RAPID GROWTH RATES OF SYNDEPOSITIONAL MARINE ARAGONITE CEMENTS IN STEEP MARGINAL SLOPE DEPOSITS, BAHAMAS AND BELIZE

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ABSTRACT: Growth rates of marine botryoidal aragonite cements from steep (35-45°) marginal slope deposits in the Bahamas and Belize have been determined by accelerator mass spectrometer radiocarbon dating of samples taken at the base and top of individual botryoids. The pore-filling cements, which range from approximately 11,000-13,000 years old, grew at average rates of 8-10 mm/100 yr with maximum rates > 25 mm/100 yr. Radiocarbon dating of coexisting skeletal components indicates that cementation was syndepositional.

Microsampling transects across individual botryoids for stable-isotope analyses show little variation in δ13C and δ18O, supporting the conclusion that cementation was extremely rapid. Although the cements show a progressive depletion in isotopic composition of approximately 1‰ (δ13C) and 2‰ (δ18O) from 13 ka to 11 ka, the average variation (ε) within individual pore-filling cements, ranging in size from 2 mm to 32 mm (bottom to top), was 0.11‰ (δ13C) and 0.14‰ (δ18O).

Results of this study provide the first quantitative data on growth rates of marine carbonate cements in a marginal slope environment. The data indicate that marginal slope deposits may lithify within several tens of years and suggest that "geologically instantaneous" cementation may be critical in stabilizing steep carbonate slope deposits at or above angles of repose.

INTRODUCTION

The rates at which carbonate sediments lithify and become limestones in marine environments is one of the fundamental questions in carbonate sedimentology. Until now this question has been answered mainly in qualitative terms, such as "rapid" or "syndepositional", based almost entirely on textual evidence. A quantitative understanding of cementation rates is, however, important in the interpretation of some marine limestones and is essential to the development of predictive sedimentologic models.

In shallow tropical seas, there is clear evidence that lithification can take place within a few tens of years. Lyell (1875, p. 551) was one of the first to report on the rapid cementation of tropical beachrock when describing the inclusion of recent human bones and artifacts in "calcite"-cemented carbonate sands on the island of Guadeloupe in the West Indies. Shinn (1969) reported shallow subtidal sands in the Persian Gulf that had been cemented by fibrous or acicular aragonite within 20 yr; the incorporation of human artifacts into the cemented sediment provided a reasonable means to estimate rates of cementation. In more dramatic example, Emery et al. (1954, p. 44) describe aragonite-cemented beach rock on Eniwetok atoll containing brass cartridge cases and steel shaft fragments left over from military operations just 7 yr earlier. Except for these kinds of observational evidence for rapid cementation in shallow marine settings, along with a few experimental studies in natural environments (e.g., Morse and Mucci 1984), little else is known about rates of cementation in marine carbonates. This is especially true for cementation in the transition zone between shallow-water platform and deeper-water basinal environments.

Aragonite cements have been reported from modern marginal slope environments in Belize (e.g., Ginsburg and James 1976; James and Ginsburg 1979), Jamaica (e.g., Land and Moore 1980), the Bahamas (e.g., Grammer and Ginsburg 1992; Grammer et al. 1993), and the Great Barrier Reef (e.g., Marshall and Davies 1981) and have been interpreted from ancient slope deposits throughout the Phanerozoic (e.g., Krebs 1969; Mazullo and Cys 1977; Mazullo 1980; Amsaass 1985; Harris 1988). Several authors have argued, mainly from textual evidence, that marine cementation along fossil slopes (either aragonite or Mg calcite) was rapid or syndepositional (Krebs 1969; Mazullo 1980; Harris 1988; Kenter and Campbell 1991) and that this syndepositional cementation helped to stabilize steep, primary depositional slopes with declivities of 35-40° (e.g., Playford 1980, 1984; Kerans et al. 1986).

The concept of "rapid" or "syndepositional" cementation is, however, extremely vague. Does cementation occur within thousands of years, hundreds of years, or perhaps even faster? Is cementation truly fast enough to rapidly stabilize primary depositional slopes at or above angles of repose? If so, what are the implications for long-term slope progradation and diagenetic alteration of these deposits? In an effort to increase our understanding of this fundamental aspect of carbonate rocks, we have combined stable-isotope analyses and high-precision radiocarbon dating of pore-filling botryoidal aragonite cements from the deep fore reef of Belize and the Tongue of the Ocean, Bahamas (Fig. 1). We report here the first quantitative evidence for rapid growth rates of aragonite cement in a marginal slope environment.

METHODS

Samples of lithified slope and forereef deposits containing pore-filling botryoidal aragonite cements were collected along the marginal slopes of the Tongue of the Ocean, Bahamas, and from Belize using free-diving research submersibles. The rocks consist of well-lithified, coarse-grained, skeletal packstones and grainstones collected in water depths of 120-170 m subsea (Fig. 1). Samples were dislodged from the interior of the slope (Bahamas) and from large talus blocks resting on the slope (Belize) through the use of small charges of explosives. In addition, cemented sediment was recovered on a sediment trap deployed along the slopes of the Tongue of the Ocean at a depth of 158 m.

A total of 178 samples of botryoidal aragonite cement from 24 different botryoids were analyzed for their stable-isotope (δ13C and δ18O) composition. The samples were extracted by microdrill in a continuous transect from the base to the top of each botryoid (Fig. 2). Samples of 0.3-0.5 mg of powdered carbonate were reacted with H3PO4 at 90°C, and the CO2 produced was analyzed using a Finnigan MAT 251 mass spectrometer. Carbon and oxygen isotopic data are reported relative to PDB and corrected for 17O as described by Craig (1957) with modifications for a triple-collector instrument.

Nineteen samples from 11 botryoids with lengths of 2-32 mm (base to top) were analyzed for radiocarbon ages. From these the 7 largest (lengths 5-32 mm) were chosen for evaluation of botryoidal aragonite growth rates by taking samples at the base and the top of each botryoidal fan (Fig. 2). An intermediate sample was also taken midway between the top and the bottom of the largest (32 mm) botryoid. Rates of cement growth were
determined by the difference in age dates between the base and top of each botryoid.

Radiocarbon measurements were carried out at the NSF Accelerator Facility at the University of Arizona with an accelerator mass spectrometer (AMS). The accelerator dating method differs from conventional radiocarbon dating in that the AMS measures the actual number of $^{14}$C atoms in a sample rather than the number of disintegrations per minute (e.g., Rucklidge 1984, Linick et al. 1986). The principal advantage of AMS dating is that samples as small as 5-10 mg of carbonate (or 0.5-1.0 mg carbon) can be analyzed, as opposed to the 30+ grams of carbonate required for conventional radiocarbon dating. This not only minimizes the potential for sampling error but also enables dating of samples too small to be dated by conventional radiocarbon techniques.

**Results**

**Petrography**

Botryoidal aragonite cements are found partially or completely filling a variety of cavities in coarse-grained, skeletal packstones and grainstones collected from the steep marginal slopes of the Tongue of the Ocean, Bahamas, and in front of the Belize barrier reefs. The term botryoidal aragonite, first used by Ginsburg and James (1976), is used to describe a spectacular type of pore-filling cement that consists of individual and coalescing mamelons of compact, fibrous aragonite.

Botryoids from the slopes of the Bahamas and Belize range in length from a few hundred microns to over 32 mm. Radiocarbon age dates vary from 11,310 $\pm$ 85 ybp to 13,935 $\pm$ 115 ybp (Grammer 1991). Petrographically the botryoids are very similar to those originally described by Ginsburg and James (1976) and more recently by Aissaoui (1985); they consist of individual or compound fans of elongate euhedral fibers with a characteristic sweeping extinction in crossed-polarized light (Fig. 3A). The botryoids exhibit no preferential growth direction within a sample and may grow out into pores from the floors, walls, or ceilings of the cavities. Many botryoids contain what appear to be discontinuity horizons marked by "dust lines" of small (1-3 $\mu$m), solid, dark, irregularly shaped inclusions and/or slight irregularities in crystal growth (Fig. 3B). Some of the discontinuity surfaces are marked by fragments of planktonic foraminifera or by small patches (5-10 $\mu$m) or thin layers ($< 10 \mu$m) of Mg-calcite micrite similar to that described by Ginsburg and James (1976). These horizons presumably represent episodic interruptions in the growth of the cement. As many as 38 discontinuity surfaces were observed in a single fan 9 mm long, although most fans contained 5-15 of these horizons. Discontinuity surfaces do not correlate between different fans growing in a single pore, suggesting that growth may have started at different times. In addition, there is no consistent relationship between the number of discontinuity horizons and the size of the fan (i.e., the largest fans do not contain the greatest number of discontinuities), even for those growing in the same pore.

**Isotopic Data**

The stable-isotope ($\delta^{13}$C and $\delta^{18}$O) compositions of the pore-filling botryoidal aragonite cements fall within established values for normal shal-
low-water marine cements (Fig. 4). Values for δ¹³C range from +3.52‰ to +4.96‰ PDB; δ¹⁸O values range from +0.60‰ to +2.85‰ PDB (Table 1). The covariant trend in both carbon and oxygen isotopic values is a function of age, with the isotopically most enriched values from cements that are approximately 14,000 yr old (Fig. 5). This depletion trend (especially for δ¹⁸O) is likely related to a change in the isotopic composition of sea water with the progressive decrease in ice volume during the last glacial cycle and with a temperature overprint (e.g., Shackleton 1987).

There is a relatively large variation in stable-isotope composition between different botryoids, especially for oxygen (~ 2‰; see Table 1), but sample transects within individual botryoids show little overall variation in the stable-isotope composition of a single pore fill (i.e., low σ; Table 1). The maximum excursion (σ) in the stable-isotope composition within a single botryoid of pore-filling cement was 0.32‰ for δ¹³C (pore size 13 mm) and 0.48‰ for δ¹⁸O (pore size 9 mm), but the average variation (σ) was significantly lower: 0.11‰ for δ¹³C and 0.14‰ for δ¹⁸O (Table 1). The small variations in isotopic compositions within individual pore-filling cements indicate that there was little change in pore-water chemistry during precipitation of individual botryoids.

Considering that there is significant isotopic variation, especially for oxygen, between the 14,000 ybp cements and the 11,000-11,500 ybp cements, the minor variations within individual pore-filling cements suggest that cementation must have been rapid. Individual pore-filling cements that grew over thousands of years would have recorded a significant temporal variation in isotopic composition.

**Growth Rates of Botryoidal Aragonite**

Growth rates of the pore-filling botryoidal aragonite cements were determined from the difference in ages between samples extracted from the bases and tops of seven individual botryoids ranging in age from 11,310 ybp to 12,650 ybp (Table 2). From the difference in mean age values for a single botryoid, the average rate of cement growth is 8.2 mm/100 yr, with maximum rates of up to 25.0 mm/100 yr. Discounting the 3 samples for which adjustment of the ± age differences could be interpreted as instantaneous growth (i.e., same age), the maximum growth rates average more than 12 mm/100 yr. Even the most conservative growth rates (i.e.,
determined by maximizing the age differences, and therefore minimizing growth rates, suggest average growth rates > 3 mm/100 yr. Note that the above rates assume constant growth of the pore-filling cements. The presence of multiple discontinuity horizons within individual pore-filling cements, however, indicates that cement growth may be episodic and that "pulses" of cement growth may therefore be even faster.

Two-Year-Old Fibrous Aragonite

Evidence supporting rapid growth of aragonite cements in a marginal slope environment is provided by fibrous aragonite that grew in 2 years or less on Bahamian slopes. In June 1960 a sediment trap was recovered that had been deployed two years before (May 1968) at a depth of 158 m along the steep marginal slopes in the Tongue of the Ocean. A mixture of skeletal and nonskeletal sands (Halimeda sp., benthic foraminifera, mollusk fragments, and peloids) were found to be cemented onto the sides of the trap. This cemented sand, with a maximum thickness of 1 cm, was distributed discontinuously around the base of the trap. Scanning electron microscopy shows abundant fibrous aragonite binding the sand grains (Fig. 6). The crystals are typically 1–3 μm wide and 30–50 μm long, although some are up to 75 μm long, most have blunt terminations (Fig. 6B). The cementation of individual grains onto the sides of the sediment trap indicates that the sands were cemented in place and not derived from shallower water as lithoclasts. Although this is an isolated example, and the growth of these cements might have been influenced by unknown external factors (e.g., the substrate for the sediment was a concrete block), it is interesting that the growth rates of these fibrous aragonites (1.5–3.75 mm/100 yr) is similar to that observed for the botryoidal aragonite cements.

**DISCUSSION**

Although steep carbonate slopes (35–45°) are well known from the geologic record (Wilson 1975), there has been considerable argument about the evolution of these steep slope. Several workers have concluded, mainly by analysis of in situ geotectonic structures, that the steep slope angles associated with some ancient examples are representative of primary depositional slopes (e.g., Bosellini 1984; Enos 1977; Haddad et al. 1984; Harris 1988; Lehmann 1978; Playford 1980; Playford et al. 1989; Ward

**Fig. 5.—** Stable-isotope values ($\delta^{13}C$ and $\delta^{18}O$) vs. radiocarbon age (AMS) for 11 different botryoids. Isotopic data represent mean values for 2–4 samples taken at same location as the age-dated samples (total number of isotopic samples, 57). Radiocarbon ages have not been corrected for the mean age of seawater (i.e., by subtracting 400 yr; Bard et al. 1987) to allow for easier comparison with previously published cement data.
TABLE 2.—Growth rates of botryoidal aragonite

<table>
<thead>
<tr>
<th>Sample</th>
<th>Age (yr)</th>
<th>Botryoid Length (mm)</th>
<th>Rate (mm/100 yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>Max</td>
<td>Min</td>
</tr>
<tr>
<td>Belize</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BB-B (T)</td>
<td>11310 ± 85</td>
<td>32</td>
<td>11.6</td>
</tr>
<tr>
<td>BB-B (M)</td>
<td>11520 ± 80</td>
<td>22</td>
<td>8.1</td>
</tr>
<tr>
<td>BB-B (B)</td>
<td>11585 ± 90</td>
<td>13</td>
<td>5.1</td>
</tr>
<tr>
<td>72-24 (T)</td>
<td>11730 ± 90</td>
<td>13</td>
<td>8.1</td>
</tr>
<tr>
<td>72-24 (B)</td>
<td>11730 ± 90</td>
<td>13</td>
<td>8.1</td>
</tr>
<tr>
<td>BB-A (T)</td>
<td>11580 ± 80</td>
<td>20</td>
<td>5.1</td>
</tr>
<tr>
<td>BB-A (B)</td>
<td>11975 ± 80</td>
<td>20</td>
<td>5.1</td>
</tr>
<tr>
<td>Bahamas</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RR-16A.1 (T)</td>
<td>12005 ± 105</td>
<td>10</td>
<td>2.1</td>
</tr>
<tr>
<td>RR-16A.2 (B)</td>
<td>12475 ± 115</td>
<td>12</td>
<td>2.1</td>
</tr>
<tr>
<td>RR-16A.2 (T)</td>
<td>12290 ± 100</td>
<td>12</td>
<td>2.1</td>
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<td>RR-16A.3 (B)</td>
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<tr>
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<td>15</td>
<td>2.1</td>
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<tr>
<td>8B-090 2b1 (T)</td>
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<td>8B-090 2b1 (B)</td>
<td>12306 ± 110</td>
<td>5</td>
<td>2.2</td>
</tr>
<tr>
<td>Lake MacLeod, Australia</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Handford et al. 1984)</td>
<td>2500 to present</td>
<td>~0.4</td>
<td>~0.2</td>
</tr>
</tbody>
</table>

*Mean growth rates are calculated using the difference in mean radiocarbon ages from top to bottom of an individual botryoid. Maximum rates are obtained by minimizing difference (±) in radiocarbon ages (rates marked with (**)) are those where radiocarbon ages may be considered to be the same. Minimum growth rates were calculated by maximizing difference in radiocarbon age dates.

et al. 1986; Yurewicz 1977). These workers suggest that early submarine cementation along with sediment binding by various organisms preserved the steep slopes at or above angles of repose, but others have concluded that the declivity of some steep slope deposits is due mainly to postdepositional compaction (McCabe et al. 1985; Devaney et al. 1986).

Arguments for "early" or "syndepositional" cementation have been based mainly on textural relationships visible in hand specimen or thin section. The problem, of course, has been the question of rates. The likelihood for slope deposits to be preserved at or above angles of repose is probably directly proportional to the rate at which the sediment lithified. Previous work on Bahamian slopes has shown that cementation is syndepositional (i.e., within a few hundred years) by comparison of radiocarbon-dated cements and coexisting skeletal components (Graham and Ginsburg 1992; Grammer et al. 1993). The results of this study, however, suggest that marginal slope deposits may lithify within several tens of years. Cements growing at 8-10 mm/100 yr would stabilize slopes at or above angles of repose in a relatively short time.

Even though rapid rates of carbonate cementation have been observed in many shallow-water marine environments (e.g., Lyell 1875; Emery et al. 1954; Shinn 1969), and Handford et al. (1984) have shown that aragonite cements can grow at 0.2-0.4 mm/100 yr in hypersaline environments, these are the first quantitative data on cement growth rates in a marginal slope environment. The Tongue of the Ocean samples, which were obtained from interior slope deposits at depths of 150-170 m (Fig. 1), have radiocarbon ages ranging from approximately 12,000 ybp to 14,000 ybp. With Fairbanks' (1989) sea-level curve for the Caribbean region as a basis of reference, these cements were precipitated in marine waters, at depths of 45-85 m in a fore reef or upper marginal slope environment. A normal marine origin for the cements is further supported by their isotopic composition, as shown in Figure 4. Although precipitation depths for the Belize samples are a bit more problematic because the samples were obtained from talus blocks resting on the slope, a similar exercise suggests that these cements may have grown at depths as deep as those from the Tongue of the Ocean. It is interesting that these depths and environments of cement growth are consistent with several examples of Paleozoic botryoidal cements documented in the literature (e.g., Krebs 1969; Davies 1977; Yurewicz 1977).

Because the concept of such rapid rates of cementation has far-reaching implications for the overall morphology of some carbonate platforms, as well as to the diagenetic history and resulting seismic character of marginal slope deposits, it is important to consider some of the possible limitations of our preliminary results. The most obvious is the number of samples analyzed to date. Although the present data base includes radiocarbon dates from only eleven different botryoids, and only seven of these were dated more than once for growth-rate information, it is significant that the cements come from two different oceanographic provinces and are separated by more than 1200 km and 7° of latitude. The similarity in growth rates and isotopic compositions of the cements between the Bahamian and Belize samples is strong albeit circumstantial evidence that we are seeing an accurate signal for the growth rates of the botryoidal aragonite cements and that these rates were unaffected by localized precipitation-enhancing conditions.

The apparent abrupt cessation in botryoidal aragonite cement growth approximately 11,000 yr ago raises further questions. Is this a function of a depositional bias, or might it record some change in the chemistry of pore waters or in the pore network in which the fluids are circulating?

The potential for a depositional bias is real. Although botryoidal aragonite cements may constitute 20% or more of the cements in the interior slope deposits from the Tongue of the Ocean (Grammer 1991), deposition
of these steep marginal slope deposits ceased abruptly around 10,500 ybp (Grammer and Ginsburg 1992). This transition occurred as the rim of the platform began to be flooded and carbonate production switched from mainly a fringing reef along the escarpment that produced coarse sands, gravels, and boulders that were deposited on steep talus slopes, to banktop sedimentation characterized by sands and muds. Because the bank-derived sediments are fine-grained, most of the sediment shed off the platform has been bypassing the steep marginal slopes because the slopes are steeper than the angles of repose for material of this size (Grammer et al. 1993). The lack of younger botryoidal aragonite cements in our data base could therefore be related to the limited deposition of sediment along these slopes in the last 10,500 yr.

Another possibility is that with the continued rise in sea level over the last 10,000-11,000 yr, the slope environments simply moved out of the highly saturated, warm, mixed-water zone above the thermocline into a colder-water regime in which aragonite precipitation is either absent or rare. This is certainly a possibility for the deeper parts of the slope, but present-day water temperatures of 24°C extend down to depths of 150-160 m (Fig. 7), and we have observed aragonite cementsation taking place at these depths today. We do acknowledge, however, that this isolated occurrence may represent extremely localized aragonite precipitation due either to the stabilization of sand grains against the sediment trap or possibly to local funneling of dense, warm waters cascading off the platform (Wilson and Roberts 1992). Further work is needed to evaluate and confirm the distribution of present-day cementation in this environment.

A third possibility for the abrupt cessation in botryoidal aragonite dates at ~ 11,000 yr is a significant reduction in permeability related to a submarine hardground surface that developed as the steep marginal slopes switched from a depositional slope to a bypass slope (Grammer and Ginsburg 1992). This submarine hardground is characterized by dense, relatively impermeable, micritic cement and sediment that would have significantly reduced the circulation of fluids through the sediment. Because botryoidal aragonite is always found in relatively large pores, suggesting precipitation in highly porous and permeable sediments, it is reasonable to assume that such a reduction in permeability would have shut down the precipitation of these cements.

Although we cannot adequately explain the temporal distribution of the botryoidal aragonite cements, the significant point is that botryoidal aragonite cements can grow in marginal slope environments at rates that are geologically virtually instantaneous. In addition to the possibility of "freezing" carbonate slope deposits at or above angles of repose, such rapid cementation would tend to quickly occlude primary porosity and decrease sediment permeability, thereby inhibiting further diagenesis, and might produce enough acoustic impedance between surrounding deposits to form a strong seismic reflection horizon.

The rapid cementation and preservation of steep carbonate slope deposits might also influence overall platform geometry and might provide a predictive tool for subsurface work (i.e., steeply dipping, prograding choniforms on seismic might correlate with coarse-grained deposits, as suggested by Kenter 1990). Another point to consider is that the inverse relationship between rates of cementation and sedimentation suggested by some (e.g., Scoffin 1987; Tucker and Wright 1990) may not be applicable to marginal slope deposits. The high rates of cementation documented in this study suggest that estimates of slope depositional and progradational rates, based on the relationship of high cementation rates being indicative of low sedimentation rates, could be misleading and erroneous.

CONCLUSIONS AND IMPLICATIONS

Radiocarbon dating indicates that pore-filling botryoidal aragonite cements in a marginal slope environment may grow at rates > 8-10 mm/yr. In addition, direct observations with a scanning electron microscope have shown that fibrous aragonite may grow up to 75 µm long within 2 yr (rates up to 3.75 mm/100 yr) in water depths of 158 m. This combined evidence of geologically nearly instantaneous cementation, or "freezing" of marginal slope deposits, has important implications for the understanding of steep carbonate slopes. Through rapid cementation, steep slope deposits may be preserved at or above angles of repose, seismic reflector horizons may be formed, and primary porosity may be rapidly occluded. In addition, the potential for geologically instantaneous cementation in the marginal slope environment should be considered when developing models for depositional and progradational rates of carbonate platforms.

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