

Climatic significance of Holocene beachrock sites along shorelines of the Red Sea: Reply

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Mozley and Burns' (2006) discussion reminds me of current discussions on paleotemperature elsewhere. In the July 29, 2005, issue of *Science*, the following statements are presented: "Two teams of researchers, studying the same evidence with the same techniques, have painted diametrically opposite pictures of a key period in the history of Earth's climate, which climatologists are probing...It's a tough issue to sort out... 'What's at stake is the regional distribution of climate,' both past and future" (Kerr, 2005, p. 687). We have to wait for more data. This is difficult work, and it is easy to be misled.

Before answering specific criticism, please note that my study was a geologic note and not a full article. My detailed article (Friedman, 2004) was published as part of a special publication series requested by the Geochemical Society as part of its tribute to Isaac R.

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In my 1968 article on carbonate sediments of the Red Sea, I expressed my appreciation to I. R. Kaplan of the California Institute of Technology for his interest in this study and for assistance in the field. I am grateful to Richard Reesman of Geochron Laboratories, Cambridge, Massachusetts, for stable isotopic analyses and to Samuel A. Bowring and the thermal ionization mass spectrometry (TIMS) laboratories of the Massachusetts Institute of Technology for strontium isotope analysis. For reviewing beachrock manuscripts, grateful thanks are extended to André Strasser, general secretary of the International Association of Sedimentologists, Péroles, Friborg, Switzerland; Leon E. Long, University of Texas at Austin; Maurice E. Tucker, president of the International Association of Sedimentologists, University of Durham, England; Isabel P. Montañez, associate editor for the *Journal of Sedimentary Research* and coeditor for *Sedimentology*, University of California, Davis; L. C. Gerhard, Kansas Geological Survey; W. M. Kazman, Richardson, Texas, and anonymous reviewers.

The geochemistry of the beachrock cement was determined by the Geochron Laboratories and Massachusetts Institute of Technology laboratories. Although I have an initial degree in chemistry and worked as an analytical chemist for Pfizer, I was not involved in the chemical analyses in this study.

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Kaplan. I refer Mozley and Burns (2006) to the details of my article.

I shall answer their criticism.

DESCRIPTION OF THE PETROGRAPHIC CHARACTERISTICS OF THE SAMPLES

The studied beachrock is composed of (1) terrigenous debris derived from nearby bedrock, (2) carbonate particles of local origin, and (3) carbonate cement (Friedman, 1988; Table 1).

The most common beachrock lithology is terrigenous calcipebblestone (Figure 1) and calcisandstone in which skeletal debris is minor or absent, terrigenous rock fragments are dominant, and carbonate cement is abundant. Terrigenous debris does not affect radiocarbon dating nor carbon or strontium isotopic measurements because in most of the samples, the debris does not generally contain carbonates. The samples selected for the study contain fossils only sporadically, or at best, fossils are entirely absent.

Terrigenous particles in the studied beachrocks consist of igneous and metamorphic rock fragments, quartz, K-feldspar, plagioclase, mica-chlorite, and/or mixed-layer clay minerals. The rock fragments include basalt, andesite, trachite, granite, granite gneiss, and quartz-mica schist. Many quartz particles exhibit wavy extinction, suggesting a metamorphic origin. Minor well-sorted, rounded, and coated calcareous skeletons include foraminifera, ostracods, bryozoans, corals, mollusks, coralline algae, echinoid spines and plates, and biogenic intraclasts. One of the samples (Elat 3-99) contains low-magnesium calcite related to calcareous particles.

The studied beachrock displays a seaward- to landward-prograding sequence with a temporal succession from land to sea.

Holail et al. (2004) discuss cementation of Holocene beachrock in the area of this study. Aragonite and high-Mg calcite are the common minerals that comprise the cement of the beachrock (cf. Shinn, 1969; Friedman and Gavish, 1971; Alexandersson, 1972; Magaritz et al., 1979; El-Sayed, 1988; Khalaf, 1988; Guo and Friedman, 1990; Holail and Rashed, 1992; Strasser et al., 1992; Strasser and Strohmenger, 1997; Friedman, 2002, 2004).

The intergranular pores of the studied beachrock are filled with cryptocrystalline high-Mg calcite cement (Holail et al., 2004). In the Gulf of Aqaba beachrock, the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of this type of cement reflect precipitation in equilibrium with seawater (Holail et al., 2004).

Table 1. X-Ray Diffraction Mineralogical Analysis*

Mineral Constituents	Relative Abundance (%)				
	Sample Identification	Elat 1-99	Elat 2-99	Elat 3-99	Elat 4-99
Quartz		28	33	37	41
Plagioclase Feldspar		40	27	20	22
K-feldspar		10	9	10	12
Low-magnesium calcite		1	7	16	7
High-magnesium calcite		5	9	9	8
Aragonite		5	8	2	3
Halite		trc**	trc	trc	trc
Kaolinite		1	1	1	2
Chlorite		3	2	2	2
Illite and mica		6	2	2	2
Mixed-layer illite-smectite (% illite layers in mixed-layer illite-smectite)		1 (30–40%)	2 (30–50%)	1 (40–50%)	1 (30–50%)
Total		100%	100%	100%	100%

*Beachrock, northwestern shore of Gulf of Aqaba, Red Sea (prograding sequence from Elat 1-99 [youngest] to Elat 4-99 [oldest]).

**trc = trace.

METHODOLOGY (ANALYTICAL METHODS)

In the field, beachrock sections were located and sampled. Subsequently, the rocks were thin sectioned. Traditional petrographic microscopy studies of the samples included the texture of the rock, composition of particles and cement, and pore types.

Special attention was given to the amount and kinds of carbonate minerals present, such as the presence of noncement carbonate particles (fossil fragments, carbonate lithoclasts, or micrite-size allochthons). The carbonate bomb was used to determine the concentration of CaCO_3 (Müller and Gastner, 1971). Staining (Friedman, 1959) differentiated aragonite, high-Mg

Figure 1. Beachrock with abundant included terrigenous pebbles paving intertidal zone and extending into supratidal zone on the west side of the Gulf of Aqaba.



calcite, and low-Mg calcite, and x-ray diffraction confirmed mineralogical composition (Müller, 1967; Gavish and Friedman, 1973; Milliman, 1974).

For $^{87}\text{Sr}/^{86}\text{Sr}$, radiocarbon, and stable isotope analysis, the carbonate rocks were cleaned thoroughly in an ultrasonic cleaner. The samples were then hydrolyzed with HCl under vacuum, and the carbon dioxide was recovered for analysis. The ^{13}C analysis was made from a small part of the same evolved gas.

For strontium-isotopic ratio error information, the 1σ error is approximately ± 0.000010 . The errors commonly quoted in strontium literature are for 2σ errors.

For O and C isotope ratios, the 1σ error is approximately ± 0.2 .

For ^{14}C ages, the errors are 1σ errors.

The term “ ^{14}C years BP” identifies the given ages as “uncalibrated” (i.e., they are not calibrated to be calendar years). Dates are based on the Libby half-life (5570 yr) for ^{14}C . The error is ± 1 s as judged by the analytical data alone. Our modern standard is 95% of the activity of National Bureau of Standards oxalic acid. The age is referenced to the year A.D. 1950.

The term “ ^{13}C corrected” identifies the given ages as conventional in that they have been corrected for natural isotope fractionation.

EXISTING LITERATURE ON BEACHROCK

Important reviews on beachrock formation are included in Ginsburg (1953), Nesteroff (1954), Russell (1960), Stoddart and Cann (1965), Friedman (1968, 1975, 1998, 2004), Scoffin (1970), Friedman and Gavish (1971), Schmalz (1971), Davies and Kinsey (1973), Siesser (1974), Gavish (1975), Friedman and Sanders (1978), Hanor (1978), Krumbein (1979), Scoffin and Stoddart (1983), Gavish et al. (1985), Hopley and Davies (1986), Meyers (1987), El-Sayed (1988), Strasser et al. (1989), Guo and Friedman (1990), Holail and Rashed (1992), Kendall et al. (1994), Gischler and Lomando (1997), Camoin (1999), Neumeier (1999), Webb et al. (1999), Kneale and Viles (2000), and Holail et al. (2004).

PURPOSE OF STUDY

One purpose of this study is to use radiocarbon, strontium isotopes, stable carbon and oxygen isotopes, and petrography to determine timing and rates of forma-

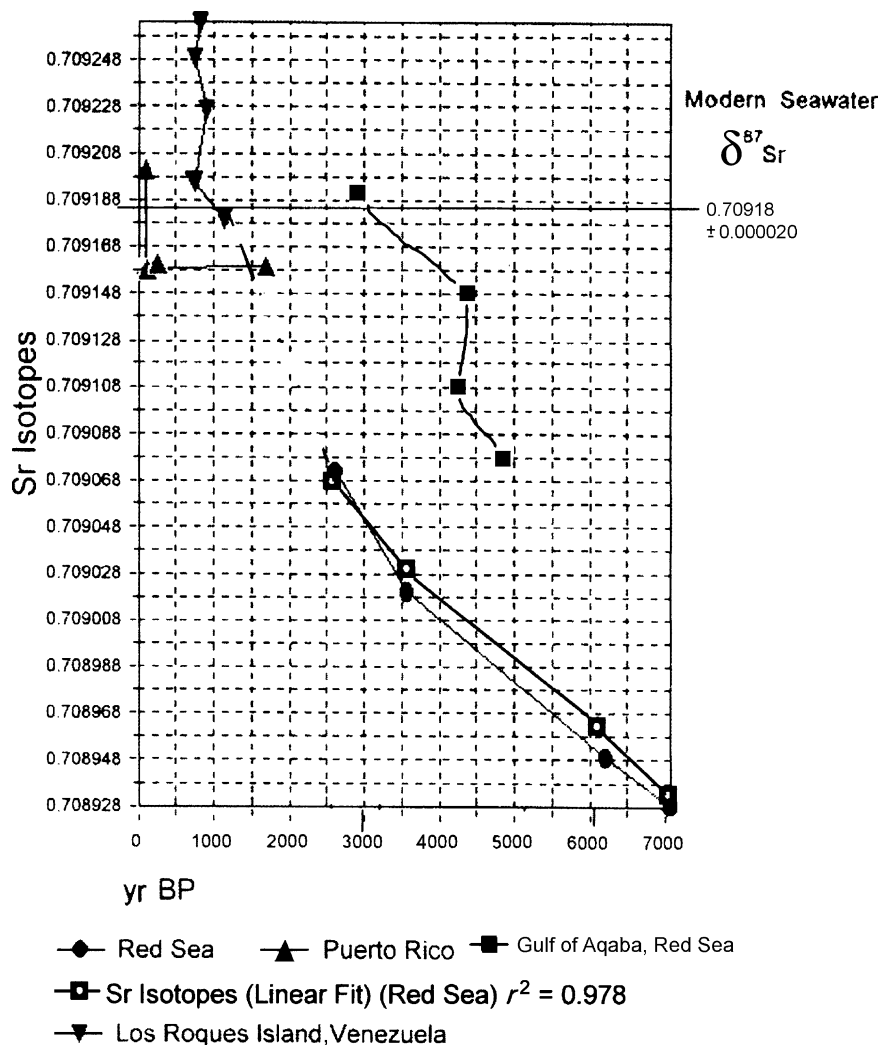
tion of the carbonate cements between the sand particles, to link Holocene geochemical and paleoceanographic changes to geologic events. These various techniques determine residence time of each beachrock level and date the timing of the sea level changes and/or tectonic activity, such as earthquakes, and the changing of temperature and composition of the seawater at each event of cementation. Values of $\delta^{18}\text{O}$ provide a telltale sign of climate change (but also the composition of seawater).

Three kinds of cement are present in the Red Sea samples (Table 1). Two- or three-generation aragonite cement consists of dark, cryptocrystalline aragonite-rimming pores. Second-generation aragonite cement consists of transparent acicular crystals that grew toward the centers of pores (Friedman and Gavish, 1971). The third kind of cement is peloidal, finely crystalline or cryptocrystalline, tan to semiopaque high-magnesium calcite (13 mol% MgCO_3).

The origin of the mineral cements in beachrock has been a subject of great interest for many years. Physical-chemical mechanisms of beachrock formation may be a consequence of the rise in ionic concentration resulting from the evaporation of sea water as it draws through the beach or by variation in the chemistry of marine vadose waters. Carbon dioxide (CO_2) degassing is a chemical process generating cement, but cyanobacteria and other microbes may also be involved, not only in stabilizing the beach sediment, but also in raising the pH by photosynthesis to a level at which calcium carbonate is precipitated. According to Davies and Kinsey (1973), pH goes up during the day to 9.5 in beachrock, but precipitation of CaCO_3 occurs at night after the waters of high pH have drained into the sediment, where precipitation occurs.

Biologically controlled CaCO_3 precipitation (principally of aragonite) by pH changes has been demonstrated in laboratory experiments using a variety of bacterial strains. Organically mediated cementation in beachrock probably occurs extracellularly (as it does in laboratory experiments involving calcium-carbonate precipitation by bacteria), as a result of fluctuations in the concentration of CO_2 and HCO_3^- that are controlled organically. Films of nonliving organic matter coating mineral particles may also be involved in chemical or biochemical processes that lead to cementation (Ginsburg, 1953; Nesteroff, 1954; Russell, 1960; Hanor, 1978; Krumbein, 1979; Meyers, 1987; Kendall et al., 1994; Camoin, 1999; Neumeier, 1999).

Figure 2. Plots of strontium isotopic ratios against radiocarbon ages for carbonate cement-prograding beachrock sequences of the Caribbean plate (Los Roques Island, Venezuela), Puerto Rico, and Gulf of Aqaba, Red Sea. For the Red Sea prograding beachrock sequence, one graph shows the data points and a second the computed linear fit ($r^2 = 0.978$). The four separate points on the right represent data from spot samples from the Gulf of Aqaba, Red Sea. The horizontal line at 0.70918 gives the present-day equilibrium $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the modern ocean.



STRONTIUM ISOTOPIC RECORD ($^{87}\text{Sr}/^{86}\text{Sr}$)

To clarify the age and geochemical data, I have added a section on strontium isotopes. Strontium-isotopic analyses of beachrock cement (Figure 2; Table 2) reflect $^{87}\text{Sr}/^{86}\text{Sr}$ secular variation in seawater. The modern seawater Sr-isotope line (horizontal line in Figure 2) is a global ocean record (Capo and DePaolo, 1990; Quinn et al., 1991; Farrell et al., 1995). When marine carbonate forms, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of ocean water is incorporated into its structure without fractionation (Faure, 1986). Carbonate cements in marine settings precipitate from waters in strontium isotopic equilibrium with the global ocean (Burke et al., 1982; Koepnick et al., 1985; Hodell et al., 1989; Veizer, 1989; Farrell et al., 1995). Plots of radiocarbon age dates against $^{87}\text{Sr}/^{86}\text{Sr}$ ratios reveal past geochemical changes and cycles of strontium isotopes in the global ocean (Veizer et al., 1999; McArthur et al., 2001).

The values for the modern-day seawater vary depending on whose lab runs them (from 0.70917 to 0.70921). In this study, the seawater values are reported as 0.70918.

Table 2. Strontium Isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) Values and Stable Isotopes ($\delta^{13}\text{C}$, $\delta^{18}\text{O}$) of Prograding Samples*

Sample Identification	$^{87}\text{Sr}/^{86}\text{Sr}$	$\delta^{18}\text{O}_{\text{PDB}}$	$\delta^{13}\text{C}_{\text{PDB}}$
Elat 1-99	0.709072	-0.1**, -0.2	+3.4**, +3.2
Elat 2-99	0.709020	-0.7	+2.8
Elat 3-99	0.708949	-1.9	+2.3
Elat 4-99	0.708928	-3.5	+1.1

*From four levels of a prograding sequence, northernmost west shore of Gulf of Aqaba, Red Sea.

**Duplicate analyses on separate aliquots of the original sample.

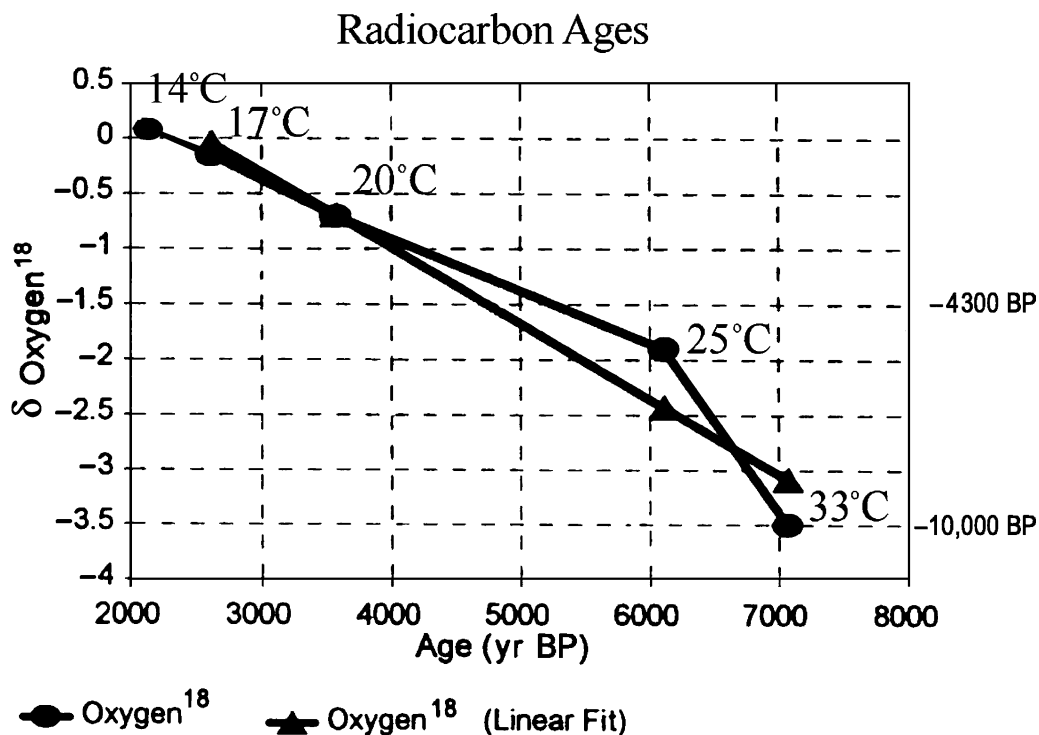


Figure 3. Plots of oxygen-isotopic ratios against radiocarbon ages of interparticle cement for Gulf of Aqaba, Red Sea prograding sequence. For data, see Table 2 and Figure 2. Plots with elliptical (rounded) pattern provide data points, triangular pattern represents linear fit ($r^2 = 0.930$). This diagram shows a progressive warming trend in the Red Sea during the past 7000 yr. Temperature of most recent age (~2 years ago) approximated from data of Nof et al. (2006).

The modern ages for beachrock yielded $^{87}\text{Sr}/^{86}\text{Sr}$ ratios close to that of modern seawater. The plot of age against $^{87}\text{Sr}/^{86}\text{Sr}$ ratios for the prograding sequence of Red Sea beachrocks follows a linear pattern ($r^2 = 0.978$) in which decreasing age generates carbonate cements of progressively higher strontium-isotope ratio comparable to that in my article (Friedman, 2005) to which Mozley and Burns (2006) object. The beachrock from other areas (South and middle America) are closer to modern seawater (Figure 2).

Strontium isotopic ratios of the beachrock cements are among the highest for Phanerozoic carbonates and probably for all geologic time.

TEMPERATURES

Following the equation and the isotopic temperature scale of Epstein et al. (1953) (Arthur et al., 1983), Figure 3 presents the computed mean sea-surface paleotemperatures and the adjusted temperatures obtained for the Gulf of Aqaba beachrock by related modern average sea-surface temperature (24°C) to

computed temperature ($t^\circ\text{C}$) for prograding beachrock samples from four levels of a beachrock sequence of the Red Sea. For the middle Holocene centuries between 7.07 ± 0.38 and 2.62 ± 0.23 ^{14}C ka, an interval of approximately 4500 yr, a decrease of wide-ranging sea-surface temperature is indicated (Figure 3). The interval 6–5 ka corresponds to the Flandrian or Atlantic period, when climate in many places was warmer and more humid, and sea levels in most oceans was +2 m (+6.6 ft). Ritchie et al. (1985) suggested a humid tropical climate with annual monsoonal rainfall of at least 400 mm (15 in.) during the middle Holocene based on sediment and pollen evidence from the eastern Sahara. Stable isotopic composition of middle Holocene fossil *Porites* spp. corals from the northern Gulf of Aqaba revealed heavier values compared with modern corals, meaning enrichment in $\delta^{18}\text{O}$ and cooler temperature (Moustafa et al., 2000). Mesopelagic pteropoda suggest an arid continental climate in the Red Sea region for the past 4000–5000 yr and a humid climate for the preceding 5000 yr (Almogi-Labin et al., 1991). Figure 3 indicates the beachrock data of the Red Sea, showing progressive cooling in the Holocene and suggesting a

major cooling event. Oxygen isotopes confirm that the climate in Britain 5000 yr ago was about 2°C warmer than the area today (Evans et al., 2001). This conclusion contradicts the general impression gained from reading news reports, which project a warming trend for the recent past (last 100 yr).

The implied temperature variation (16°C warmer at 7.7 ka) may indicate a dramatic change in climate. Bard (2002) cites this temperature swing at 8.2 ka. He claims that unstable models of temperature swing are “in fact, very hard to answer” (Bard, 2002, p. 32). “The climate system is complex because it is made up of several components (such as the atmosphere, oceans, and ice sheets), each of which has its own response times and thermodynamic properties” (Bard, 2002, p. 32).

The computed sea-surface temperatures cited in this discussion were determined to indicate a trend of temperature changes and not specific paleotemperatures. The assumption that the present temperature of 17°C was identical at 2.62 ka is not necessarily valid; the purpose of the computations is to imply a direction of change during an approximately 4500-yr Holocene interval.

A recent issue of *Science* magazine titles its discussion of calendar ages as “The Boon and Bone of Radiocarbon Dating” (Guilderson et al., 2005).

To explain that the Red Sea (Gulf of Aqaba) data are different from the various examples, which Mozley and Burns (2006) cite, I have added data from Holocene beachrocks of South America (Venezuela) and middle America (Puerto Rico) (Figure 2). The numbers and trends are completely different. This difference may be the reason that explains why Mozley and Burns (2006) find a “discrepancy between Friedman’s interpretation and the existing literature.”

I collected additional beachrock samples from the Gulf of Aqaba from four random sites (Figure 2). I have not computed the Epstein temperatures, but their trend parallels that of the prograded sample sequence of Figure 2.

EPILOGUE

Evidence for coincidence of high sea level with cold climate and low sea level with warm climate is that extremes of climate and sea level coincide. In other words, the colder the climate, the lower the sea; and the warmer the climate the higher the sea. Extremes of climate and sea level do not appear to coincide. For one,

evidence (based on carbonates) suggests a warm peak 10,000–12,000 yr ago when sea level was low (–50 to –110 m [–164 to –360 ft]). In the other example, faunal evidence suggests cold climate about 4300 yr ago, when the sea was at its present high level (Friedman and Sanders, 1970).

SUMMARY

After 40 yr of beachrock research on deposits from all over the world, I conclude that the data in my 2005 article are current and fitting interpretations of the subject studied. I do not dispute Mozley and Burns’ (2006) interpretations of other areas to which they have referenced.

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