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DIAGENESIS OF MIDDLE TERTIARY CARBONATES IN THE TOA BAJA WELL, PUERTO RICO

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Abstract. The Toa Baja Well drilled in northern Puerto Rico to a depth of 2705 m (8872 ft.) penetrated over 550 m (1800 ft.) of Tertiary carbonates. The limestone-dominated portion of the well consists mostly of shallow-water backreef carbonates. Metastable carbonates have been either calcitized, dolomitized or dissolved. The petrographic character of the Tertiary carbonates in the Toa Baja Well, and those reported by Monroe [1980], the cathodoluminescence petrography, and the stable isotopic compositions indicate that these carbonates were rapidly cemented in the marine environment (limiting compaction), that replacement of metastable carbonates by calcite and precipitation of sparry calcite took place mostly in meteoric diagenetic environments and dolomitization probably occurred in a meteoric-marine mixing zone. Given the history of numerous drainage systems that dissected the Tertiary carbonates throughout their depositional history [Monroe, 1980] and the repeated Cenozoic sea level oscillations [Monroe, 1980; Seiglie and Moussa, 1984], it is likely that alteration of metastable carbonates took place during lowstands. Interstratified fluvial deposits suggest the continued influence of meteoric fluids in local highlands [Monroe, 1980].

Introduction

The Toa Baja #1 well was drilled to evaluate the depositional history of the northern Puerto Rico sedimentary sequence and to assess postdepositional changes in these sediments. Major questions posed for the shallow carbonate dominated sediments of the Toa Baja #1 well (Figure 1) are: what type of diagenetic modifications are involved, when these occurred (early vs. late), whether diagenetic modifications involved hot (burial) fluids, and the fate of organic matter and possible hydrocarbon generation or involvement. In an attempt to clarify the nature of diagenetic modification of the Middle Tertiary carbonates present in the Toa Baja #1 well petrographic and stable isotope studies have been undertaken.

The limestone-dominated portion of the Toa Baja Well ranges from 25 m (80 ft.) down to 570 meters (1875 ft.) in depth. The carbonates consist mostly of shallow-water backreef carbonates of Tertiary age [Montgomery et al., 1991]. Detrital influx is prominent in various portions of the stratigraphic sequence in the well (Figure 1). Most of these detrital sediments are fluvial in origin, and record the evolution of paleodrainage systems that were periodically active throughout the Tertiary [Monroe, 1980]. The penetrated carbonates outcrop throughout the north coast of Puerto Rico and are described by Monroe [1980]. From the known depositional history of successive regressive-transgressive events and the various episodes of fluvial influence during lowstands [Seiglie and Moussa, 1984; Monroe,1980], it can be expected that major diagenetic modifications would have taken place in freshwater meteoric or vadose environments, possibly including the meteoric-marine mixing zone. Moussa et al. [1987] inferred alteration in freshwater diagenetic environments for the dolomitized portions of the Aymamon limestone, while Monroe [1980] suggested influences of marine-derived fluids. Based on petrographic criteria and limited carbon and oxygen isotopic data, Monroe [1980] inferred meteoric diagenetic stabilization for the non dolomitized Aymamon.

Methods

All petrographic observations are based on well cuttings that were sieved washed and retained on a 230 mesh sieve (fine

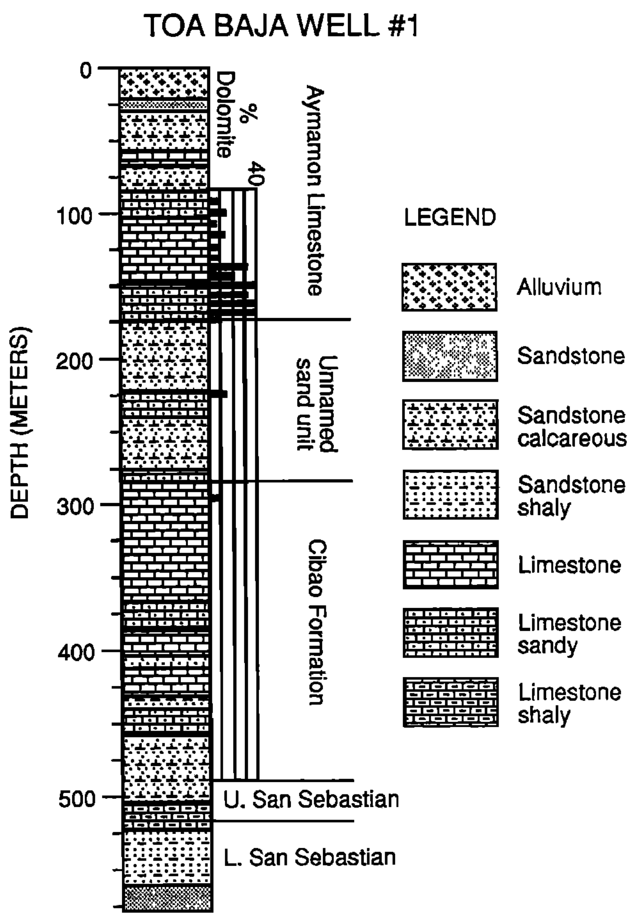

Fig. 1. Inferred lithology for the Toa Baja #1 Well. Formation boundaries/assignments from Montgomery et al. [1991]. Dolomite percentages refer to percentage of total carbonate, division in units of 10%.

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sand or larger) and embedded in epoxy, from which thin sections and polished chips were produced. All chips were stained using Alizarin Red and Potassium Ferricyanide solutions to differentiate dolomite and calcite and identify iron-rich carbonate phases. Cathodoluminescence petrography was performed using a Nuclide ELM-2 cold cathode luminoscope. Operating conditions were 10 kV at 0.5 ma. Microscale samples averaging 0.1 mg powdered carbonate were extracted from polished slabs using a microscope-mounted drill assembly with drill bits of 500 µm in diameter. Samples then were reacted with anhydrous phosphoric acid at 72°C and analyzed using a Finnigan MAT251 ratio mass spectrometer. All stable isotope analyses were performed at the University of Michigan Stable Isotope Laboratory. All values are reported relative to PDB standard.

Petrography

In general, limestone fragments consist of variable amounts of benthic foraminifera, red algae, echinoderm fragments, coral and molluscan debris. Most of these are embedded in a micritic matrix and occasionally they are rimmed by fibrous marine cements. Quartz-rich calcareous sandstones and siltstones are all cemented by calcite spar or microspar. The diagenetic history of carbonate rocks encountered in the Toa Baja well can be summarized as follows: a) early cementation in the marine environment, b) dissolution or replacement of aragonitic components by blocky calcite, c) fabric-retentive replacement of high magnesium calcite components by low magnesium calcite, d) infilling of skeletal and intraskeletal porosity by equant/blocky calcite spar, e) dolomitization of selected skeletal components and micrite cements/matrix.

Early diagenesis in the marine environment is evidenced by the presence of rims of fibrous cements, presumably calcite or high magnesium calcite. Fibrous cement rims range in width from 5 to 100 µm. Early cementation by fibrous cements is prominent in the youngest carbonate at depths of 40 m to 76 m (130 to 250 ft.). In all carbonate cuttings, there is a noticeable lack of compaction features such as deformation of skeletal grains, particularly of pellets or the mud-size fraction, suggesting early cementation prior to any significant burial of the carbonates.

Former aragonitic components such as coral fragments and molluscan debris have been either dissolved leaving moldic porosity or they have been replaced by blocky calcite with no preservation of skeletal fabric. Preserved aragonitic components are noticeably lacking. In the exposed Middle Tertiary carbonates of northern Puerto Rico, molluscan faunas are present mostly as molds and/or casts of fine grained carbonates [Monroe, 1980]. Thus in the cuttings recovered in the Toa Baja Well it is likely that molluscs preserved in such a manner are underrepresented. Large molluscan molds infilled by blocky calcite, common in outcrops will likely go undected in the cuttings and will be represented as fragments of carbonate spar. Former high magnesium calcite components such as benthic foraminifera and echinoids have been replaced by low magnesium calcite with fairly good preservation of skeletal micro-structure.

Dolomitized grains appear first at 88 m (290 ft.) (Figure 1), making up between 5 to 10% of total grains down to 135 m (440 ft.). Between 140 and 175 m (460 and 570 ft.), dolomitized grains make up 30 to 40% of the grains. Throughout the whole carbonate-dominated intervals, dolomite is encountered in trace amounts mostly replacing carbonate mud or micrite lithic fragments as rhombs of 5 to 100 µm. The observed occurrence of dolomite in the lower portions of the Aymamon are consistent with the observation of Moussa et al. [1987] and Monroe [1980].

Although pyrite is present at various intervals, it is always present as single fragments not associated with any carbonate. Pyrite is only encountered in the clastic-rich intervals and can be presumed to be associated with the detrital portion of the cuttings. It is possible that pyrite could be formed in localized anoxic environments within the clastic rich units. From the available information is impossible to determine the origin and timing of pyrite formation. Rounded to subrounded, limonite and hematite clasts, were also observed and are probably weathering products of detrital material or detrital grains themselves.

Not all of these styles of diagenetic modification are present at all depths. From the cuttings alone, it is impossible to determine the relative timing of these events at any given depth. However, it can be reasonably proposed that early submarine cementation preceded all other events. It is likely that dissolution/replacement of skeletal aragonite occurred simultaneously with stabilization of high magnesium skeletal calcites and/or dolomitization.

CL-petrography

Three types of luminescent carbonate were observed. These include: a) calcite cement in quartz sandstones/siltstone, b) micritic matrix of carbonate clasts, and c) calcite spar occurring as individual grains or infilling skeletal porosity or molds. The majority of the skeletal fragments are non luminescent. Exceptions to the non-luminescent character of skeletal grains are occasional foraminifers and bryozoans in the intervals associated with clastic influx.

In general, micritic cements as matrix or infilling voids were found to be dully luminescent. The sparry calcites infilling skeletal porosity, molds, replacing molluscan fragments or occurring as solitary grains were brightly luminescent. Sparry calcite cementing quartz sandstone/siltstones is also brightly luminescent. Occasionally, cements in these sandstone/siltstone cuttings exhibit up to four generations of alternating brightly luminescent and non-luminescent crystal growth bands.

Isotopic data

The bulk of the carbon and oxygen isotopic values for the carbonates in the Toa Baja Well fall within two distinct fields (Figure 2). The $\delta^{18}O$ of dolomitized grains range from 2.0 to 3.1 ‰ and $\delta^{13}C$ ranges from 0.8 to -1.9 ‰. Carbonate spar (calcite and dolomite), recrystallized skeletal grains (calcite), calcitic benthic foraminifera and calcite-cemented silt and micrite fall in a trend ranging from -4.5 to -1.3 ‰ $\delta^{18}O$ and -8.2 to 1.2 ‰ $\delta^{13}C$. Outliers to these two groups are two values obtained from two sparry calcites sampled at 45 and 100 m (150 and 330 ft.). These spars have anomalously light oxygen isotopic compositions when compared with the bulk of the calcitic samples. With the exception of the heavy oxygen

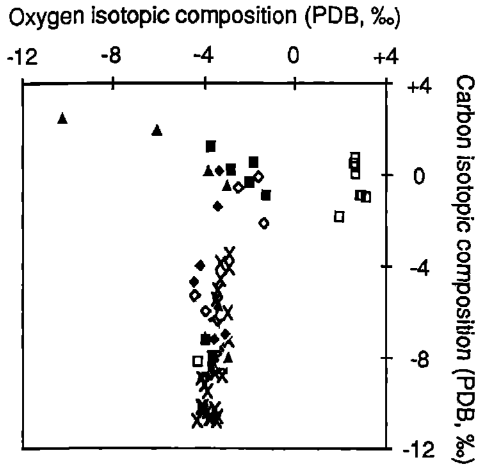

Fig. 2. Carbon and oxygen isotopic composition of selected carbonate components. Open squares = dolomite spar and dolomitized grains, solid squares = calcitic benthic foraminifera, solid diamonds = calcite silt/micrite, open diamonds = recrystallized skeletal grains, and solid triangles = sparry calcite. The X's are modern meteoric calcite (cave calcite) from González [1989].

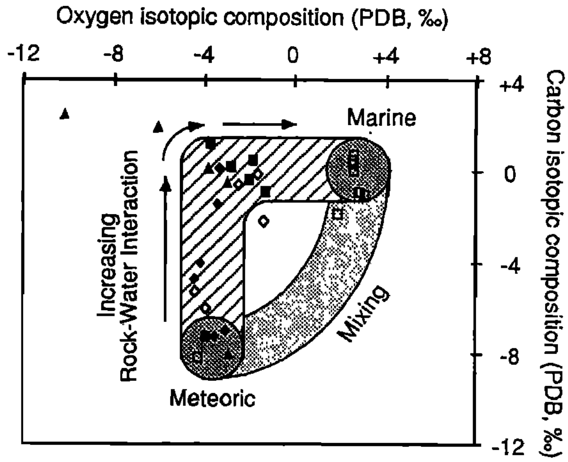

Fig. 3. Interpreted shifts in carbon and oxygen isotopic composition during meteoric and meteoric-marine diagenesis. [After Lohmann, 1982,1988]. The hyperbolic shaded portion represents the range of carbonate isotopic compositions that can be produced in a mixing zone. The fields labeled "Marine" and "Meteoric" represent carbonate isotopic compositions formed by end-member fluids. The inverted "J" cross-hatched portion represent calcite/carbonate isotopic compositions produced from a meteoric fluid undergoing increasing rock water interactions. Symbols as in Figure 2.

isotopic compositions of dolomitized grains, no systematic changes in stable isotopic composition are detected with increasing depth.

Discussion

As would be expected from the known depositional history of the Tertiary carbonates of northern Puerto Rico the observed diagenetic features suggest that major modifications took place within the freshwater phreatic or the marine-freshwater mixing environments, with early cementation taking place in the marine phreatic environment. The presence of fibrous marine cements and the lack of compaction deformation suggest early cementation prior to compaction, with all of other diagenetic modifications postdating early marine cementation.

With the exception of the outliers mentioned above, the observed stable isotopic composition of the calcitic carbonates conform to trends expected from freshwater phreatic diagenesis. The limited range of oxygen isotopic compositions and highly variable carbon isotopic compositions and the oxygen isotopic enrichment with the heavier carbon values are best explained by alteration in a meteoric environment (Figure 3). Present day meteoric carbonates (cave calcite) of northern Puerto Rico define a similar "meteoric calcite line" (Figure 2). The luminescent character of the calcitic components and dolomite spars also conform to alteration in a meteoric environment. Brightly luminescent carbonates were most likely deposited under reducing phreatic conditions.

The two calcite spar samples that have light $\delta^{18}O$ compositions are probably of detrital origin. Hydrothermal calcite veins commonly associated with pyrite, barite, and rarely with lead and zinc sulfides are found scattered throughout the lower Tertiary and Upper Cretaceous volcanics, volcaniclastics and plutonic rocks of the central portions of the island [e.g., Berryhill, 1966; Nelson and Monroe, 1966].

Two alternative scenarios are possible for dolomitization. The first of these would involve two separate events in which dolomitized grains having heavy carbon and oxygen isotopic compositions are formed by marine fluids [Land, 1985], while the dolomite spar exhibiting depleted carbon and oxygen isotopic compositions are formed by meteoric fluids. As the major dolomite abundances are associated with the uppermost Aymamon, it is likely that dolomitization took place under a diagenetic regime associated with the major marine offlap that produced the extensive erosional unconformity on top of the Aymamon [Monroe, 1980] or during the submergence of the Aymamon in times of deposition of Pliocene Quebradillas Formation [Moussa et al., 1987].

The distribution of dolomite in outcrops of the Aymamon, occurring along coastal outcrops [Monroe, 1980], suggests that dolomitization was limited to seaward portions of the Aymamon. The occurrence of dolomite in the subsurface in the Toa Baja Well as well as its presence in other deep wells in northern Puerto Rico [Monroe, 1980] suggests that dolomitization took place in a limited geographic "zone" extending from seaward areas inland through the subsurface. A dolomitizing front with such spatial distribution would be formed by a meteoric-marine mixing zone. The isotopic composition of both dolomitized grains and dolomite spar could then be explained by dolomite being precipitated only by the end-member fluids. Dolomitized grains exhibiting heavy $\delta^{18}O$ and $\delta^{13}C$ compositions being precipitated in the marine-dominated portion of the mixing zone, and dolomite spars with depleted $\delta^{18}O$ and $\delta^{13}C$ compositions formed in the freshwater dominated portion of the mixing zone.

Conclusions

The petrographic character of the Tertiary carbonates in the Toa Baja Well, and those reported by Monroe [1980], the cathodoluminescence petrography, and the stable isotopic compositions indicate that these carbonates were rapidly cemented in the marine environment. Replacement of metastable carbonates by calcite and precipitation of sparry calcite took place mostly in meteoric diagenetic environments. Dolomitization probably occurred in a meteoric-marine mixing zone. Given the history of numerous drainage systems that dissected the Tertiary carbonates throughout their depositional history [Monroe, 1980] and the repeated Cenozoic sea level oscillations [Monroe, 1980; Seiglie and Moussa, 1984], it is likely that alteration of metastable carbonates took place during lowstands. Interstratified fluvial deposits suggest the continued influence of meteoric fluids in local highlands. It is evident that further detailed studies (on cores and outcrops) are needed to decipher the relationships between sea-level (eustatic or tectonic) oscillations and chronology of meteoric diagenesis in Tertiary carbonates of northern Puerto Rico.

Clearly the Middle Tertiary carbonates penetrated by the Toa Baja Well have not been subjected to high temperature alteration. Fluids seems to have been limited to marine, meteoric or a mixture of these two. Hydrocarbons are not present and gaseous hydrocarbons, if ever present, played no role in the diagenetic alteration of these carbonates.

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