

# Isotopic fingerprints of microbial respiration in aragonite from Bahamian stromatolites

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## ABSTRACT

**Authigenic aragonite preserves a carbon isotopic record of heterotrophic microbial influences on dissolved inorganic carbon (DIC) in microenvironments within shallow subtidal stromatolites from Highborne Cay, Bahamas. A greater amount of aragonite precipitates when and where respiration, rather than photosynthesis, influences local DIC, which is consistent with sulfate reduction promoting carbonate precipitation and calcium release during decay of exopolymeric substances. Thus, heterotrophs play a more direct role than phototrophs in stromatolite lithification. Cyanobacteria are spatially associated with aragonite containing heterotrophic isotopic signatures. Hence, the absence of an autotrophic isotopic signature in the rock record does not imply the absence of photosynthetic organisms.**

**Keywords:** microbe-mineral interactions, carbonate geochemistry, isotopes, stromatolites, Bahamas.

## INTRODUCTION

Understanding microbial roles in lithifying stromatolites is critical to the interpretation of the origin of ancient stromatolites and the early evolution of life. Stromatolites represent a mineral record of ancient carbonate chemistry, including microbial influences on local dissolved inorganic carbon (DIC). All microbial communities cycle CO<sub>2</sub>, changing local carbonate mineral stability and influencing the δ<sup>13</sup>C of DIC. When carbonates precipitate, they record the δ<sup>13</sup>C signature of local DIC, capturing microbial influences on isotopic ratios (e.g., Des Marais et al., 1989; Guo et al., 1996; Stephens and Sumner, 2002). Thus, the isotopic composition of carbonates can record ancient microbial CO<sub>2</sub> cycling, providing insights into the environmental distribution of microbial influences on environmental chemistry.

Modern stromatolites provide the opportunity to characterize how microbial carbon isotopic shifts can be incorporated into the rock record, and microbial δ<sup>13</sup>C shifts have been identified in modern lacustrine and hypersaline stromatolites (e.g., Guo et al., 1996; Schidlowski 2000). Isotopic shifts in marine stromatolites have not been sufficiently resolved to demonstrate microbial influences on carbonate precipitation (Browne, 1993). Likewise, studies of marine microbial carbonates have not provided convincing documentation of microbial isotopic shifts; previous results have been interpreted as evidencing “non-enzymatic fractionation” close to values precipitated from seawater equilibrium in some studies (e.g., Camoin et al., 1999), and were

considered negligible, within equilibrium of seawater or “non-enzymatic organomineralization,” in others (Reitner et al., 2000).

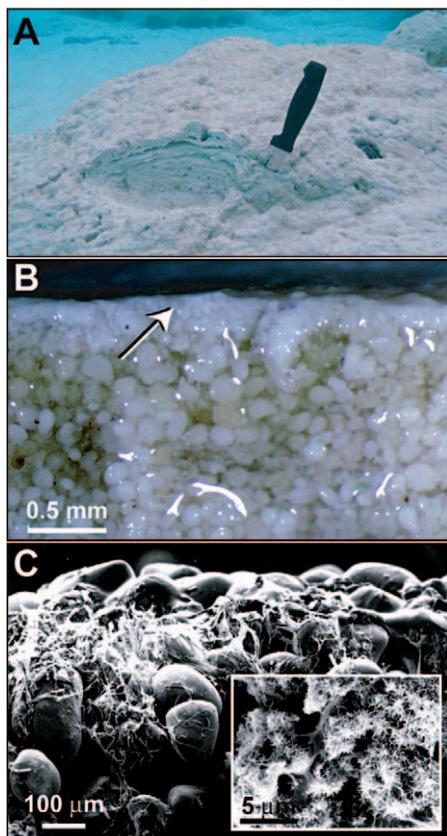
The difficulty in observing isotopic signatures may be due to the competing influences of photosynthetic CO<sub>2</sub> uptake, sulfate reduction, and degradation of organic matter on the isotopic composition of DIC and carbonate saturation states (e.g., Nadson, 1928; ZoBell, 1946; Krumbein, 1979; Visscher and Stolz, 2005). By carefully subsampling modern Bahamian stromatolites, we have obtained the first carbon isotopic results from modern marine stromatolites that demonstrate that heterotrophic processes dominate when marine carbonate precipitates leading to stromatolite lithification.

## MATERIAL AND METHODS

On Highborne Cay (76°49'W; 24°43'N), Exuma Cays, Bahamas, shallow subtidal stromatolites grow in the back-reef lagoon of an algal-ridge fringing reef (Reid et al., 1999). Laminated ridge and columnar stromatolites grow to 50 cm high in <1 m of water at low tide. Variations in microbial mat structure and activity include three end-member communities (Reid et al., 2000). An unlithified, extracellular polymeric substances (EPS)-rich community dominated by the filamentous cyanobacterium *Schizothrix* sp. (Golubic and Browne, 1996) traps and binds grains deposited on stromatolites, including 150–180-μm-diameter ooids, as well as other grains consisting of skeletal fragments, shell fragments, and unidentified clasts. A diverse phototrophic and heterotrophic community forms a contin-

uous EPS film associated with surficial aragonite crusts, which persist as quasicontinuous, ~50-μm-thick micritic laminae at depth in the stromatolites (Reid et al., 2000; Visscher et al., 2000). With time, this heterotrophic community can mature into a community containing abundant *Solentia* sp., an endolithic coccoidal cyanobacterium. *Solentia* bores through sand grains, backfilling boreholes with aragonite and fusing grains when boreholes cross grain contacts (Macintyre et al., 2000). Successions of these three communities produce laminated stromatolites with variable cementation in different layers. Cementation increases with depth due to precipitation of <5-μm-long aragonite needles (Fig. 1C, inset) attached to crusts, attached to grains, and in EPS between grains.

Four stromatolites, A–D, were sampled to characterize microbial roles in aragonite precipitation. Stromatolite A was marked with a carborundum layer on 16 January 2004 and was sampled on 14 March 2004. All stromatolite A samples accreted to or precipitated on the stromatolite between January and March 2004. The other stromatolites were not marked, and the timing of precipitation is unknown. Stromatolite layers were dissected into component parts and then reacted in bleach for 8–9 h to remove organic matter. The pH of bleached test samples remained constant and below 9, suggesting no carbonate precipitation during processing. Coarse-grained constituents (ooids, other grains, and crusts) were picked manually from disaggregated samples and petrographically characterized to ensure proper classification. To separate fine sediment and aragonite needles from coarse components, we suspended samples in water equilibrated with stromatolitic sediment and retained the fine components that remained in suspension longest. This process was repeated 1–2 times to isolate the finest sediment. Petrographic characterization of fine sediment samples demonstrated that some samples consisted solely of carbonate <5 μm, whereas others contained a small proportion of 5–30 μm sediment. Thus, samples were divided into two groups: fine, and fine and grains. This division was confirmed with scanning electron microscope imaging. After separation, samples were soaked in bleach for an additional

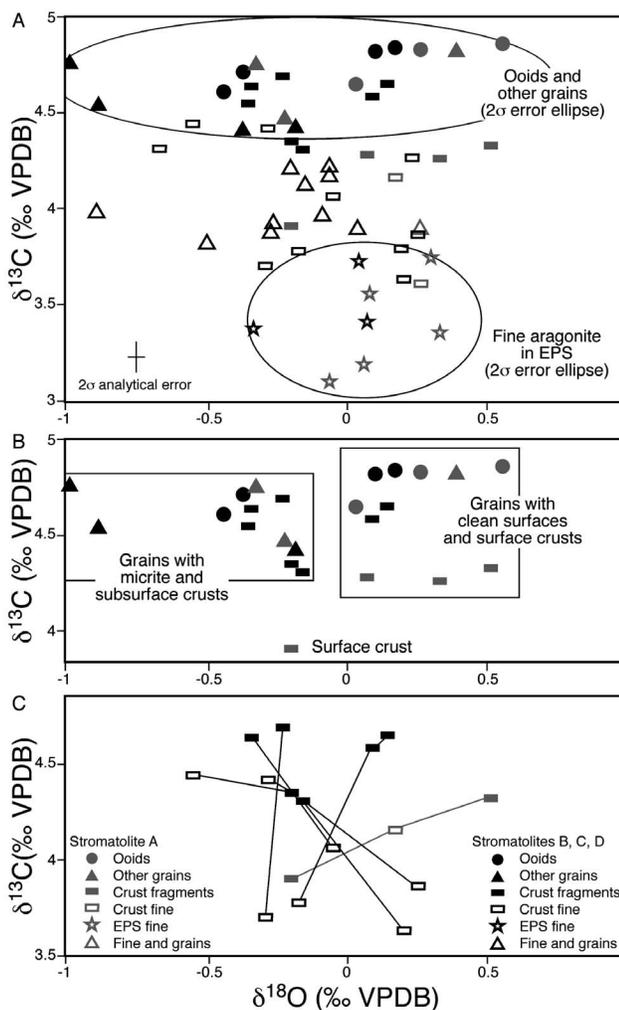


**Figure 1.** A: Highborne Cay stromatolite viewed underwater showing prominent lamination and complex surface morphology. B: A vertical cut section of top surface crust (arrow). C: Scanning electron microscope (SEM) image of surface mat extracellular polymeric substances (EPS) biofilm draped on top of sediment trapped and bound by filamentous cyanobacteria. Fine carbonate, aragonite needles (inset) precipitate in association with EPS decay and heterotrophic microbial activity.

8 h to dissolve remaining organic material, washed 3 times with neutral pH water, centrifuged, and air dried.

Carbonates were isotopically analyzed with a Kiel III automated carbonate device interfaced to a Finnigan Delta-plus stable isotope ratio mass spectrometer. Results were corrected for standard drift and isobaric interferences and are expressed relative to Vienna Pee Dee belemnite (VPDB). Instrument precision was  $0.15\text{‰}$  for  $\delta^{18}\text{O}$  and  $0.1\text{‰}$  for  $\delta^{13}\text{C}$  ( $2\sigma$ ).

Organic carbon isotopic samples were air dried and treated with 1 M HCl to remove inorganic carbon. More labile components may have been hydrolyzed during treatment, but the  $2\text{‰}$  range in results exceeds expected isotopic shifts due to sample processing (e.g., Schubert and Nielsen, 2000). Samples were analyzed on a Europa CN device interfaced to a continuous-flow stable isotope ratio mass spectrometer. Absolute standard deviation of  $\delta^{13}\text{C}_{\text{org}}$  analysis was  $0.1\text{‰}$  ( $2\sigma$ ).



**Figure 2.** Isotopic composition of aragonite. A: Ooids and other grains are enriched in  $^{13}\text{C}$  relative to fine aragonite that precipitated in extracellular polymeric secretion (EPS). B: Clean, surface ooids and other grains that lack micritic coatings and substantial *Solenitaria* boring are slightly enriched in  $^{18}\text{O}$  relative to those associated with micrite. Crusts are similarly enriched with the exception of one sample from stromatolite A. C: Crusts are isotopically heterogeneous, as demonstrated by the variability in fragments from the same crust and fine carbonate separated from these fragments. Lines connect multiple analyses from the same crust.

U and Th isotopes were measured on two samples composed of 510 mg and 518 mg of stromatolite-bound sediment from different depths in the same stromatolite. Before analysis, samples were chemically purified following published procedures (Cheng et al., 2000, and references therein). U and Th isotopes were measured on a Finnigan MAT 262 RPQ+ multicollector mass spectrometer. Measured  $^{234}\text{U}/^{238}\text{U}$  activity ratios were  $1.147 \pm 0.0016$  dpm (disintegrations per minute) and  $1.1437 \pm 0.0027$  dpm, respectively, indicating a seawater signal (Cheng et al., 2000).

## RESULTS

Sediment trapped in two stromatolite layers yielded U/Th ages of  $1548 \pm 55$  and  $1590 \pm 47$  yr, which are consistent with previously published ages for oolitic sands elsewhere in the Bahamas (Martin and Ginsburg, 1965). These results demonstrate that trapped and bound grains in stromatolites represent an old, well-mixed population, and surface grains reflect the same population as those in stromatolite interiors.

Organic  $\delta^{13}\text{C}$  of surface mats ranges from

$-7.28\text{‰}$  to  $-9.20\text{‰}$ , which is  $11.2\text{‰}$ – $13.2\text{‰}$  lower than the local seawater DIC composition of  $\delta^{13}\text{C} = 4.04\text{‰}$ . Cyanobacteria, the dominant organic carbon source, produce organic carbon that is  $\sim 25\text{‰}$  lighter than ambient DIC (Preuss et al., 1989), unless carbon fixation is faster than diffusional  $\text{CO}_2$  equilibration with the ambient environment (Des Marais et al., 1989; Sumner, 2001). The presence of relatively  $^{13}\text{C}$ -enriched organic carbon is consistent with  $\text{CO}_2$  limitation during photosynthesis.

Carbonate  $\delta^{13}\text{C}$  ranges from  $+3.1\text{‰}$  to  $+4.8\text{‰}$ , and different stromatolite components have different values. The  $\delta^{13}\text{C}$  values of ooids and other grains range from  $+4.41\text{‰}$  to  $+4.86\text{‰}$  and are more  $^{13}\text{C}$ -enriched than other components (Fig. 2B). The  $\delta^{13}\text{C}$  values of micritic crusts range from  $+4.26\text{‰}$  to  $+4.69\text{‰}$ , which is slightly  $^{13}\text{C}$ -depleted relative to average ooids and other grains. One crust analysis, from stromatolite A, is significantly depleted in  $\delta^{13}\text{C}$  relative to other crusts and a second sample from the same crust (Fig. 2B). Also, fine carbonate samples separated from crusts have different isotopic composi-

tions than larger fragments of the same crust (Fig. 2A). Two samples of fine carbonate are slightly  $^{13}\text{C}$ -enriched relative to their associated larger crust fragments (hereafter called "crusts"), but most are  $^{13}\text{C}$ -depleted, some up to 1‰ (Fig. 2C). Thus, the  $\delta^{13}\text{C}$  of crusts is heterogeneous. Fine-fraction carbonate samples separated from EPS-rich layers and consisting of  $<5\ \mu\text{m}$  aragonite crystals (Fig. 2C, inset) are the most  $^{13}\text{C}$ -depleted with  $\delta^{13}\text{C} = 3.1\text{‰}$ – $3.7\text{‰}$ . Samples that include a few small grains have  $\delta^{13}\text{C} = 3.8\text{‰}$ – $4.2\text{‰}$ , which is consistent with physical mixing of grain and aragonite needle end members.

Carbonate  $\delta^{18}\text{O}$  ranges from  $-0.98\text{‰}$  to  $+0.55\text{‰}$  (Fig. 2A). Ooids and other grains have the largest  $\delta^{18}\text{O}$  range; those with clean, glassy surfaces from the upper 1–3 mm of stromatolites are enriched in  $^{18}\text{O}$  relative to ooids and other grains bored by *Solentia* and those with varying amounts of surficial micrite from deeper in the stromatolites. The  $\delta^{18}\text{O}$  values of the crusts similarly cluster into surface and subsurface groups (Fig. 2B). Although the  $\delta^{18}\text{O}$  range of fine-fraction samples is similar to that of grains and crusts (Fig. 2A), they lack  $\delta^{18}\text{O}$  differentiation with depth.

## DISCUSSION

The isotopic composition of ooids and other grains is consistent with Bahamian surface sediments in the Bahamas (Shinn et al., 1989; Swart and Eberli, 2005), although aragonite that precipitates in equilibrium with  $\text{HCO}_3^-$ -dominated DIC with  $\delta^{13}\text{C}$  of  $\sim 4\text{‰}$ , as measured in the Bahamas, should have  $\delta^{13}\text{C}$  of  $\sim 6.7\text{‰}$ . The lower  $\delta^{13}\text{C}$  values are consistent with fluctuations in DIC  $\delta^{13}\text{C}$  over time, reflecting variations in water advection, photosynthesis, and respiration on the Bahamian platforms (Swart and Eberli, 2005). We interpret grain  $\delta^{13}\text{C}$  values as reflecting equilibrium precipitation from average seawater over  $\sim 1500$  yr. In contrast, fine precipitates extracted from EPS are  $^{13}\text{C}$ -depleted relative to grains. This signal is unlikely to be due to isotopic disequilibrium during rapid precipitation because only carbon isotopic values are distinct from the ambient marine signature;  $^{18}\text{O}$  is also depleted during rapid carbonate precipitation (e.g., McConnaughey, 1989). Thus, low  $\delta^{13}\text{C}$  values for fine sediment suggest that respiration rates within stromatolites were rapid enough to alter the  $\delta^{13}\text{C}$  of local DIC. An isotopic shift of  $1\text{‰}$ – $2\text{‰}$  requires a 20% contribution from respired DIC if respired organic carbon is 12‰ lower than oceanic DIC, as observed in the Bahamas. A microbial contribution to DIC could either increase or decrease  $\text{CO}_3^{2-}$  activity, depending on pH buffering and degassing (Visscher and Stolz, 2005). However, evidence of precipitation of aragonite in EPS demonstrates that the aragonite saturation index did not sub-

stantially decrease, consistent with abundant sulfate reduction, which can increase both DIC and pH (Visscher and Stolz, 2005) and  $\text{Ca}^{2+}$  release during EPS decay (Paerl et al., 2001; Kawaguchi and Decho, 2002; Decho, 2003; Dupraz et al., 2004).

Crusts show a slight depletion in  $^{13}\text{C}$  relative to grains. Because crusts form at the surfaces of stromatolites (Reid et al., 2000), rapid exchange of DIC between the crust and ambient seawater may inhibit maintenance of a local pool of microbial-influenced DIC in the crust, leading to aragonite that is nearly in equilibrium with ambient seawater. The small  $^{13}\text{C}$  depletion could reflect some precipitation in nooks of the mat where exchange with open seawater was slow enough that respiration influenced the  $\delta^{13}\text{C}$  of DIC. Although rapid isotopic equilibration with seawater is a reasonable explanation for the isotopic composition of crusts, chemical gradients in Highborne Cay stromatolites include  $600\ \mu\text{M}$   $\text{O}_2$  and 0.9 pH variations due to microbial activity (Visscher et al., 1998, 2000). These gradients, measured on similar mats, demonstrate that carbonate chemistry in the top 2 mm of the mat is not in equilibrium with seawater, and DIC exchange between the crust and ambient seawater is not as rapid as microbial  $\text{CO}_2$  cycling. Thus, aragonite isotopic compositions do not reflect rapid DIC exchange and must reflect local microbial processes within the mat, including both photosynthesis and respiration. The presence of only small isotopic shifts implies that competing microbial isotopic influences are only slightly out of balance as recorded by intervals of aragonite precipitation. Isotopic heterogeneity in crusts demonstrates that this balance shifts in space and time.

The accumulation of organic matter in the stromatolites requires that, on average, photosynthetic  $\text{CO}_2$  fixation is greater than respiration. Furthermore, respiration continues at night, whereas photosynthesis occurs only during daylight hours, so average daytime photosynthetic removal of  $\text{CO}_2$  must be greater than daytime release of  $\text{CO}_2$  by heterotrophs, as observed in Highborne Cay stromatolites (Visscher et al., 1998; Decho et al., 2005). Large increases in pH within stromatolites during peak  $\text{O}_2$  production demonstrate photosynthetic influences on carbonate chemistry (Visscher et al., 2000, 2002), but the absence of  $^{13}\text{C}$  enrichment in the carbonate demonstrates that aragonite is not predominantly forming during this high pH interval. Even though pH increases promote aragonite precipitation, precipitation could be inhibited by EPS production, possibly due to binding of  $\text{Ca}^{2+}$  by acidic organic molecules produced during active photosynthesis (Paerl et al., 2001; Decho, 2003). The absence of  $^{13}\text{C}$  en-

richment demonstrates that most precipitation does not occur through photosynthetic influences on carbonate chemistry. Rather, the slight  $^{13}\text{C}$  depletion of crusts relative to grains may be due to more abundant aragonite precipitation at night when heterotrophic processes dominate. EPS and low-molecular-weight dissolved organic carbon flux experiments demonstrate peaks in heterotrophic  $\text{CO}_2$  release several hours after peak photosynthesis, and  $\text{Ca}^{2+}$  release coupled to EPS decay may enhance aragonite precipitation, particularly if sulfate reduction is one of the major heterotrophic processes (Decho et al., 2005; Visscher and Stolz, 2005). The slight  $^{13}\text{C}$  depletion in the stromatolite crusts is consistent with the influences on carbonate chemistry predicted by these biological models and adds further evidence that photosynthesis is not the driving factor for lithification of these stromatolites.

Subsurface grains, ooids, and crusts have  $\sim 0.5\text{‰}$  lower  $\delta^{18}\text{O}$  values relative to those on the surface. Given the  $\sim 1500$  yr average age of ooids and grains in the stromatolites, temporal variations in temperature and salinity are unlikely to have caused the observed variations in  $\delta^{18}\text{O}$ . Furthermore, subsurface aragonite needles have  $\delta^{18}\text{O}$  values that overlap both surface and subsurface grain  $\delta^{18}\text{O}$  values, eliminating an overall environmental difference from top to stromatolite interior. However, fluctuations in pH may explain  $\delta^{18}\text{O}$  variations. The oxygen isotopic composition of DIC varies with pH due to changes in the relative abundance of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  (Zeebe, 1999). If the subsurface grains partially recrystallized at higher pH than ambient water (pH = 7.9), they would have lower  $\delta^{18}\text{O}$  values than surface grains. Grain recrystallization associated with *Solentia* boring (Macintyre et al., 2000) could cause part of this shift if aragonite precipitates in *Solentia* bores at a pH significantly greater than 7.9. Also, mat pH varies significantly with time and depth, and times of peak sulfate reduction correspond to pH  $> 8.3$  in many parts of the mats (Decho et al., 2005; Visscher et al., 2002). Differences in  $\delta^{18}\text{O}_{\text{DIC}}$  between pH = 7.9 and 8.3–8.7 are  $+0.4\text{‰}$  to  $1.4\text{‰}$  (Zeebe, 1999), which are consistent with the  $\sim 0.5\text{‰}$  isotopic shift observed for crusts. A  $\delta^{18}\text{O}$  depletion of  $1.4\text{‰}$  should correspond to an increase in  $\delta^{13}\text{C}$  due to photosynthesis, as observed in two analyses of fine carbonate from crusts (Fig. 2). Variations in grain and ooid  $\delta^{18}\text{O}$  values require that aragonite associated with *Solentia* sp. boring precipitates at higher pH as well. In contrast, the range in  $\delta^{18}\text{O}$  of floating precipitate suggests that it precipitates at various pH values, consistent with diel pH changes within the microbial mat.

## CONCLUSIONS

Authigenic aragonite in Highborne Cay stromatolites preserves an isotopic record of heterotrophic microbial influences on DIC in microenvironments within the stromatolites. More aragonite precipitates when and where respiration influences local DIC than photosynthesis, which is consistent with sulfate reduction promoting carbonate precipitation in modern marine environments and EPS release of Ca<sup>2+</sup> during decay. The absence of photosynthetic isotopic signatures suggests that aragonite does not tend to precipitate during peak photosynthesis. Subtle  $\delta^{18}\text{O}$  shifts between surface and subsurface samples may record variations in pH.

The identification of variable microbial isotopic shifts in marine stromatolites opens new opportunities to evaluate the timing and influence of microbial communities on carbonate precipitation. Heterotrophic processes are the only ones captured in the isotopic signatures reported here, even though photosynthetic cyanobacteria are abundant and actively manipulating carbonate chemistry. Understanding the temporal and spatial relationship of precipitation is critical to capturing these signatures; the absence of an isotopic signature for photosynthesis in no way demonstrates an absence of cyanobacteria. The 1‰–2‰ shifts over 100  $\mu\text{m}$  spatial scales will be difficult to identify in ancient stromatolites after continued burial, lithification, and diagenesis (see discussion in Andrews and Brasier, 2005). Thus, microbial isotopic signatures in marine stromatolites are only likely to be identified in exceptional circumstances and if the carbonate components that precipitate on spatial scales of microbial communities can be isolated.

## ACKNOWLEDGMENTS

We thank T. Eisenhauer for the U/Th measurements at IFM-GEOMAR, and P. Visscher for discussions on sulfate reduction. Thanks are due to the Highborne Cay staff for help and logistical support of field work. We appreciate the constructive criticism and reviews by J.E. Andrews, R. Riding, and E.P. Verrecchia. Funding was provided by the Bio-complexity program, U.S. National Science Foundation. This is Research Initiative on Bahamian Stromatolites contribution 35.

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Manuscript received 1 April 2006

Revised manuscript received 12 June 2006

Manuscript accepted 16 June 2006

Printed in USA