounted as affecting the measured strontium concentrations. Potassium and sodium concentrations vary from relatively high (400–1000 ppm K, 1000–2000 ppm Na) in pre-eruption, fracture-fill cements within the carbonate clasts to below detection in later stage, luminescent cements. Concentrations of sulfur (up to 1200 ppm) are generally significant only in places with high sodium and potassium concentrations, but not all analyses include measurements for sulfur.

Sample 144-878A-44M-2, 0-5 cm (407.6 mbsf)

This sample is primarily composed of sand- to granule-sized carbonate and volcanic particles (Fig. 5A). Many carbonate grains contain fractures that are filled with clear equant sparry calcite and the majority of the carbonate grains have thin (up to 2 mm) rinds of finegrained, greenish gray material similar to micrite. Some carbonate clasts contain crystals and crystal aggregates of pyrite. The volcanic and carbonate materials form a closely packed grainstone texture cemented by clear equant calcite (up to 40 μ m-diameter crystals).

The results of a microprobe analysis of this sample are shown in Figure 5B. We analyzed along a transect from a micritic carbonate grain (points 1-3), through the greenish gray outer rind (points 4-6), into brightly luminescent equant spar cement (points 7-9). All points analyzed had a low magnesium content (<0.5 wt%). The iron concentration is consistently high (approximately 1000 ppm) in the micrite relative to much lower concentrations in the luminescent cement. The manganese concentration is higher in the cement than in the grain; the raised concentration accounts for the luminescence of the cement. Other elements are fairly constant in concentration throughout, with the exception of the points through the greenish gray rind. The rind shows low calcium and very high iron, potassium, and sodium concentrations; it probably contains noncarbonate materials such as clay or other silicates. This suggests that the rind formed during or shortly after eruption from interaction with young, warm volcanic material. The high iron concentrations could be attributed to alteration in reduced pore fluids; however, the low manganese and calcium concentrations and the sympathetic variations among iron, potassium, and sodium concentrations suggest that the composition of the rind is contaminated with noncarbonate minerals.

A second microprobe transect across this sample (Fig. 6A) was measured from the center of one of the micritic clasts (points 1–3), across a small internal (pre-eruption) fracture filled with nonluminescent equant sparry calcite (points 4–7), and back into micrite (point 8). The analytical results are shown in Figure 6B. Both sodium and potassium concentrations are relatively high (800–1800 ppm Na, 250–900 ppm K) in the micritic material, which suggests an origin in a hypersaline, restricted marine environment. Significant sulfur concentrations (up to 500 ppm) in the micrite support this hypersaline interpretation; the sulfur concentrations are uniformly low (typically <250 ppm) throughout this transect.

Sample 144-878A-46M-1, 85-89 cm (419.35 mbsf)

This is a grainstone of sand-sized micritic particles and poorly preserved fragments of mollusk shells that are completely replaced



Figure 4. **A.** Thin-section photomicrograph of Sample 144-878A-71R-1, 119–123 cm (656.09 mbsf), lower carbonate platform, under cathodoluminescence, shows the location of an electron microprobe transect. Analyses were spaced along the line of transect using a beam diameter of approximately 4 μ m. Scale bar represents 0.25 mm. **B.** Results of the microprobe analysis. The analysis traverses nonluminescent coarse spar (points 1–3), through a zone of tightly banded luminescence in the coarse spar (points 3–16), into nonluminescent bladed fringing spar cement (points 17–20) and a micritic grain (points 21–23).

Figure 5. **A.** Thin-section photomicrograph of Sample 144-878A-44M-2, 0-5 cm (407.6 mbsf), polymictic breccia, under cathodoluminescence, shows the location of an electron microprobe transect. Analyses were spaced along the line of transect using a beam diameter of approximately 4 μ m. Scale bar represents 0.25 mm. **B.** Results of the microprobe analysis. Transect through a portion of a micritic carbonate grain (points 1–3), to the greenish gray outer rind (points 4–6), into a brightly luminescent equant spar cement (points 7–9).

Figure 6. **A.** Thin-section photomicrograph of a second area in Sample 144-878A-44M-2, 0-5 cm (407.6 mbsf), polymictic breccia, shows the location of an electron microprobe transect in a carbonate clast. Analyses were spaced along the line of transect using a beam diameter of approximately 4 μ m. Plane-polarized light. Scale bar represents 0.3 mm. **B.** Results of the microprobe analysis. Transect from the center of a micritic clast (points 1–3), across a small internal (pre-eruption) fracture filled with nonluminescent equant sparry calcite (points 4–7), and back into micrite (point 8).

with coarse, blocky, strongly luminescent, sparry cement (Fig. 7A). The outsides of these particles are commonly coated with thick (up to 3 mm), irregular layers of micrite, which may be algal encrustations. The sandy portions of the rock are completely cemented with very fine-grained, clear, equant, sparry calcite. Minor interstitial mud occurs throughout.

The results of an electron microprobe transect of six points from sandy grainstone (points 1–2), through the micritic layers (points 3–4), and into brightly luminescent spar (points 5–6) are displayed in Figure 7B. The analyses show distinct variations in manganese and iron. These elements covary from moderately high concentrations (1100 ppm Mn, 600 ppm Fe) in the fine equant spar of the grainstone, to very low concentrations (<200 ppm Mn, <110 ppm Fe) in the micritic layers, to very high manganese and high iron concentrations (2400– 3000 ppm Mn, 300–500 ppm Fe) in the coarse luminescent spar. Based on the luminescence characteristics of this zone, the coarse spar that replaces a mollusk shell fragment formed after eruption in somewhat reducing fluids. The micritic coat of the shell contains abundant strontium and sulfur (approximately 500 ppm Sr and 1250 ppm S), significantly higher concentrations than found in the grain (<93 ppm Sr, 200 ppm S) and coarse spar (<93 ppm Sr, <100 ppm S).

Sample 144-878A-50R-3, 32-36 cm (458.11 mbsf)

This is a well-sorted, porous grainstone of closely packed, sandsized, micritic particles (Fig. 8A). They were initially cemented with what appears to be micritic meniscus cement. Porosity is partially occluded by very coarse-grained, euhedral to subhedral calcite that is brightly luminescent. In a few places, a single cement crystal encloses several smaller micritic grains (poikilitic texture).

The results of an electron microprobe transect of Sample 144-878A-50R-3, 32–36 cm (458.11 mbsf), is displayed in Figure 8B. Eleven points were analyzed from the edge of a micritic grain (points 1–5), into a proximal cement crystal (points 6–8), and then into a crystal closer to the center of the pore space (points 9–11). There is a pronounced increase in iron (up to 1000 ppm) and manganese (up to 3000 ppm) in the luminescent spar, compared to values obtained from the micrite, which are close to or below the detection limits for iron and manganese. Strontium is present in measurable amounts in the micrite (up to 250 ppm), and the sodium concentration (up to 150 ppm) remains relatively constant throughout the transect.

Lower Platform Carbonates

Electron microprobe analyses of pore-filling calcite cements in grainstones from the lower platform interval show strong fluctuations in strontium, sulfur, iron, and manganese concentrations. Sodium and potassium concentrations are generally very low (typically 100–200 ppm Na, below detection limits for K). Isolated dolomite grains in this interval contain significant amounts of sodium and sulfur (100–300 ppm Na, 100–400 ppm S), which are interpreted as indications of a saline environment of dolomite formation, possibly incorporating sulfate microinclusions. Some of the results presented in van Waasbergen and Haggerty (this volume) are summarized below.

Sample 144-878A-73R-1, 14-19 cm (674.34 mbsf)

This is a coarse grainstone of bioclasts (Fig. 9A–B). Abundant primary pore space is occluded with several generations of cements, which include fringing, inclusion-rich, bladed spar as well as clear, fine-grained, equant spar and coarse, clear, void-filling, blocky spar. The electron microprobe traversed this sample (Fig. 9B) from the micritic portion of a detrital grain (points 1–3), through bladed, inclusion-rich, fringing spar (points 4–7) and equant blocky spar (points 8–15), and back through fringing cement (points 16–19) into another micritic grain (points 20–22). The results show variations in trace elements, especially strontium and sulfur concentrations, which

appear to be the highest in the fringing cement. There is an antithetic variation between iron and manganese concentrations and an alternation in abundance of these elements, which probably explains the distinct luminescent banding observed in these samples. A sympathetic variation between sulfur and strontium is also present, although the relationship is not consistent for all data points. Elevated concentrations of strontium (up to 820 ppm) in bladed, inclusion-rich, fringing spar may be an indication that this was originally fibrous aragonite, neomorphosed to calcite.

Sample 144-878A-71R-1, 119-123 cm (656.09 mbsf)

This is a coarse grainstone of bioclasts including altered mollusk fragments and coral. Coated grains and lithic fragments of packstone and wackestone are also common particle types. Cementation has occurred in two stages: an early fringing, bladed spar followed by coarse, void-filling, blocky spar. These cements fill the original intergranular pore space as well as the secondary space where mollusk shell material was removed. The bladed spar is nonluminescent, whereas the coarse blocky spar contains zones of very closely spaced, luminescent and nonluminescent bands (Fig. 4A), which remain inside the present crystal boundaries. A short probe transect through the latest stage, blocky spar cement (Fig. 10A) shows only low concentrations of trace elements (Fig. 10B). A second, longer probe transect (Fig. 4A-B) in this sample crosses from nonluminescent coarse spar (points 1-3), through a zone of tightly banded luminescence in the coarse spar (points 4-16), into nonluminescent bladed fringing spar cement (points 17-20) and a micritic grain (points 21-23). Most of the trace elements in the coarse cement are present in very low amounts (none above 250 ppm). Manganese and iron concentrations fluctuate strongly in the banded luminescent zone with slightly offset peaks. Typically, higher iron concentrations coincide with higher sodium concentrations, whereas low iron concentrations coincide with only points where strontium concentrations are above detection limits.

The euhedral calcite crystal in Sample 144-878A-75R-1, 126–130 cm (694.76 mbsf; Fig. 11A), displayed little fluorescence and was thought to be dolomite before the electron microprobe analysis. One of the analyses (point 4) showed highly elevated sulfur (3841 ppm), sodium (1201 ppm), and strontium (575 ppm) concentrations (Fig. 11B); iron and manganese concentrations were below detection limits.

Dolomite crystals in Sample 144-878A-75R-1, 32–37 cm (693.82 mbsf; Figs. 12A–B and 13A–B) contain significant amounts of sodium (100–200 ppm) and sulfur (up to 405 ppm), as well as very minor amounts of iron (when present). Small neomorphic areas of calcite within the dolomite crystal show elevated sodium values (>200 ppm).

Discussion of Microprobe Results

The electron microprobe analyses of grains and cements in the uppermost part of the breccia zone show a consistent pattern of a reducing diagenetic environment following deposition of the limestone clasts with the basalt clasts. The preexisting limestone clasts that became incorporated into the polymictic volcanogenic breccia near the top of the section were lithified in an early-stage diagenetic environment that was slightly reducing with high salinity. This diagenetic environment that was slightly reducing with high salinity. This diagenetic environcentrations in the micrite. Below Core 144-878A-46M (420 mbsf), trace element values in the micritic particles that we analyzed with the electron microprobe show marine, oxygenated values. The preexisting clasts of limestone deposited within the breccia came from two different early diagenetic environments: (1) a slightly reducing environment with high salinity fluids and (2) an oxygenated marine environment.

High concentrations of strontium and sulfur in micrite coating a shell fragment in Sample 144-878A-46M-1, 85–89 cm (419.35 mbsf; Fig. 7A), probably represent the chemistry of the warm, saline marine waters in which the coating formed. The sediment was lithified before eruption in slightly reducing waters, as documented by the moderate

Figure 7. **A.** Thin-section photomicrograph of Sample 144-878A-46M-1, 85–89 cm (419.35 mbsf), polymictic breccia, under cathodoluminescence, shows the location of an electron microprobe transect. Analyses were spaced along the line of transect using a beam diameter of approximately 4 μ m. Scale bar represents 0.3 mm. **B.** Results of the microprobe analysis. A transect of 6 points across sandy grainstone (points 1–2), through micritic layers (points 3–4), into brightly luminescent spar (points 5–6).

Figure 8. **A.** Thin-section photomicrograph of Sample 144-878A-50R-3, 32-36 cm (458.11 mbsf), polymictic breccia, under cathodoluminescence, shows the location of an 11-point electron microprobe transect. Analyses were spaced along the line of transect using a beam diameter of approximately 4 μ m. Scale bar represents 0.3 mm. **B.** Results of the electron microprobe transect. The analyses traverse the edge of a micritic grain (points 1–5), into a proximal cement crystal (points 6–8), and into a crystal closer to the center of the pore space (points 9–12).

2 4 6 8 10 12 14 16 18 20 22 Point along transect
Figure 9. A. Thin-section photomicrograph of Sample 144-878A-73R-1, 14–19 cm (674.34 mbsf), lower carbonate platform, shows the location of a 22-point
electron microprobe transect. Crossed nicols. Scale bar represents 0.3 mm. B. Results of the electron microprobe transect. The analyses traverse the micritic portion
of a detrital grain (points 1–3), through bladed, inclusion-rich fringing spar (points 4–7), equant blocky spar (points 8–15), and back through fringing cement (points

100

0

16-19), into another micritic grain (points 20-22).

Figure 10. A. Thin-section photomicrograph of Sample 144-878A-71R-1, 119–123 cm (656.09 mbsf), lower carbonate platform. Arrow indicates the location of a short electron microprobe transect through a clear, late-stage, calcite spar cement. Plane polarized light. Scale bar represents 0.3 mm. B. Results of the microprobe analysis.

Points along transect

Figure 11. A. Thin-section photomicrograph of Sample 144-878A-75R-1, 126–130 cm (694.76 mbsf), lower carbonate platform. Arrow indicates location of a 12-point electron microprobe transect through a single inclusion-rich calcite crystal in a wackestone matrix. Individual microprobe spots are approximately 6 µm in diameter. Crossed nicols. Scale bar represents 50 µm. B. Results of the electron microprobe transect. Several of the analyses show distinct spikes in concentrations of magnesium, sodium, and sulfur, which may be attributable to the presence of sulfate microinclusions.

Figure 12. **A.** Thin-section photomicrograph of Sample 144-878A-75R-1, 32-37 cm (693.82 mbsf), lower carbonate platform, shows a 21-point electron microprobe transect through a single dolomite crystal in a large stylolite in wackestone. This crystal displays faint concentric fluorescent zoning under blue-violet light; zonation is not apparent under UV fluorescence. Individual microprobe spots are approximately 6 μ m in diameter. Plane polarized light. Scale bar represents 50 μ m. **B.** Results of the electron microprobe transect.

Figure 13. A. Thin-section photomicrograph of a second area in Sample 144-878A-75R-1, 32–37 cm, shows an electron microprobe transect through a single unzoned dolomite crystal. Individual microprobe spots are approximately $6 \mu m$ in diameter and form a curved track across the crystal. The irregular dark spot near the lower right corner of the crystal is a low-Mg zone. Plane polarized light. Scale bar represents 50 μm . B. Results of the electron microprobe transect.

iron and manganese values in the fine equant spar. Posteruption cements formed in more strongly reducing fluids. This interpretation concurs with the fluid-inclusion analysis, which shows the presence of H_2S trapped in the paleo-pore fluids of the sample.

In Sample 144-878A-50R-3, 32-36 cm (458.11 mbsf; Fig. 8B), a reducing diagenetic environment is indicated for the formation of the posteruption cement but not for the micritic clasts. The early diagenetic environment of the clasts before deposition in the breccia appears to be marine, based on sodium and strontium concentrations and the marine isotopic signature of the micrite. The interpretation of a later stage, reducing, diagenetic environment within the polymictic breccia is supported by the strong presence of H₂S in the paleo-pore fluids in a sample only 16 cm beneath Sample 144-878A-50R-3, 32-36 cm.

Unlike the previously discussed samples, the micrite in Sample 144-878A-50R-3, 32–36 cm, shows very low concentrations of trace elements. This suggests deposition in shallow marine water. The low but measurable, strontium concentrations (above detection limits) in the micrite support this interpretation.

Trace and major element compositions for samples from the lower platform interval show distinct fluctuations in trace elements in latestage, pore-filling calcite cements, which might be interpreted as fluctuations in pore-fluid compositions during later diagenesis.

Isolated dolomite rhombs in Sample 144-878A-75R-1, 126–130 cm (694.76 mbsf; Figs. 12A and 13A), show high values for sodium and sulfur, which are similar to the Galicia Margin dolomites (Daniel and Haggerty, 1988; Haggerty and Smith, 1988) formed by hypersaline fluids and not by mixing-zone fluids. Daniel and Haggerty (1988) also noted distinct spikes in the sulfur, sodium, and strontium concentrations in these Upper Jurassic–Lower Cretaceous dolomites from the Galicia Margin. Haggerty and Smith (1988) subjected these dolomites to mineral pyrolysis and showed that the microinclusions were sulfate minerals. The highly elevated sulfur, sodium, and strontium concentrations, with a lack of iron or manganese (below detection limits, if present) in Sample 144-878A-75R-1, 126–130 cm, from MIT Guyot, have been interpreted, therefore, to be a microinclusion of a sulfate mineral. This concurs with an interpretation of a hypersaline environment.

From analyses of zoned and unzoned dolomite crystals in Sample 144-878A-75R-1, 32–37 cm (693.82 mbsf; Figs. 12A–B and 13A–B), the crystals are interpreted to have formed in high-salinity fluids under possible mildly reducing conditions. Analysis of the volatile components of the fluid inclusions reveals the presence of H_2S , which would support the interpretation of dolomite formation in a reducing environment.

Although the micritic clasts in the polymictic breccia are stratigraphically several hundred meters above the dolomite-bearing carbonates, a striking similarity in the hypersaline environments of formation can be detected. The polymictic breccia was deposited from phreatomagmatic eruptions that tore through a preexisting basalt and limestone platform. The micritic clasts in the breccia came from the underlying platform, therefore. Hence, the dolomite rhombs and the micritic clasts were formed in a related hypersaline environment.

Stable Isotope Geochemistry of MIT and Takuyo-Daisan Carbonate Platforms

Results

The results of the stable isotope analyses of the samples from MIT Guyot are presented in Table 1, and those from Takuyo-Daisan Guyot in Table 2; also see Appendix. Figure 14 shows cross plots of these data for each of the guyots, and Figure 15 displays variations in the isotopic composition of these platform carbonates with respect to depth. The stable isotopic composition of limestones from MIT Guyot (Figs. 14 and 15) ranges from -6.2% to -0.5% $\delta^{18}O$ (mean -2.76%), and from -2% to +6% $\delta^{13}C$ (mean 3.04%); limestones from Takuyo-Daisan Guyot (Figs. 14 and 15) range from -2.4% to -0.4% $\delta^{18}O$ (mean -1.81%), and from +1.2% to +3.6% $\delta^{13}C$ (mean 2.59%).

The majority of the isotopic compositions of the carbonates from MIT and Takuyo-Daisan guyots are typical Cretaceous shallowmarine values. Lohmann (1988) summarized the secular variation of carbon and oxygen isotopic compositions of marine calcite cements during the Phanerozoic. The average Cretaceous carbon and oxygen isotopic compositions are +3% δ^{13} C and -2% δ^{18} O for reefal limestones (Lohmann, 1988).

When the isotopic compositions are plotted vs. sub-bottom depth (Fig. 15), one sees a predominantly normal marine trend for the upper limestone platform on MIT Guyot and a slight shift toward negative values in the carbon isotopic composition near the top of the breccia interval. The mid-breccia interval has a wider range of stable isotope ratios than the overlying platform, which suggests diagenetic fluids of variable composition. Toward the bottom of the breccia zone, the stable isotope ratios are normal marine. The lower platform unit on MIT Guyot shows a trend of increasingly more negative oxygen isotopes toward the contact with the underlying basalt. The profile of the stable isotopic composition of the platform limestone from Takuyo-Daisan Guyot plotted vs. depth is unremarkable; the compositions are essentially marine.

The most extreme oxygen isotopic value occurs at 236 mbsf (Sample 144-878A-26M-1, 27-30 cm) in the upper platform interval on MIT Guyot. A late-stage, coarse-spar cement shows an oxygen isotope ratio of -6.4‰, and a carbon isotope ratio of +2.7‰, indicating precipitation from warm marine waters, or potentially meteoric waters if the water/rock ratio is low. Another significant shift occurs in Core 144-878A-44M (407 mbsf) at the very top of the breccia zone. Here, a carbon isotope ratio of -2.0% was measured on a micritic clast in the volcanic breccia. A slight negative shift in the carbon isotope ratios persists to a lesser extent down to approximately Core 144-878A-52R (475 mbsf). The oxygen isotopic compositions of the carbonate components over this interval are toward the negative side of normal marine values (between -3‰ and -3.5‰), indicating that the waters were warm if they were marine. These values are also compatible with precipitation from an ¹⁸O depleted fluid either from meteoric influence in conjunction with a very low water/rock ratio, or from thermal influence associated with the phreatomagmatic eruption.

Discussion

The stable isotope geochemistry does not show pervasive meteoric influences that might account for the karstlike features observed in the SeaBeam bathymetry of the summits of MIT (Fig. 2) and Takuyo-Daisan (Fig. 3) guyots. Early diagenetic events, including exposure episodes, should leave signatures in some component of the limestone. The observed diagenetic trends are easily explained as resulting from the slow subsidence of the guyot through the water column. Only Sample 144-878A-44M-2, 0–5 cm (407.6 mbsf), from near the top of the polymictic volcanogenic breccia, contained a mudstone clast that produced carbon and oxygen isotope ratios indicative of subaerial diagenesis, or a peritidal environment influenced by organic matter and/or atmospheric CO_2 . A few other samples may have isotopic signatures potentially related to meteoric diagenesis if a low water/rock ratio was involved.

Where samples of various components were taken from the same interval, oxygen isotope ratios trend toward more positive values in increasingly younger diagenetic elements. The lowest oxygen isotope ratios were found in neomorphosed mollusk shell fragments, with values becoming more positive in micrite matrix subsamples, and more positive still in later stage, sparry cement overgrowths. This trend may be attributed to diagenesis in increasingly colder marine waters and may indicate that most of the visible diagenetic elements were formed or stabilized during subsidence after final submersion of the platform. If this is the case, then most of the visible dissolution occurred very early in the diagenesis of the sediments, either as a result of meteoric influences or from a very shallow aragonite lysocline.

Figure 14. Cross plot of carbon and oxygen stable isotopic composition of carbonates from Site 878 on MIT Guyot and Site 879 on Takuyo-Daisan Guyot.

Figure 15. Oxygen and carbon stable isotopic composition of carbonates from Site 878 on MIT Guyot and Site 879 on Takuyo-Daisan Guyot plotted vs. depth. Boundaries of major stratigraphic intervals at Site 878 are indicated.

Table 1. Isotopic analyses, Site 878 (MIT Guyot).

-							
Core, section,	013.0	c18 c	Depth				
interval (cm)	9C	0°*6	(mbsf)	Description			
144.0704							
144-8/8A-	2.00	1.00	2.05	D. H. J. J. J. J. J. H.			
1R-CC, 10-12	2.89	-1.22	3.25	Bulk sample: indurated charky wackestone			
2R-1, 14-17 2D 1 66 67	2.37	-1.93	9.64	Bulk sample: porous wackestone			
AP 1 0 2	0.34	-1.58	19.00	Bulk sample: fossiliferous/moldic wackestone			
4R-1, 0-3	2.56	-3.30	20.5	Bulk sample: fine wackestone			
4R-1, 56_61	1.07	-2.04	20.5	Bulk sample: norous candy packstone			
7R-1, 7-10	1.97	-1.02	57.37	Bulk sample: polous saluy packstone			
8R-1 17-20	1.75	-2.00	67.17	Bulk sample: white wackestone			
8R-1 17-20	1.57	-1.03	67.17	Light gray porous wackestone pear edge of grain			
8R-1 26-30	1.59	-2.81	67.26	Bulk sample: fine pelletoidal grainstone			
9R-1 33-36	2.02	-2.50	76.93	Bulk sample: norous wackestone			
12R-1 10-15	2.02	-1.90	105.6	Coarse spar at edge of large mollusk fragment			
12R-1, 10-15	3.46	-2.30	105.6	Partially preserved mollusk shell material			
12R-1, 10-15	2.16	-2.11	105.6	Bulk host wackestone			
13R-1, 16-20	1.88	-2.92	115.2	Bulk sample: porous wackestone			
18R-1, 31-35	2.37	-3.13	163.7	Bulk host wackestone			
18R-1, 31-35	4.86	-4.60	163.7	Coarse spar in replaced mollusk shell fragment			
18R-1, 40-43	1.74	-3.09	163.8	Bulk grainstone of skeletal fragments			
26M-1, 27-30	2.65	-2.08	236.1	Bulk grainstone with fine equant spar cement			
26M-1, 27-30	2.67	-6.45	236.1	Coarse spar in large mollusk-mold			
30M-1, 34-38	3.00	-1.81	274.8	Bulk grainstone with abundant spar cement			
31M-1, 37-44	3.01	-2.02	284.4	Bulk wackestone matrix of floatstone sample			
31M-1, 37-44	2.88	-1.66	284.4	Youngest spar cement filling large cavity			
31M-1, 37-44	3.03	-1.78	284.4	Early spar cement in large cavity			
39M-1, 4-13	3.22	-1.59	360.9	Bulk sample: porous pelletoidal packstone			
42M-1, 32-36	3.38	-2.90	390.1	Bulk sample: massive, well indurated mudstone			
42M-1, 32-36	1.98	-1.68	390.1	Bulk sample: massive, well indurated mudstone			
43M-1, 17-20	2.56	-3.10	399.5	Bulk packstone			
44M-2, 0–5	-2.00	-3.58	407.6	Volcanogenic breccia: center of mudstone clast			
46M-1, 85-89	2.29	-2.87	419.3	Bulk wackestone			
46M-1, 85-89	1.40	-0.51	419.3	Coarse spar in gastropod mold			
49R-1, 45-49	0.33	-3.02	445.5	Volcanogenic breccia: bulk mudstone clast			
49R-1, 55-60	2.38	-3.47	445.6	Volcanogenic breccia: edge of packstone clast			
50R-3, 32-36	3.32	-3.39	458.1	Volcanogenic breccia: large mudstone clast			
51R-5, 4-7	3.15	-3.35	470.0	Volcanogenic breccia: wackestone fragment			
51R-5, 4-7	3.17	-2.24	470.0	Coarse spar in center of large mollusk grain			
51R-5, 4-7	2.55	-3.84	470.0	Partially preserved mollusk shell			
52R-1, 113-117	1.91	-2.71	475.2	Volcanogenic breccia: large wackestone clast			
54R-4, 0-8	4.06	-3.76	497.3	Volcanogenic breccia: center of mudstone clast			
54R-4, 53-58	4.23	-3.30	497.84	Volcanogenic breccia: center of wackestone clast			
56P 2 105 100	4.32	-2.73	497.84	Volcanogenic breccia: greenish-gray matrix			
56P 2 145 150	3.00	-1.07	514.39	Pulls weekestere metrix			
56P 3 145 150	2.01	-2.00	516.25	Buik wackestone matrix			
56R-3 145-150	2.44	-1.24	516.25	Spar vainlat through host waskestone			
57R-4 130-141	3.02	-0.84	526.66	Coarse clear spar filling gastropod mold			
57R-4, 139-141	4 20	-2.84	526.66	Bulk packstone with large mollusk fragments			
58R-2 40-44	4.26	-4.09	532 30	Volcanogenic braccia: mudstone clast in braccia			
58R-2 40-44	3.85	-3.62	532.30	Volcanogenic breccia: hrown material near clast			
58R-2, 82-87	5.16	-3.83	532.50	Bulk nackstone with spar-filled molds			
58R-2, 82-87	5.53	-2.46	532 72	Bulk packstone with spar-filled molds			
59R-2, 72-77	3.41	-3.66	542 32	Bulk sample: well indurated mudstone			
60R-2, 89-94	2.56	-4.34	552.06	Bulk sample: mudstone clast in breccia			
61R-3, 29-34	4.18	-3.21	562.50	Volcanogenic breccia: center of wackestone clast			
61R-6, 98-102	3.46	-3.68	567.44	Volcanogenic breccia: center of packstone clast			
62R-6, 74-77	3.86	-4.18	576.33	Volcanogenic breccia: matrix with volcanic clasts			
62R-6, 74-77	3.82	-4.67	576.33	Volcanogenic breccia: matrix near carbonate clast			
62R-6, 74-77	3.82	-3.84	576.33	Volcanogenic breccia: center of mudstone clast			
63R-2, 13-18	1.84	-2.99	579.42	Volcanogenic breccia: center of mudstone clast			
63R-3, 133-138	3.07	-2.96	582.42	Volcanogenic breccia: center of wackestone clast			
64R-1, 56-61	1.67	-3.23	588.16	Volcanogenic breccia: center of wackestone clast			
64R-4, 81-85	4.11	-2.57	592.78	Bulk sample: small loose clasts of fine mudstone			
65R-5, 135-138	3.87	-2.38	603.93	Bulk sample: packstone with volcanic fragments			
65R-6, 4-9	5.36	-1.70	604.12	Bulk sample			
66R-1, 0-5	4.11	-1.65	606.60	Bulk sample: packstone of sandsized peloids			
67R-1, 33-36	4.52	-1.86	616.63	Bulk sample: porous grainstone			
71R-1, 119-123	4.03	-2.12	656.09	Bulk sample			
72R-1, 0-5	4.55	-2.87	664.60	Bulk sample			
73R-1, 5–9	3.54	-2.49	674.25	Bulk sample			
73R-1, 52-57	3.85	-2.40	674.72	Bulk sample			
74R-1, 0-6	2.90	-4.22	683.90	Bulk sample			
75R-1, 32-37	5.03	-2.24	693.82	Bulk sample			
75R-1, 126-130	4.69	-2.22	694.76	Bulk sample			
76R-1, 49-54	4.17	-2.50	703.49	Bulk sample			
/6R-1, 111-113	3.95	-2.78	704.11	Bulk sample			
7/R-1, 48-51	2.79	-5.22	712.98	Bulk sample			
/8K-1.0-4	4.02	-3.49	722.10	Bulk sample			

Volatile Components in Fluid Inclusions from MIT and Takuyo-Daisan Carbonate Platforms

Results

The gas contents of the fluid inclusions from MIT and Takuyo-Daisan platform carbonates lack appreciable amounts of hydrocarbons. These fluid inclusions are characterized as water dominated, containing appreciable carbon dioxide, and displaying important peaks at AMUs of 28 and 34. The mass charge ratio of 28 is interpreted as $(N_2)^+$ and the $({}^{12}C^{16}O)^+$ fragment of CO₂, whereas AMU of 34 is interpreted as $(H_2S)^+$ and $({}^{16}O^{18}O)^+$ (molecular oxygen). We found this molecular oxygen contribution at AMU of 34 to be negligible. The mass charge ratios of 33 and 35 have only minor H_2S

Table 2. Isotopic analyses, Site 879 (Takuyo-Daisan Guyot).

Core, section, interval (cm)	$\delta^{13}C$ $\delta^{18}O$		Depth (mbsf)	Description			
144-879A-							
1R-1, 15-20	2.60	-1.94	0.15	Intergranular spar in coarse molluscan grainstone			
1R-1, 15-20	3.60	-1.10	0.15	Partially preserved mollusk fragment			
2R-1, 40-43	2.21	-2.07	6.40	Bulk sample: moldic wackestone			
3R-1, 79-84	1.78	-2.04	16.29	Shell fragment in boundstone(?)			
5R-1, 31-37	2.92	-1.72	34.91	Rudstone: spar cement between coated grains			
5R-1, 31-37	3.10	-1.53	34.91	Rudstone: micritic part of coated grain (oncoid?)			
5R-1, 82-87	2.78	-1.98	35.42	Bulk sample: fine skeletal grainstone			
10R-1, 19-25	3.30	-2.04	83.09	Bulk sample: porous, fine-grained packstone			
16R-1, 104-108	2.23	-0.40	141.84	Crystal spar chunks from molds			
17R-1, 54-57	1.23	-2.14	150.94	Bulk sample: mottled gray packstone			
18R-1, 11-13	2.98	-2.39	160.21	Bulk sample: fine grained packstone			

Figure 16. Cross plot of the nitrogen and hydrogen sulfide indexes, using data from Site 878 on MIT Guyot (solid squares) and Site 879 on Takuyo-Daisan Guyot (open squares). See text for explanation of indexes.

contributions; H_2S has its main peak at AMU of 34. Hence, AMUs of 33 and 35 are used to indicate background. H_2S is considered present if the response on AMU of 34 is sufficiently greater than the mean of AMUs of 33 and 35. We used the height of the response of the mass spectrometer at the AMUs of 33, 34, and 35 to calculate an H_2S index for reducing environments. The index formula is two times the mass spectrometer response at AMU of 34, divided by the sum of the mass spectrometer response at AMUs of 33 and 35. The ratio of the AMUs must be greater than 1.0 to consider H_2S is present; the higher the ratio is above 1.0, the greater the certainty that H_2S is present in the sample.

A similar process for a nitrogen index can be applied using the height of the mass spectrometer response at AMUs of 28 and 44. An AMU of 28 represents $(N_2)^+$ and the $({}^{12}C{}^{16}O)^+$ fragment of CO₂, and

an AMU of 44 represents CO_2 . Both molecules are found in air, although N_2 comprises 78% of the gas in air and CO_2 only 0.033%. CO_2 may also be found in other diagenetic environments and is usually the second most abundant component in fluid inclusions. Therefore, the ratio of the mass spectrometer response at AMU of 28 divided by the response at AMU of 44, which is considered as background, can be used as a nitrogen or air index. If the ratio is greater than 1.0, then the presence of air inclusions is indicated.

Analysis of the bulk gases derived from potentially multiple generations of fluid inclusions in 77 samples from MIT and Takuyo-Daisan guyots, plotted against the air and hydrogen sulfide indexes (Fig. 16), reveals at least four populations of samples: (1) those with air inclusions, (2) those with hydrogen sulfide inclusions, (3) those

Figure 17. Fluid-inclusion data from Site 878 plotted as nitrogen index vs. depth. Data points above the line marking the nitrogen index of 1.0 are significant.

with both air and hydrogen sulfide inclusions, and (4) those that contain neither air nor hydrogen sulfide at significant levels.

Figure 17 displays the nitrogen index analyses of 66 MIT Guyot samples against depth. Air inclusions are interpreted to be associated with nine samples yielding a ratio greater than 1.0; these are from the following sub-bottom depths: 57.4, 105.6, 409.9, 576.3, 588.2, 597.8, 598.3, 664.6, and 703.5 mbsf. Figure 18 documents the presence of fluid inclusions in samples from Site 878 on MIT Guyot that trapped fluids from a reducing environment. Samples that did not have a ratio greater than 1.0 are from the following sub-bottom depths: 105.6, 436.6, 598.3, 604.1, and 722.1 mbsf.

The volatile components of the fluid inclusions analyzed from MIT Guyot samples show the presence of H_2S , which invokes a reducing environment for part of the diagenetic history of these samples. Also, there is evidence for some air inclusions in the platform limestones from MIT Guyot. The shallowest sample analyzed from this guyot is from 9.6 mbsf; it displays a signature for reducing conditions associated with part of its diagenetic history. Therefore, we cannot determine if the uppermost portion of the platform was exposed.

Figure 19 displays the nitrogen index of 11 Takuyo-Daisan Guyot samples against depth. Of the 11 samples, only one sample has a ratio greater than 1.0; it is from 0.15 mbsf and is interpreted as evidence of air inclusions associated with exposure of the upper platform surface. Figure 20 documents the presence of fluid inclusions in samples from Site 879 on Takuyo-Daisan Guyot that trapped fluids from a reducing environment. Three of the 11 samples did not have a ratio greater than 1.0; these samples are from the following sub-bottom depths: 16.3, 141.8, and 150.9 mbsf.

The volatile components of the fluid inclusions analyzed from Site 879 indicate the presence of H_2S which invokes a reducing environment for part of the diagenetic history of these samples. The shallowest sample analyzed from this guyot is from 0.15 mbsf and displays a distinct signature for subaerial exposure associated with part of its diagenetic history.

Discussion

If large-scale subaerial karst occurred on the MIT and Takuyo-Daisan platforms, dolines or sinkholes could be generated by the involvement of the meteoric vadose infiltration zone, the meteoric vadose percolation zone, or both zones of diagenesis. If exposure occurred, regardless of the abundance of cement that was generated during that time, small microinclusions of air and meteoric water would be trapped in the cement. If the limestones were strictly subjected to marine diagenesis over time, then they would contain only marine waters. Reducing environments may occur just beneath the sediment/water interface to deeper sub-bottom depths in pore waters that were initially derived from either meteoric phreatic or marine phreatic settings, and can be generated in microenvironments by bacterial activity.

We compared the results of the fluid-inclusion analyses with the other data sets to determine if there is any collaborative evidence for the interpretations of the pore-fluid environments associated with the fluid inclusions. In the "Petrography" section (this chapter), we described fenestral porosity in Sample 144-878A-13R-1, 16–22 cm, from MIT Guyot (115 mbsf). This sample is located 10 m beneath a

Figure 18. Fluid-inclusion data from Site 878 plotted as hydrogen sulfide index vs. depth. Data points above the line marking the hydrogen sulfide index of 1.0 are significant.

sample interpreted to have air inclusions. The thin geopetal laminae may be vadose silt, and the porosity may be generated by dissolution in meteoric water.

Another piece of collaborative evidence is from Sample 144-878A-44M-2, 0–5 cm (407.6 mbsf); it is only a meter beneath the top of the polymictic breccia. This sample yielded the most negative carbon isotope ratio (–2.0‰ δ^{13} C) of all the MIT platform limestones analyzed; another sample only 2 m beneath it (at 409.9 mbsf) indicates the presence of air inclusions.

The intense cathodoluminescence associated with late-stage cements in the polymictic volcanogenic breccia and the lower platform carbonates may be interpreted as evidence of reducing environments associated with these late-stage cements. This supports the fluidinclusion analyses that show inclusions of anoxic fluids in this interval. The presence of the iron and manganese detected by electron microprobe analyses in samples from this interval also confirms the findings using the H₂S index. Those limestones or their components were subjected to a reducing environment during part of their diagenetic history.

By using the nitrogen index to analyze for the presence of air inclusions in these platform limestones, we are able to document the occurrence of a vadose environment associated with a portion of the diagenetic history of some samples. From the 66 samples analyzed, 2 indicate at least local vadose diagenesis at Site 878 and may be related to subaerial exposure of the platform in the top 200 m. These occur at approximately 57 and 105 mbsf. Several other samples were analyzed from the upper 200 m of this platform, but they provide no strong evidence of air inclusions. If prolonged exposure of the upper 100 or 200 m of the MIT carbonate platform occurred, then it is not recorded with inclusions in the cements or grains of these limestones. Takuyo-Daisan Guyot also has an irregular topography, but the only evidence revealing a vadose diagenetic environment was found in the uppermost sample from 15 cm below the seafloor. There is no strong evidence from the other 10 analyses of air inclusions in these platform limestones. If a large-scale vadose environment with prolonged extensive exposure formed the irregular surface topography on this guyot and left a relict rim as a diagenetic feature, it is not recorded in the cements or grains in these samples.

DISCUSSION

Generation of Surface Topography of MIT and Takuyo-Daisan Guyots

Van Waasbergen and Winterer (1993) interpreted, from SeaBeam bathymetry, the occurrence of closed depressions, stream channels and terraces on the tops of many northwestern Pacific guyots. These features are cited as indications of 100–200 m of subaerial exposure before the final drowning of the guyots. A comparison of the guyot topography with modern uplifted islands and atolls, and lowstand terraces in front of modern reefs and banks, shows remarkable similarity to modern subaerial karst morphology (van Waasbergen and Winterer, 1993).

Site 879 is located on the southern marginal rim of Takuyo-Daisan Guyot (Fig. 3). Insufficient geochemical evidence exists to demonstrate that this perimeter ridge is a relict feature from subaerial karst diagenesis as suggested by van Waasbergen and Winterer (1993). The dissolution of low-energy lagoonal limestone facies and the lithification of high-energy rim deposits during exposure were suggested by van Waasbergen and Winterer (1993) as producing a diagenetic rim of

Figure 19. Fluid-inclusion data from Site 879 plotted as nitrogen index vs. depth. Data points above the line marking the nitrogen index of 1.0 are significant.

limestone. If this feature was lithified by meteoric diagenesis, then the stable isotope geochemistry should reveal some evidence of the meteoric environment, and the analysis of the volatiles in the fluid inclusions should reveal a series of samples with air inclusions. Drilling results indicate that the rim feature is a product of the stacking of intermittent shoal deposits (Premoli Silva, Haggerty, Rack, et al., 1993). Arnaud Vanneau and Premoli Silva (this volume) present paleontologic and sedimentologic data that indicate the carbonate environments at this site ranged from open-marine and wave-exposed deposits to lagoonal and restricted environments. A 100-m-tall buildup composed of accumulations of skeletal debris and shoal deposits is difficult to explain without some kind of diagenetic influence; perhaps it was in the form of early lithification in near-surface-marine fluids.

If early marine cementation by aragonite or high Mg-calcite occluded the primary pore space, and then large-scale subaerial exposure occurred, these minerals would be dissolved and/or replaced with meteoric low Mg-calcite. Low Mg-calcite is stable in both the meteoric and marine environments until reaching depths associated with the calcite lysocline. Therefore, low Mg-calcite should be less susceptible to diagenetic alteration (Veizer, 1983). Shipboard observations of the drilling rate, or rate of penetration of the drill bit, and the nature of the limestone recovered from the drill holes at all sites revealed a correlation of better recovery associated with limestones that were better cemented (Premoli Silva, Haggerty, Rack, et al., 1993). Therefore, even with poor recovery, we should have recovered a series of samples in the upper 100–200 m containing low Mg-calcite that precipitated in the meteoric environment, if it were present.

The intensity and duration of diagenesis sufficient to generate 100to 200-m-deep sinkholes would be expected to imprint a strong geochemical signature into the rock record. An exposed periplatform rim might have been faulted away and deposited downslope. No strong and consistent geochemical evidence for subaerial exposure was documented from material dredged from the slopes of the many guyots that showed pronounced surface relief (van Waasbergen, 1993).

Other mechanisms for generating features that mimic the appearance of sinkholes on a submerged carbonate platform must be considered. There are at least two other potential ways of developing these features.

The first mechanism suggested is related to the aragonite compensation depth (ACD) and the generation of marine karst. The reactions in the ACD essentially mimic the reactions in the meteoric phreatic environment as far as texture and dissolution characteristics of limestones (Schlager and James, 1978; Haggerty, 1983; Freeman-Lynde, 1986), but the geochemical signature is a telltale difference. This dissolution in the marine realm is enhanced by the oxygen minimum zone and is presently located at approximately 400 mbsl in the Pacific (Berner and Honjo, 1981; James and Choquette, 1983). This dissolution begins at a significantly shallower depth than the calcite lysocline. Aragonite and Mg-calcite are dissolved at intermediate depths in the marine realm.

Paull et al. (in press) have shown that an active exchange occurs between guyot-interior pore waters and the surrounding seawater. We speculate that if active exchange occurs between these marine waters and the platform-interior pore waters, then it may be possible to dissolve aragonite and Mg-calcite from within the platform and develop vugs or caverns. It is doubtful that sufficient dissolution would occur to produce large-scale collapse features in the guyot summit.

Analyses of the limestones from Sites 878 and 879 display primarily marine signatures and evidence of reducing pore-water conditions. The dissolution associated with the ACD and aragonite lysocline may have aided the development of vugs or cavities within the platform. At times in the past, the oxygen minimum zone may have become essentially anoxic if productivity was high in the overlying surface waters. This zone would produce corrosive, anoxic marine waters that could

Figure 20. Fluid-inclusion data from Site 879 plotted as hydrogen sulfide index vs. depth. Data points above the line marking the hydrogen sulfide index of 1.0 are significant.

enhance the dissolution of carbonates. This potentially could produce an irregular surface topography on the guyot summit, but it is unlikely that it would produce 100- to 200-m deep depressions.

The second method suggested for generating an irregular topography is through dissolution of evaporites at depth within the section. If the section of evaporites was relatively thick, dissolution of the evaporites may result in collapse of the overlying section. This phenomenon generates an irregular topography called cobblestone topography in the Mediterranean Sea (Kastens and Spiess, 1984). This topography is characterized by closed depressions 50 to 100 m deep and several kilometers across that resemble karstic dolines.

We did not recover any evaporite deposits on Leg 144; from indirect evidence, however, we are able to infer that evaporites may have been deposited laterally to the drilled location in the lower platform. The electron microprobe analyses document high sodium, potassium, strontium, and sulfur concentrations in the carbonates from MIT Guyot and indicate a hypersaline environment. The oxygen isotope ratios of the grains and early cements from MIT and Takuyo-Daisan guyots may indicate formation in warm saline water. Analysis of samples from MIT Guyot shows the presence of some dolomite crystals in the lower carbonate platform, and molds from dolomite in the limestone clasts of the volcanogenic breccia. The high sodium and sulfur concentrations in the dolomite also indicate a hypersaline environment of formation. In addition, there is potential evidence of sulfate microinclusions in calcite in the lower platform, and at least two samples in the lower platform have air inclusions. This combination of data supports the presence of a hypersaline environment that may have produced evaporites in nearby areas on the platform. Evaporites are highly soluble in seawater, and pressure may enhance their solubility. Therefore, subsidence of a platform into the marine realm may result in dissolution of the evaporite beds after deposition of the overlying strata. Dissolution of evaporite beds within the platform may produce collapse features. If evaporite beds were relatively shallow at the time of dissolution, we speculate that cobblestone topography would be produced. If the evaporite beds were very deep in the platform at the time of dissolution, it is unlikely that features mimicking sinkholes would be produced.

Another method of generating the irregular topography is related to a source of sulfur, possibly from the dissolution of evaporites at depth within the platform and/or a hydrothermal source. If sulfur-rich fluids within the platform became reducing and were mobilized upward along fractures, faults, or other circulation pathways, then dissolution of carbonates could occur along the way. Morse and Mackenzie (1990) note that partial sulfate reduction may result in carbonate dissolution. After these reducing fluids reached the shallower depths of an oxidizing environment, this new environment may alter the reduced fluids back to sulfate and potentially sulfuric acid, producing additional dissolution of carbonates. Interestingly, Hill (1990) proposed a mechanism for the dissolution of carbonates associated with the formation of Carlsbad Caverns, resulting from leaching of anhydrite beds. Mobilization of sulfur-rich reduced fluids up faults into an oxidizing meteoric environment resulted in the formation of sulfuric acid and carbonate dissolution (Hill, 1990, 1992).

We have documented the presence of sulfur-rich, reducing, paleopore fluids in both the MIT and Takuyo-Daisan carbonate platforms from the fluid-inclusion data. The microprobe analyses of the carbonate cements also exhibit high sulfur concentrations. The source of the sulfur in the paleofluids is presently undetermined. It may be related to hydrothermal activity, volcanic deposits, evaporites, etc. Although no evaporites were recovered as a source for generating sulfur-rich fluids, we have already presented indirect evidence for their possible existence. We speculate that it is more likely that the movement of these sulfur-rich fluids upward along faults or vertical fractures would produce dissolution mimicking sinkholes. This process represents a new form of marine diagenesis.

Considering all the geochemical evidence presented, we conclude that the irregular topography on MIT and Takuyo-Daisan guyots is not primarily the result of subaerial karst. At least two limestone samples from the upper platform of MIT Guyot contain air inclusions. If these limestone samples were not deposited in shoals or an intertidal setting, then they are recording exposure of the platform not related to the local environment. Minor exposure of the platform could initiate dissolution in some areas that may become depressions or even sinkholes. We speculate that the deep depressions (100-200 m) on the surface of these guyots may be unrelated to karst or may be formed by enhancement of preexisting, minor, subaerial karst features by other marine dissolution mechanisms. Dissolution of aragonite in the ACD may solution-enlarge preexisting areas or develop new vugs or cavities within the platform that could collapse. After submergence of the platform into the marine realm, the collapse of the upper platform from the dissolution of evaporites or the dissolution of carbonates generated from the sulfur-rich fluids may have occurred. The surface topography on these guyots may have formed by a combination of several mechanisms rather than from one major subaerial exposure of several hundred meters of carbonate platform.

None of these mechanisms would explain the occurrence of terraces and apparent stream valleys on 11 of 21 northwest Pacific guyots investigated by van Waasbergen and Winterer (1993). MIT and Takuyo-Daisan guyots do not exhibit terraces and apparent stream valleys.

Comparison with Other Leg 144 Guyots

Stable isotope ratios of limestones from MIT and Takuyo-Daisan guyots show generally marine diagenetic processes, with very little evidence for freshwater diagenesis. The most negative (lightest) oxygen isotopic values at any given interval tend to be in the oldest components (replaced mollusk shells), and the most positive (heaviest) values in the most recent cements, suggesting diagenesis occurred during subsidence into deeper, cooler marine waters. The stable isotope ratios of the carbonates in the breccia interval at MIT Guyot are more variable than in the overlying and underlying platforms, which suggest more variable compositions and/or oxygenation of the pore fluids during diagenesis of the preexisting limestone or diagenesis within the breccia interval.

Figure 21 shows the carbon and oxygen isotopic composition of samples from Wodejebato Guyot, Sites 874 and 877. The ratios at Site 874 and 877 are largely marine (Wyatt et al. and Opdyke et al., both this volume), with only few strongly negative values for oxygen in the upper 75 m of the platform (Fig. 22). The upper 50 m of the section is also characterized by abundant fabric-selective and solution-enhanced porosity. In the uppermost portion of the platform at Site 873 (Lincoln et al., this volume), an exposure surface overlain by an intermittently exposed transgressive sequence is documented from sedimentological criteria and stable isotope geochemistry.

At Sites 874 and 877 (Wyatt et al. and Opdyke et al., both in this volume), a careful review of the oxygen isotope data reveals a trend of increasing oxygen isotope ratios with progressively younger diagenetic components. Most of the material shows marine values, with the exception of some replaced mollusk shells. These mollusk shells show distinct, strongly negative oxygen isotope ratios. Their traceelement chemistry (high strontium) is interpreted to be incompatible with a meteoric origin for this material (Opdyke et al., this volume). However, a low water-rock ratio might preserve the high strontium content of aragonite when it is transformed to calcite, while still lowering the oxygen isotope ratio.

At Site 871 on Limalok Guyot, the carbon and oxygen isotopic compositions are also largely marine (Wyatt et al., this volume). Three intervals in the cores recovered from Hole 871C have been

interpreted as exhibiting meteoric diagenesis with low water/rock ratios (Wyatt et al., this volume). This interpretation is based upon δ^{18} O values of $\leq -3\%$, coinciding with a decrease in the percentage of cement or increase in the porosity of the limestone. These zones of meteoric diagenesis occur at the top of the carbonate platform and at approximately 38 and 66 m beneath the surface of the platform.

Both of the drilled carbonate platforms on guyots in the Marshall Islands display increased porosity and strongly negative oxygen isotopic values in the upper 75 m of the platform. These characteristics were interpreted as evidence of meteoric diagenesis (Wyatt et al. and Lincoln et al., both in this volume). At MIT and Takuyo-Daisan guyots, no strongly negative oxygen isotopic values are present in the upper 75 m of the platform.

Perimeter ridges are present on Wodejebato and Takuyo-Daisan guyots. On Wodejebato Guyot, two ridges parallel each other along the northern and northeastern edges of the summit platform. They are separated by a trough about 50 m deep. The inner perimeter ridge, drilled at Sites 874 and 877, is composed of framework limestone of algae, coral, and rudists as well as associated bioclastic shoals and lagoonal deposits (Premoli Silva, Haggerty, Rack, et al., 1993; Lincoln et al., this volume). The outer perimeter ridge, drilled at Sites 875 and 876, is porous skeletal calcarenite, and muddy skeletal packstone of benthic foraminifers, mollusks, red algae, and echinoderms (Lincoln et al., this volume). These sediments were eroded or redeposited from the coeval marginal-reef deposits of the inner perimeter ridge (Lincoln et al. and Enos et al., both in this volume). The perimeter ridge on Takuyo-Daisan Guyot, drilled at Site 879, is composed of shoal deposits in the form of skeletal rudstone, floatstone, packstone, and grainstone dominated by mollusk debris, peloids, and benthic foraminifers. Intervals with abundant oncoids are common. Muddy wackestone fabrics predominate, indicating that the sediments forming the perimeter ridge on Takuyo-Daisan Guyot were deposited primarily in an interior part of the carbonate platform (Premoli Silva, Haggerty, Rack, et al., 1993). Only the uppermost 50 m of the section on Takuyo-Daisan Guyot contains textures and biotic associations that reflect deposition in a platform-margin environment.

The perimeter ridge at Takuyo-Daisan Guyot has different lithologic characteristics than the ridges drilled on Wodejebato Guyot. The mid-Cretaceous limestones from the southern perimeter rim of Takuyo-Daisan Guyot were deposited in an interior platform environment; however, before the demise of this platform, the environment significantly changed. The uppermost mid-Cretaceous limestones from Takuyo-Daisan Guyot were deposited in a shoal environment similar to the Late Cretaceous bioclastic shoals deposited in the inner perimeter ridge of Wodejebato Guyot. At Takuyo-Daisan Guyot, no indication of an in-situ bioherm was recovered from the one site on the southern rim.

At all the guyots drilled on Leg 144, with the exception of Takuyo-Daisan Guyot, multiple generations of manganese-oxide hardgrounds cap the carbonate platforms. These can be used to calculate the time span between the cessation of platform accumulation and the inception of pelagic sedimentation. The time span between the inferred age of the youngest shallow-water sediments and the oldest generation of pelagic sediments trapped in the hardgrounds averages 1 to 2 m.y. (Haggerty and Premoli Silva, this volume).

An exception occurs on Wodejebato Guyot, where the oldest pelagic sediment within the hardgrounds is 5 m.y. younger than the shallow-water platform at inner Sites 873 and 877. At Site 874 on Wodejebato Guyot, the calculated time span was only 2 m.y. The longer time gap between the shallow-water facies and the hardgrounds at Site 873 concurs with the data that a second emersion event was more pronounced in that vicinity on the guyot (Haggerty and Premoli Silva, this volume).

At MIT Guyot, a hiatus of only 1.5 m.y. was found before pelagic sedimentation (Haggerty and Premoli Silva, this volume). This small gap in the geologic record at MIT Guyot, in comparison with the other guyots, is indirect evidence of the unlikely occurrence of large-scale,

Figure 21. Cross plot of carbon and oxygen stable isotopic composition of carbonates from Sites 874 (Wyatt et al., this volume) and 877 (Opdyke et al., this volume) on Wodejebato Guyot.

Figure 22. Oxygen and carbon stable isotopic composition of carbonates from Sites 874 (Wyatt et al., this volume) and 877 (Opdyke et al., this volume) on Wodejebato Guyot plotted vs. depth.

subaerial emersion of 100–200 m of the platform. This typical 1- to 2-m.y. hiatus observed on the Leg 144 guyots implies that shortly after cessation of their growth, these carbonate platforms, independent of their age, sank rapidly below the photic zone.

CONCLUSIONS

The upper portions of the Leg 144 carbonate platforms tend to differ in their surface topography. Little cementation has occurred, and dissolution leaves largely moldic porosity. Most of the stable isotopic analyses show primarily marine influences, with a cooling trend from early diagenesis in surface waters to later diagenesis and cementation in deeper, cooler waters. Some samples from Site 871 (Limalok Guyot), Sites 873 and 874 (Wodejebato Guyot), and Site 878 (MIT Guyot) displayed a stable isotopic signature strongly indicative of subaerial exposure. Analysis of fluid-inclusion compositions supports at least two small intervals of vadose diagenesis at Takuyo-Daisan Guyot.

Dolomitization in the lower platform interval at MIT Guyot probably occurred in a hypersaline rather than a mixing-zone environment, as shown by the trace-element compositions of the crystals. Strong fluctuations in trace elements, especially manganese and iron, in pore-filling cements in polymictic volcanogenic breccia and the lower platform unit of MIT Guyot suggest diagenetic fluids fluctuated in composition and/or degree of oxygenation.

Any meteoric influences that might account for the karstlike features on the tops of MIT and Takuyo-Daisan guyots remain very subtle. The trend in the oxygen isotopes is primarily marine. Therefore, if any early diagenesis (including an exposure episode) left its mark, then it is only in a very small portion of the material. Perhaps the generation of the 100- to 200-m-deep depressions on the surface of MIT and Takuyo Daisan guyots involves dissolution of carbonates associated with the ACD and/or dissolution of carbonates associated with sulfurrich fluids. The latter mechanism is a new form of marine diagenesis. Either of the two mechanisms cannot explain the occurrence of terraces and stream channels interpreted from SeaBeam bathymetry on the surfaces of many other northwestern Pacific guyots.

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144-878A-44M-2, 0–5 cm 1 2 3 4 5 5 6 7 8 9	37,94 34,23 32,91 36,41 15,20 35,80 38,16 37,15 37,05 2) 40,32	$\begin{array}{c} 0.19\\ 0.36\\ 0.27\\ 0.24\\ 0.58\\ 0.08\\ 0.06\\ 0.44\\ 0.59\end{array}$	868 868 712 1315 7586 326 121 205	311 194 257 397 2256 117	707 848 424 452 2513	241 734 772 127	358 495 NA	BD BD BD
1 2 3 4 5 6 7 8 9	37.94 34.23 32.91 36.41 15.20 35.80 38.16 37.15 37.05 2) 40.32	$\begin{array}{c} 0.19\\ 0.36\\ 0.27\\ 0.24\\ 0.58\\ 0.08\\ 0.06\\ 0.44\\ 0.59\\ \end{array}$	868 868 712 1315 7586 326 121 205	311 194 257 397 2256 117	707 848 424 452 2513	241 734 772 127	358 495 NA	BD BD BD
2 3 4 5 6 7 8 9	34.23 32.91 36.41 15.20 35.80 38.16 37.15 37.05 2) 40.32	$\begin{array}{c} 0.36 \\ 0.27 \\ 0.24 \\ 0.58 \\ 0.08 \\ 0.06 \\ 0.44 \\ 0.59 \end{array}$	868 712 1315 7586 326 121 205	194 257 397 2256 117	848 424 452 2513	734 772 127	495 NA	BD BD
3 4 5 6 7 8 9	32.91 36.41 15.20 35.80 38.16 37.15 37.05 2) 40.32	$\begin{array}{c} 0.27 \\ 0.24 \\ 0.58 \\ 0.08 \\ 0.06 \\ 0.44 \\ 0.59 \end{array}$	712 1315 7586 326 121 205	257 397 2256 117	424 452 2513	127	NA	BD
45 67 89	36.41 15.20 35.80 38.16 37.15 37.05 2) 40.32	$\begin{array}{c} 0.24 \\ 0.58 \\ 0.08 \\ 0.06 \\ 0.44 \\ 0.59 \end{array}$	1315 7586 326 121 205	2256 117	2513	127		DD
6 7 8 9	13.20 35.80 38.16 37.15 37.05 2) 40.32	0.38 0.08 0.44 0.59	326 121 205	117	2313	100	NA	BD
7 8 9	33.60 38.16 37.15 37.05 2) 40.32	0.08 0.06 0.44 0.59	121 205	11/	108	215	NA	BD
89	37.15 37.05 2) 40.32	0.44 0.59	205	BD	BD	127	NA	BD
9	37.05 2) 40.32	0.59	100 To 100	BD	113	3760	253	BD
	2) 40.32		386	BD	56	4216	242	BD
144-878A-44M-2, 0-5 cm (area	40.32							
1	0.0 80	0.21	169	910	1498	BD	463	BD
2	39.79	0.20	BD	878	1865	BD	NA 205	BD
3	41.02	0.25	BD	249	1408	BD	305 NIA	BD
4 5	30.70	0.21	BD	140	1101	165	RD	BD
6	41 31	0.14	BD	257	904	BD	BD	BD
7	41.00	0.33	BD	272	1158	BD	NA	BD
8	41.09	0.00	BD	BD	BD	380	NA	BD
144-878A-46M-1, 85-89 cm								
1	40.44	0.31	302	BD	BD	1076	BD	BD
2	37.12	0.35	314	BD	113	1114	158	BD
3	40.82	0.39	BD	BD	85	127	653	460
4	40.61	0.40	BD	BD	198	127	1200	547
3	41.71	0.45	494	BD	BD	2950	NA 126	BD
144 979 A 50D 2 22 26 am	41.55	0.27	233	вυ	BD	2102	120	BD
1	40.30	0.41	RD	BD	85	BD	NA	224
2	40.12	0.45	BD	BD	170	BD	NA	174
3	40.11	0.41	BD	BD	85	114	NA	BD
4	40.28	0.45	BD	BD	85	BD	NA	174
5	39.30	0.25	314	BD	56	190	NA	BD
6	39.78	0.32	844	BD	BD	3127	NA	BD
7	39.47	0.34	977	BD	141	1912	NA	BD
8	40.21	0.29	1037	BD	BD	3557	NA	BD
9	40.10	0.29	736	BD	56	2646	NA	BD
10	39.94	0.29	687	BD	BD	2/4/	NA	BD
11	39.89	0.26	1025	163	330	20/1 NA	NA	BD
144-878A-71P-1 119-123 cm	57.01	0.27	1025	105	557			55
1	40.85	0.32	BD	BD	BD	BD	NA	BD
2	40.84	0.32	BD	BD	BD	BD	NA	BD
3	40.90	0.37	BD	BD	BD	BD	NA	BD
4	40.78	0.28	169	BD	56	89	BD	BD
5	41.11	0.33	BD	BD	BD	228	NA	BD
6	41.35	0.34	BD	BD	BD	114	NA	BD
7	40.93	0.26	BD	BD	BD	BD	BD	BD
8	41.09	0.38	121	BD	BD	BD	NA	BD
10	30.80	0.44	155	BD	85	BD	NA	BD
11	40.79	0.23	157	BD	BD	BD	126	BD
12	40.78	0.39	BD	BD	BD	BD	NA	BD
13	41.05	0.20	BD	BD	56	127	NA	BD
14	37.33	0.14	121	BD	BD	BD	NA	BD
15	41.31	0.13	BD	BD	BD	BD	NA	BD
16	43.55	0.37	BD	BD	85	89	NA	BD
17	40.79	0.43	205	BD	198	BD	NA	BD
18	41.12	0.43	BD	BD	BD	BD	NA	149
19	39.96	0.31	BD	BD	BD	BD	126	BD
20	40.18	0.47	BD	BD	BD	BD	NA	BD
21	39.96	0.50	BD	BD	BD	BD	NA	BD
22	37.78	0.31	BD	BD	BD	BD	NA	BD

APPENDIX Detailed Results of Microprobe Analyses

Notes: Additional microprobe analyses are listed in van Waasbergen and Haggerty (this volume). BD = below detection limit; NA = not analyzed.