Where Carbonates begin...

Northwest Quaternary bench of Curacao, Dutch Antilles Island

Photographed by B.W. Fouke

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Abstract

A new quantitative approach uses the 87Sr/86Sr compositions of pristine and chemically altered marine invertebrate low-Mg CaCO₃ skeletons to determine the depositional and diagenetic age of mixed carbonate and siliciclastic depositional systems tracts. This technique has direct application to marine and terrestrial sedimentary systems that contain brachiopod and bivalve skeletal low-Mg CaCO₃, significantly expanding the range of shell material suitable for 87Sr/86Sr age dating.

Texturally and chemically altered low-magnesium calcite skeletal material records the progressive stages of meteoric diagenesis of the Seroe Domi Formation limestones on Curaçao, Netherlands Antilles. The elemental and isotopic geochemical composition of these altered shells is compared with taxonomically equivalent unaltered Recent shells, and quantitatively modelled with respect to mechanical mixing and water-rock interaction processes. This permits reconstruction of the 87Sr/86Sr of the original shells and their replacement calcites for use with Sr isotope age models. Results indicate that deposition of the Seroe Domi Formation during the Miocene-Pliocene-Pleistocene was punctuated by periods of subaerial exposure caused by the combination of tectonic uplift and eustatic lowering of sea level.

Ostrea frons oyster shells from the base of the 350 m-thick Seroe Domi Formation exhibit 87Sr/86Sr versus 13C and 1/Sr covariations suggesting that the shell compositions represent a mechanical mixture of original shell calcite and replacement calcite. The asymptotes of hyperbolic mixing curves fitted with unaltered and completely-altered shell compositions indicate that the oysters had an initial 87Sr/86Sr of 0.70877 (±0.00002). This implies that deposition occurred during the Middle Miocene (13.8 ± 1.4 Ma) and is consistent with foraminifer biostratigraphy. Modeling also suggests that the replacement calcite precipitated from meteoric water that was depleted in 13C, Sr and Mg, and enriched in Mn. An 87Sr/86Sr of 0.70883 in completely altered O. frons shells implies that subaerial exposure took place no later than the Middle to Late Miocene (11.2 ± 1.4 Ma).

Texturally unaltered and completely altered shells of Thecidellina barretti brachiopods and O. frons oysters from near the top of the Seroe Domi Formation have indistinguishable 87Sr/86Sr compositions. The unaltered shells contain Sr isotope ratios of 0.70904 to 0.70906, which suggest a Pliocene depositional age consistent with scleractinian coral biostratigraphy and that shell alteration took place soon after deposition during the Plio-Pleistocene.

Introduction

Because of its relative thermodynamic stability, texturally altered low-magnesium calcite (LMC) skeletal material is commonly used to reconstruct the 87Sr/86Sr composition of seawater at the time that a marine limestone was deposited. This assumes that the skeletal LMC has not been chemically altered, and therein establishes a comparative seawater 87Sr/86Sr standard for depositional and diagenetic reconstructions (e.g. Lowenstam, 1961; Popp et al., 1986a, b; Swart et al., 1987; Banner et al., 1988; Saller and Koepnick, 1990; Hodell et al., 1991). However, significant geochemical alteration of LMC skeletal material may take place without accompanying textural alteration (Rush and Chafetz, 1990). Therefore, seawater 87Sr/86Sr reconstructions made exclusively from texturally unaltered skeletal LMC are diagenetically suspect.

In this study, LMC skeletal material known to be diagenetically altered from the Neogene Seroe Domi Formation on Curaçao, Netherlands Antilles, is evaluated by combining models created to fingerprint mechanical mixing (Langmuir et al., 1978) and water-limestone interaction (Banner and Hanson, 1990). The approach is to collect compositional data from texturally unaltered, partially altered and completely altered Seroe Domi Formation LMC shells, as well as from Recent taxonomically-equivalent shells and the host limestones. These components, representing the incipient and endmember stages of alteration, are then quantitatively modeled to reconstruct the original shell calcite and diagenetic fluid compositions. Therefore, instead of obstructing diagenetic reconstructions, altered shells provide the intermediate control points necessary to accurately back-calculate original compositions. The results are used to reconstruct an intraformational seawater 87Sr/86Sr standard for the Seroe Domi Formation. Synthesis of this standard with field relationships, sedimentology and biostratigraphy has been used to establish the depositional and dolomitization history of the Seroe Domi Formation (Fouke, 1993, 1994; Fouke et al., 1996). This use of altered LMC skeletal material should significantly increase the number of geologic settings in which 87Sr/86Sr depositional and diagenetic age modelling can be applied.

GEOLOGIC SETTING

The Seroe Domi Formation is a 350 m-thick sequence of mixed carbonate and siliciclastic limestones that stand in relief on the leeward coast of the island of Curaçao, Netherlands Antilles (Fig. 1). The formation is composed of 3 stratigraphic subunits and 8 lithofacies that were were discontinuously deposited during the Miocene-Pliocene-Pleistocene (Fig. 2; Fouke, 1993, 1994; Fouke and Reeder, 1992; Fouke et al., 1996). Because the Seroe Domi Formation has never been buried, the potential
spectrum of diagenetic waters can be limited to seawater and meteoric groundwaters, as well as altered near surface derivatives of these waters and their mixtures.

Subunit 1, the basal 30 m of limestone, is a sequence of interbedded shelf to reef-front derived carbonate flows and pelagic oozes. The presence of the foraminifers Melonis pompiloides and Laticarinina pauperata suggest that Subunit 1 was deposited in deep-water (>500 m) fore-reef and carbonate slope environments on the leeward flanks of the Curaçao horst. Subunit 2, a 250-m section of siliciclastic-rich carbonate sands derived from erosion of the basement, which are overlain by 70 m of coralgal grainstones and boundstones. In situ reefs in the upper part of Subunit 2 indicate that depositional water depths shallowed to within the photic zone (<100 m). Subunit 3 siliciclastic sandstones and conglomerates were also derived from erosion of the Curaçao basement, and deposited within erosional chutes and caves formed in the uppermost Subunit 2 limestones. Subunits 1, 2, and 3 of the Seroe Domi Formation are then onlapped by a stepped sequence of Quaternary Limestone Terraces.

SAMPLES AND METHODS

Shells of the oyster Ostrea frons and brachiopod Thecidellina barretti were collected from Subunit 1 Lithofacies 1 and Subunit 2 Lithofacies 6 and 7 limestones of the Seroe Domi Formation on Curaçao (St. Michielsberg, Seru Spreit, and St. Annabaai; Figs. 1 and 2). Recent specimens of T. barretti and O. frons were collected in shallow marine environments near Piscaderabaai (Fig. 1). Geochemical analysis was completed on loose shells by mounting them in epoxy plugs and cutting sections perpendicular to the hinge line. Sectioned shells and whole-rock thin-section chips were then polished and petrographically examined using plane-light, cathodoluminescence, and SEM photomicrograph mosaics were constructed to serve as guides for microsample drilling. Each microdrilled sample powder was then ground to 75 µm mesh, and X-rayed for mineralogical homogeneity on a SCINTAG XRD at Stony Brook.

Figure 1. Geographic map of the island of Curaçao, Netherlands Antilles. The outcrop belt of the Seroe Domi Formation on the leeward coast of Curaçao is in black (after DeBuisonje, 1974). Labeled outcrops and bays distinguish localities in which Recent and Seroe Domi Formation skeletal material was collected for the present study. Inset depicts the location of Curaçao within the southern Caribbean Sea.

The cross-section is oriented perpendicular to the leeward coast of Curaçao at St. Michielsberg. Listed below the cross-section is a summary of the sedimentologic and Sr isotope evidence observed in Subunits 1, 2, and 3.

Figure 2. Geologic cross-section of Curaçao summarizing the stratigraphic relationships of the Curaçao Lava Formation basement, Seroe Domi Formation, and the overlying Quaternary Limestone Terraces. The cross-section is oriented perpendicular to the leeward coast of Curaçao at St. Michielsberg. Listed below the cross-section is a summary of the sedimentologic and Sr isotope evidence observed in Subunits 1, 2, and 3.

Carbon and oxygen isotopes were analyzed on a Finnegan-MAT 251 mass spectrometer with an on-line common acid bath in the Exploration and Production Technology Department of Texaco Oil Company in Houston, Texas. Data are reported as 18O and 13C-values for CO2 gas relative to PDB in the per mil standard notation 18O = [18Rsample/18Rstandard] - 1 \times 1000 where R =18O/16O. One-third of the samples were run in duplicate, yielding an analytical precision of 0.1 per mil for O and 0.2 per mil for C. In-run reproducibility of results was determined relative to the NBS 20 Solenhofen Limestone standard, and yielded a precision of 0.1 per mil for O and 0.2 per mil for C. Fractionation occurs between the 18O/16O ratio in the carbonate and the CO2 gas produced as a result of reaction with phosphoric acid. Therefore a fractionation factor of T = [5.25 \pm (0.08) \times 102JT-2 + 1.003970 \pm (0.000034)], as suggested by Swart et al. (1991) for the common acid bath technique, has been applied to calcite analyses. No phosphoric acid
fractionation correction has been applied to the dolomite analyses.

Cation abundances (Ca, Mg, Sr, Mn, Mn, and Fe) were determined by dissolving 20 mg of sample powder in ultrapure nitric acid, diluting the sample in 3x purified deionized water (with a resistance of <18 Ohms), and analyzing the solutions on a Beckman Spectra Span VB DCP (Direct Current Argon Plasma) at Stony Brook. All samples were analyzed in triplicate, with analytical uncertainties and detection limits of each element reported in the data tables. Major elements were analyzed separately from trace elements in sample splits that were diluted 100x. Standards were prepared by gravimetric dilution from single stock solutions.

DCP analyses of Ca, Mg, Fe and Mn were cross-checked with in situ elemental abundances on an electron probe microanalyzer (EPMA) at Stony Brook using a Cameca Camebax electron probe operating at 15 kV and 0.015 uA (for Ca and Mg) or at 30 kV and 0.015 uA (for Fe and Mn). Ten replicate analyses were made for each spot and averaged results were used for all comparisons. No systematic increases or decreases in counts were observed during any of the replicate analyses, suggesting that volatilization was not a problem. Carbonate and dolomite standards were run throughout. Estimated precision is expressed as 95% confidence limits, which are calculated from replicate analyses. For Ca and Mg, these are typically 1.5% relative, or approximately 0.8 mol% MCO3. For Mn and Fe, confidence limits are generally less than 4 wt%.

**PETROGRAPHIC CHARACTERIZATION**

Petrographic criteria were established in order to consistently categorize Seroe Domi Formation oyster and brachiopod shells according to the extent to which they have been texturally altered. Texturally unaltered or pristine specimens are shells that are non-cathodoluminescent (CL), and exhibit shell fabrics identical to those observed in the modern specimens. Partially altered specimens include shells with local areas of mottled CL, and patchy distributions of smoothed to irregular dissolution fabrics. Completely altered shells exhibit pervasive bright to mottled CL and widespread dissolution fabrics with no trace of original shell fabric. This terminology for the three successive degrees of skeletal alteration will be used throughout the following discussion.

**Oyster and Brachiopod Shells**

The shell of *O. frons* is 2 to 5 cm in longest dimension, 0.25 to 0.4 cm-thick, and composed of four structural layers that include the encasing periostracum, the hypostracum, and the inner and outer calcitized ostracum (Simkiss and Wilbur, 1989). The ostracum exhibits a variety of crystal morphologies, which include prismatic, fibrous, spherulitic and granular microcrystalline structures. The fibrous crystals are generally the most abundant and occur as 0.15 to 0.35 cm-thick layers of elongate LMC prisms that have grown inward from the periostracum within a bonding organic matrix to produce broad shell laminae (Simkiss and Wilbur, 1989). Specimens of *O. frons* sampled from the Seroe Domi Formation Subunit 1 and 2 grainstones exhibit the entire textural range of unaltered, partially altered, and completely altered shell fabrics (Fig. 3). These various fabrics are randomly distributed within shell populations from a single bedding plane, and did not exhibit a regular stratigraphic or geographic distribution. Shells of Recent *O. frons* chosen for analysis contain some fungal and algal microborings, but are otherwise texturally unaltered and non-cathodoluminescent.

**Figure 3.** Scanning electron micrographs of shell ultrastructure within specimens of Subunit 1 Lithofacies 1 *Ostrea frons*. Pictured sample is number 2/15/89-V7 from St. Michielsberg. A. Layers of prismatic crystals in the outer calcitized ostracum in texturally unaltered shells. B. Layers of fibrous crystals in the outer calcitized ostracum of texturally unaltered shells. C. Polished section of layered fibrous crystals in a partially texturally altered specimen, exhibiting dissolution pits along layers. D. Rounded, slightly dissolved prismatic crystals in a partially texturally altered specimen.

Most articulate brachiopod shells are composed of an inner primary prismatic layer and an outer secondary fibrous layer encased by the periostracum, both of which are deposited by different areas of the mantle (Williams, 1977). However, in addition to many other unique life history and physiologic affinities of thecideid brachiopods (Jackson et al., 1981; Fouke and LaBarbera, 1986), the fibrous secondary shell material does not form a layers but occurs only in superficial ovate patches up to 35 µm in diameter on the inner wall of the pedicle valve, and in teeth and socket ridges (Williams, 1973). Therefore, the LMC *Thecidellina barretti* shells are predominantly primary layer granular to accicular calcite crystals up to 15 µm in length (Williams, 1973). As was the case for the oyster shells, *T. barretti* specimens from single horizons exhibit the full range of texturally altered, partially altered, and completely altered shells (Fig. 4), which are randomly distributed at each locality within a single bedding plane. No texturally pristine ancient or Recent *T. barretti* shells were observed to luminescence.

**Host Limestone Paragenesis**

Detailed descriptions of the Seroe Domi Formation paragenetic sequence are presented in Fouke (1993, 1994) with the earliest pre-dolomitization diageneis summarized here.
The Subunit 1 Lithofacies 1 limestones containing *O. frons* shells exhibit extensive meteoric leaching and dissolution fabrics, and a 15 to 30 µm-long columnar "bladed" LMC cement precipitated within biomolds from meteoric fluids (depleted 18O and 13C compositions; Fouke et al., 1996). The Subunit 2 Lithofacies 7 limestones containing shells of *O. frons* and *T. barretti* also have extensive meteoric leaching and dissolution fabrics. However, the bladed calcites observed in Subunit 1 Lithofacies 1 are distinctly absent from the Subunit 2 Lithofacies 7 (Fouke et al., 1996).

### GEOCHEMICAL CHARACTERIZATION

Results of the geochemical analysis of Seroe Domi Formation and Recent oyster and brachiopod shells are presented in Table 1. In general, all Seroe Domi Formation shells, including the texturally pristine specimens, exhibit varying extents of depletion in Sr, Mg, 18O, and 13C relative to the Recent oyster and brachiopod shell material (Figs. 5 and 6).

The Recent shells of *O. frons* are depleted in 18O (-0.12 to -0.54 o/oo) and slightly depleted in 13C (-0.15 to -0.33 o/oo) relative to a Mio-Plio-Pleistocene estimated seawater calcite (ESC; +1 to +3.8 o/oo 18O and +0.5 to +2.5 o/oo 13C; Shackleton and Kennett, 1975; Shackleton and Cita, 1979; Miller et al., 1987, 1988; Fig. 5). Mg, Mn, and Fe abundances are consistently low, while Sr concentrations reach 748 ppm (Fig. 6). The Recent *T. barretti* shells are isotopically less depleted in 13C (1.31 to 1.94 o/oo) than *O. frons*, but more depleted in 18O (-0.67 to -0.91 o/oo; Figs. 5 and 6). Conversely, the Recent brachiopod up to 7.1 mol% MgCO3 and 1574 ppm Sr, which is significantly higher than the oysters (Fig. 6).

*O. frons* shells from Subunit 1 Lithofacies 1 Seroe Domi Formation limestones contain Sr isotope ratios that range from 0.708781 in texturally unaltered shells to 0.708831 in completely altered shells (Fig. 6). This increase of 0.00005 is the largest diagenetic shift in 87Sr/86Sr observed within any monospecific sample population in this study. The Lithofacies
Oysters also have lower stable isotopic compositions with respect to the ESC, ranging from -1.58 to -2.06 o/oo 18O and -3.22 to -4.37 o/oo 13C (Fig. 5). Sr and Mg concentrations become significantly depleted with increasing textural alteration, with Sr decreasing from 233 to below 2 ppm and Mg decreasing from 0.8 to 0.4 mol% MgCO3.

Conversely, completely altered shells exhibit simultaneous increases of as much as 205 ppm Mn and 161 ppm Fe.

Subunit 2 Lithofacies 7 Pliocene T. barretti shells are geochemically distinct from coeval lithofacies 7 O. frons, with the exception of a nearly identical range in 87Sr/86Sr (0.709035 to 0.709050; Fig. 6). However, as was the case for the oysters, this yields an undetectable difference of only 0.00001 between unaltered and completely altered shells. Lithofacies 7 brachiopod oxygen isotopes are depleted by up to 2 o/oo in 18O with respect to both the Lithofacies 1 and 7 oysters, displaying a tighter distribution of -0.38 to -1.00 o/oo (Fig. 5). Conversely, the carbon isotopes exhibit broad range of compositions from -0.88 o/oo in the texturally unaltered shells to -3.83 in the altered shells. Trace element abundances also have a broad ranges, with 1.9 to 5.2 mol% MgCO3, 94 to 1082 ppm Sr, and Mn and Fe enrichments of up to 344 ppm and 914 ppm respectively (Fig. 6).

INTERPRETATION OF SHELL ALTERATION

Several studies have documented the simultaneous enrichment of Mn, Mg, Fe, and 87Sr, and simultaneous depletion of Sr, 18O, and 13C in the low-Mg calcite shells during the progressive stages of meteoric diagenesis (e.g. Veizer and Compston, 1979; Brand and Veizer, 1980, 1981; Veizer, 1983a, b; Popp et al., 1986a, b; Brand and Morrison, 1987; Rush and Chavez, 1990; Wadleigh and Veizer, 1992). The rate, extent and textural style of this low-temperature LMC to LMC transition is controlled by the rate of Mn mobilization and the availability of Mg from the surrounding groundwater.

Table 1. The geochemical compositions of Recent and Seroe Domi Formation Ostrea frons oyster and Thecidellina barretti brachiopod shells.

Table 2. Sr isotope model ages of skeletal material from the Seroe Domi Formation. Skeletal 87Sr/86Sr values have been evaluated with the regression age model of Hodell et al. (1991).
formation is dependent upon the complex interplay of several parameters, including: 1) differences in the compositions of the respective solid and fluid reservoirs; 2) the partition coefficients and fractionation factors for individual elements and isotopes; 3) the local volumetric ratios of interacting solid and fluid; 4) the local extent of reaction; 5) the relative ratio of fluid-rock interaction events that have taken place; and 6) the influences of fluid or solid mixing (Brand and Veizer, 1980; Veizer, 1983; Banner and Hanson, 1991).

Water-Rock Interaction Versus Mechanical Mixing

The relative fluid/rock ratios necessary for different isotopic and elemental systems to simultaneously equilibrate during water-rock interaction can be modelled with iterative mass balance equations (Banner and Hanson, 1990). While it is unnecessary for the system being modelled to have reached equilibrium, it is necessary to assume that the system is advancing toward equilibrium. This implies that the replacement process proceeds via the pervasive textural and geochemical alteration of the skeletal LMC. The other conceptual endmember regarding low-temperature LMC to LMC transitions is that the replacement occurs in small discrete areas rather than pervasively. This would create a patchwork of replacement calcites within a relatively unaltered host matrix of original shell material, the scale of which could range from Å’s to µm’s and is below standard petrographic resolution. Therefore, the 100 µm resolution of the microdrilling technique would create a bulk mixture between the original shell material and the local areas of replacement calcitization. In both the pervasive and discrete replacement cases, it is the composition of samples representing the intermediate stages of the alteration process, and not the initial and final fluid and solid compositions, that would permit the distinction between water-rock interaction and mechanical mixing processes. However, it is possible that water-rock interaction and mechanical mixing pathways may be identical due to compositional similarities. Therefore the effectiveness of these modelling approaches in determining the diageneric mechanism depends upon accurate estimates of the initial solid and fluid compositions, as well as the extent and direction of diagenesis in the natural system during alteration. All of these criteria are met by comparing partially to completely altered fossil LMC skeletal material with taxonomically equivalent extant shells.

Subunit 1 Lithofacies 1 Oyster Shell Alteration

Texturally unaltered specimens of Lithofacies 1 O. frons shells are significantly lower in 18O, 13C, Sr and Mg, and slightly enriched in Mn and Fe, relative to modern O. frons shells (Figs. 5 and 6). This indicates that the texturally unaltered Lithofacies 1 oysters have been diagenetically altered (e.g. Veizer, 1983), and therefore do not reflect original seawater 87Sr/86Sr ratios.

The isotopic and elemental enrichment or depletion observed in all of the Lithofacies 1 oysters is consistent with the
relative progression from unaltered to altered textures. A hyperbolic mixing curve has been calculated for the Lithofacies 1 oysters using the endmember unaltered and completely altered shell compositions, which indicates that the 13C would be reset prior to the 87Sr/86Sr during the mixing process (Fig. 7; Langmuir et al., 1978). The 13C versus 87Sr/86Sr compositions of the intermediate partially altered Lithofacies 1 O. frons shells closely correlate with this mixing curve, while the 87Sr/86Sr versus 1/Sr companion plot exhibits a strong linearity ($r = 0.94$; Fig. 7). Therefore, this implies that the observed oyster shell compositions represent a binary mixture between original LMC shell and the replacement LMC (Langmuir et al., 1978). Furthermore, the interaction of Lithofacies 1 oyster shell calcite with normal meteoric groundwaters low in HCO3 and Sr/Ca abundances (Stoessel et al., 1989), would equilibrate 87Sr/86Sr prior to resetting the 13C (Fig. 7). The observed equilibration of C isotopes prior to 87Sr/86Sr in the Lithofacies 1 oysters would require a meteoric water containing at least 1200 ppm HCO3 and 0.15 Sr/Ca, which is unlikely for both meteoric and marine waters in these near-surface environments (Drever, 1982; Stoessel et al., 1989). However, the tight clustering of 18O versus 13C compositions prevents further discrimination between mixing or water-rock evolution (Fig. 5).

The Mg versus Mn and Sr/Ca versus Mn plots of Lithofacies 1 O. frons shell compositions initially appear to suggest alteration during water-rock interaction, in which Sr and Mg are completely equilibrated prior to Mn equilibration (Fig. 8). However, the strong evidence for mechanical mixing provided by the 13C versus 87Sr/86Sr crossplot implies that this more accurately represents the mixing of shell LMC with replacement LMC that became progressively enriched with respect to Mn during progressive alteration (Fig. 8). The sensitivity of Mn solubility to redox conditions (e.g. Morse and Bender, 1990), the abundance of Mn sources available on Curaçao (e.g. clastic basement, carbonates, seawater), and the significant temporal variations in Mn concentrations observed in other Seroe Domi Formation calcite and dolomite cements (Fouke, 1994), combine to suggest that mixing with a calcite of evolving Mn abundances is geologically plausible. In order for mixing to produce the observed low abundance narrow range of Sr/Ca and Mg, each Lithofacies 1 oyster shell necessarily must represent almost complete replacement by the evolving Mn calcite, which is also suggested by the depleted tightly clustered O versus C isotope distributions (Fig. 5).

The above geochemical evidence suggests that the textural and compositional alteration of the Lithofacies 1 O. frons shells represents the mixing of shell LMC with replacement LMC rather than water-rock interaction. Therefore, the asymptotes and intercepts of the hyperbolic mixing curves will be used to place maximum and minimum constraints on the endmember compositions of the original shell material and the replacement calcite (Langmuir et al., 1978). The hyperbolic asymptotes of 87Sr/86Sr versus 13C (Fig. 7), Sr, Mn, and Mg plots (Fouke, 1993) consistently suggest a minimum original O. frons skeletal 87Sr/86Sr of 0.70887. In addition, this suggests a minimum replacement LMC composition of -4.6 o/oo 13C, 0.003 ppm Sr, 0.6 mol% Mg, and 165 ppm Mn, which is con-
sistent with the precipitation of this calcite from meteoric waters (e.g. James and Choquette, 1883; Meyers and Lohmann, 1985; Lohmann, 1987; Saller and Moore, 1989; Goldstein et al., 1991). An independent evaluation of this original 87Sr/86Sr composition is provided by the intersection of the range of Sr abundances observed in Recent oyster shells (430 to 738 ppm; Table 1) with the regression line through the 87Sr/86Sr versus 1/Sr data (Fig. 7). This suggests a complementary estimate of the original 87Sr/86Sr of 0.708782 to 0.708810 as defined by the 95% confidence interval of the regression line (Fig. 7). In addition, the intersection of a mechanical mixing line connecting the mean Recent and Lithofacies 1 shell compositions with the estimated replacement calcite 13C suggests that the replacement calcite has a 18O composition of approximately -2.3 o/oo (Fig. 5).

**87Sr/86Sr CHRONOSTRATIGRAPHY**

The previously presented geochemical evaluations of Seroe Domi Formation oyster and brachiopod shells indicate that the 87Sr/86Sr signatures of the texturally unaltered LMC has been altered to varying extents during meteoric diagenesis. Therefore, estimates of the original shell 87Sr/86Sr compositions for chronostratigraphic reconstructions in the Subunit 1 Lithofacies 1 oysters have been derived from the asymptotes and intersects of hyperbolic mixing curves. Conversely, because similar quantitative modelling was not possible for Subunit 2 Lithofacies 7 brachiopods and oysters, the small spread in 87Sr/86Sr between unaltered and completely altered shells suggests that the unaltered Sr isotopic composition is a reliable estimate of the original shell composition. Several recent studies of ODP and DSDP of the 87Sr/86Sr in calcitic foraminifer tests (Hodell et al., 1989, 1990, 1991; Miller et al., 1991) have independently applied in the following Seroe Domi Formation reconstructions (Tab. 2).

**Depositional Age**

Modelled hyperbolic asymptotes of the Subunit 1 Lithofacies 1 Ostrea frons shell compositions suggest that the original 87Sr/86Sr at the time of precipitation from seawater was 0.70877, implying a depositional age of 13.8 ±1.4 Ma (Hodell et al., 1991; Tab. 2; Fig. 11). This model age and its associated age uncertainties overlap with the Praeorbulina glomerosa (Blow) range zone of 15.2 to 16.2 Ma (Berggren et al., 1985) suggested by Subunit 1 planktonic foraminifer biostratigraphy (Fouke et al., 1995). The texturally unaltered Subunit 2 Lithofacies 7 Ostrea frons and T. barretti shells suggest that the original shell 87Sr/86Sr was approximately 0.70904, which implies precipitation from a Late Pliocene to Early Pleistocene seawater at 2.3 ±0.6 Ma (after Hodell et al., 1991; Tab. 2; Fig. 11). This model age is consistent with the scleractinian coral assemblage that implies a Late Pliocene to Early Pleistocene depositional age (Fouke et al., 1995). A single specimen of Ostrea frons sampled from Subunit 2 Lithofacies 6 packstones yields an 87Sr/86Sr of approximately 0.70903 (+0.00002), suggesting a Late Miocene to Pliocene age of 4.8 Ma ± 0.5 Ma (after Hodell et al., 1991; Tab. 2; Fig. 11). Although it was not possible to complete a rigorous analysis of other shells from this horizon, this age is consistent with the stratigraphic occurrence of Lithofacies 6, which is underlain by Lithofacies 1 and overlain by Lithofacies 7 (Fouke et al., 1996).
Timing of Diagenetic Alteration

The $^{87}$Sr/$^{86}$Sr model age of completely altered skeletal material has also been applied to interpret the timing of meteoric diagenesis of the Seroe Domi Formation limestones. The groundwaters that altered the Subunit 1 and 2 shell material may have derived Sr from different sources, which include: 1) the host Subunit 1 and 2 limestones; 2) contemporaneous seawater; 3) the basalts and siliclastics comprising the Curaçao basement; and 4) younger carbonates (Fouke, 1993). However, the observed increases in shell $^{87}$Sr/$^{86}$Sr with progressive textural alteration suggest that the diagenetic waters did not contain less-radiogenic Sr derived from the basement. In addition, the lack of early bladed LMC cements in Subunit 2 Lithofacies 6 deposits directly overlying Subunit 1 deposits suggests that Subunit 1 limestones were stabilized in meteoric fluids prior to the Late Miocene-Pliocene deposition of Lithofacies 6 (Fouke, 1994). Therefore there were no younger limestones at this time from which to source more-radiogenic Sr. Similarly, diagenetic evidence with respect to the distribution of calcite and gypsum cements in Subunit 2 Lithofacies 7 limestones suggests that Lithofacies 7 diagenesis occurred prior to the Pleistocene deposition of Lithofacies 8 and the overlying Quaternary Limestone Terraces (Fouke 1993; Fouke et al., 1996). Therefore the source of Sr in the meteoric fluids that altered Subunit 1 and 2 limestones can be restricted to contemporaneous seawater and/or the host limestones.

These observations suggest that Sr in the meteoric fluids that stabilized Lithofacies 1 and 7 limestones had an $^{87}$Sr/$^{86}$Sr that was either equivalent to, or less-radiogenic than, contemporaneous seawater at the time of subaerial exposure. Therefore, the following $^{87}$Sr/$^{86}$Sr model ages reconstructed from completely altered shell material will provide a maximum estimate of the age of stabilization. The completely texturally altered specimen of Lithofacies 1 Ostrea frons analyzed in this study has a Sr isotope ratio of $0.708832 \pm 0.00002$, suggesting that skeletal replacement during subaerial exposure took place no earlier than 11.2 $\pm$ 1.4 Ma (after Hodell et al., 1991; Tab. 2; Fig. 11). This period of exposure correlates with the -200 m drop in sea-level associated with the onset of Antarctic glaciation (Shackleton and Kennett, 1975; Haq et al., 1988). Given the deep-water (500+ m water depths) environment of Subunit 1 deposition, subaerial exposure of the Subunit 1 limestones at the Middle to Late Miocene transition would have required the combined effects of tectonic uplift and eustatic sealevel lowstand.

SUMMARY AND CONCLUSIONS

A modeling approach has been presented that utilizes the $^{87}$Sr/$^{86}$Sr composition of pristine and chemically altered marine invertebrate low-Mg CaCO$_3$ skeletons, which can be directly and universally applied to reconstruction of the timing of deposition and diagenesis in other marine and terrestrial sedimentary systems containing fossilized brachiopod and bivalve shells. The geochemical composition of altered low-magnesium calcite oyster (Ostrea frons) and brachiopod (Thecideillina barretti) shells from the Seroe Domi Formation record the incipient stages of meteoric diagenesis. Quantitative analyses of these altered shells with respect to mechanical mixing and water-rock interaction processes have been used to determine their original and altered $^{87}$Sr/$^{86}$Sr signatures for chronologic interpretations of the ages of deposition and diagenesis. The results suggest that the Seroe Domi Formation has experienced multiple episodes of marine deposition and meteoric stabilization due to the combined effects of tectonic uplift and eustatic sealevel changes.

Subunit 1 Lithofacies 1 O. frons shells from the basal 30 m of the Seroe Domi Formation are depleted in 18O, 13C, Sr, and Mg, but enriched in Mn and Fe with respect to Recent shells. These trends suggest that all specimens, including texturally pristine shells, have experienced significant meteoric diagenesis that has reset their original seawater Sr isotopic compositions. $^{87}$Sr/$^{86}$Sr versus 13C covariations suggest that these oyster shell chemistries are the result of the mixing of skeletal calcite and replacement calcite rather than progressive water-rock interaction. The hyperbolic asymptotes of mixing curves and the comparison of $^{87}$Sr/$^{86}$Sr versus 1/Sr with the 87Sr/86Sr of 0.70887 Sr isotope regression age modelling, coupled with biostratigraphy, implies that Subunit 1 deposition took place during the Middle Miocene. The composition of completely altered Lithofacies 1 O. frons shells took place in meteoric waters during the Middle to Late Miocene transition.

Subunit 2 Lithofacies 7 O. frons and T. barretti shells from the uppermost 100 m of the Seroe Domi Formation are also depleted in 18O, 13C, Sr, and Mg, and enriched in Mn and Fe, indicating that the shells have experienced meteoric diagenesis. However, while the observed shift in $^{87}$Sr/$^{86}$Sr of only 0.00001 between unaltered and completely altered shells prevents quantitative mixing and water-rock interaction modeling, it does suggest that unaltered shell $^{87}$Sr/$^{86}$Sr has not been significantly changed. The Sr isotopic composition of unaltered O. frons and T. barretti suggests an original minimum $^{87}$Sr/$^{86}$Sr of approximately 0.70904, which is consistent with the biostratigraphy and suggests a Pliocene depositional age. Completely altered Lithofacies 7 oysters and brachiopods exhibit $^{87}$Sr/$^{86}$Sr signatures of 0.70905 to 0.70906, suggesting that subaerial exposure and meteoric alteration no earlier than the Late Pliocene to Early Pleistocene transition.

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REFERENCES


NOTICE!!!

Member Reminder:

Last year’s Board and this year’s Board in their joint meeting in June of 2007 decided to discontinue the WTGS Bulletin in its original hardcopy format as part of the standard annual membership dues. Instead, the new standard annual membership dues fee will only include a digital (Adobe PDF file) version of the Bulletin, to be downloaded from the website (www.wtgs.org). Members who wish to continue receiving a hardcopy version will have an option box to check on the 2008/2009 Membership Renewal Form. Adding the hardcopy version of the Bulletin will cost an additional $20.