CARBON ISOTOPE DISCREPANCY BETWEEN PRECAMBRIAN STROMATOLITES AND THEIR MODERN ANALOGS: INFERENCES FROM HYPERSALINE MICROBIAL MATS OF THE SINAI COAST

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Abstract. The isotopic composition of organic carbon from extant stromatolite-type microbial ecosystems is commonly slanted toward heavy $\delta^{13}C$ values as compared to respective compositions of average organic matter (including that from Precambrian stromatolites). This seems the more enigmatic as the bulk of primary producers from benthic microbial communities are known to fix carbon via the C3 pathway normally entailing the sizable fractionations of the RuBP carboxylase reaction.

There is reason to believe that the small fractionations displayed by aquatic microorganisms result from the limitations of a diffusion-controlled assimilatory pathway in which the isotope effect of the enzymatic reaction is largely suppressed. Apart from the diffusion-control exercised by the aqueous environment, transport of CO_2 to the photosynthetically active sites will be further impeded by the protective slime (polysaccharide) coatings commonly covering microbial mats in which gas diffusivities are extremely low. Ineffective discrimination against ^{13}C becomes, however, most pronounced in hypersaline environments where substantially reduced CO_2 solubilities tend to push carbon into the role of a limiting nutrient (brine habitats constitute preferential sanctuaries of mat-forming microbenthos since the emergence of Metazoan grazers $\sim$0.7 Ga ago). As the same microbial communities had been free to colonize normal marine environments during the Precambrian, the CO_2 concentration effect was irrelevant to the carbon-fixing pathway of these ancient forms. Therefore, it might not surprise that organic matter from Precambrian stromatolites displays the large fractionations commonly associated with C3 photosynthesis. Increased mixing ratios of CO_2 in the Precambrian atmosphere may have additionally contributed to the elimination of the diffusion barrier in the carbon-fixing pathways of ancient mat-forming microbiota.

1. Introduction

As is testified by a growing pile of relevant publications, the fossil structures depicted in Figure 1 and commonly termed 'stromatolites' have, of late, met with increasing attention (see Awramik, 1982; Krumbein, 1983; and Walter, 1983, for recent reviews). In the most general sense, stromatolites represent biosedimentary laminations that have resulted from the matting behavior of benthic prokaryotes, notably cyanobacteria. Though constituting genuine relics of former life, these generally unimpressive bun-shaped laminae would probably not command much interest if it were not for the fact that the microbial ecosystems responsible for their formation had monopolized – along with their planktic variant – all biologically hospitable environments on our planet during the first three billion years of recorded Earth history (i.e., prior to the appearance of the oldest Metazoa some 0.7 Ga ago).

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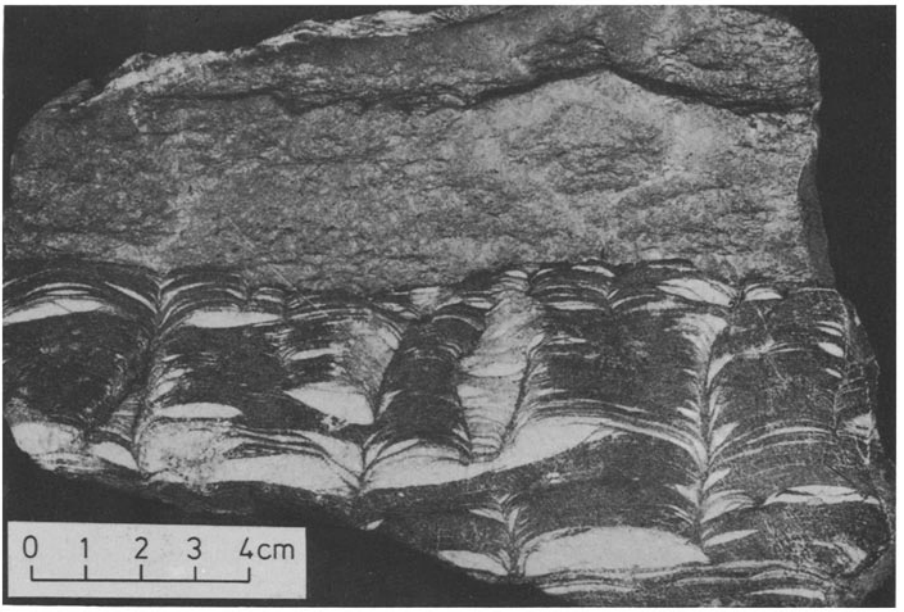

Fig. 1. Archaean stromatolite from the Bulawayan Group, Zimbabwe (~2.6 Ga). The specimen comes from the classical Huntsman Quarry locality near Bulawayo originally described by MacGregor (1940) that had figured until recently as the oldest fossil occurrence of a laminated microbial ecosystem (note succession of bun-shaped and partially interfering laminae representing lithified mats). This stromatolitic limestone contains about 0.5‰ organic carbon whose $\delta^{13}C$ values range between −26 and −33‰ [PDB] (Schopf *et al.*, 1971; Eichmann and Schidlowski, 1975).

Results of isotope surveys carried out since the mid-sixties on the organic carbon (or 'kerogen') content of the most ancient stromatolites were decidedly consistent with their morphological interpretation as fossil microbial mats. In fact, $\delta^{13}C$ spreads[1] displayed by the kerogen constituents of Precambrian stromatolites (Hoering, 1967; Schopf *et al.*, 1971; Eichmann and Schidlowski, 1975) fall right into the isotopic mainstream of sedimentary organic matter through geologic time (see Figure 2) that is roughly defined by the range $\delta^{13}C = -27 \pm 6\,‰$ [PDB] and appears to be basically constant with time (Hayes *et al.*, 1983; Schidlowski *et al.*, 1983).

In marked contrast to these findings it had been noted, however, that the biomass of recent cyanobacterial mats was, in the majority of cases, distinctly enriched in heavy carbon. Among the first measurements reported were those of Behrens and Frishman

[1] Differences in carbon isotope composition are expressed in the conventional δ-notation giving the permil deviation of the $^{13}C/^{12}C$ ratio of a sample (sa) relative to that of a standard (st), mostly Peedee belemnite (PDB), i.e.,

$$\delta^{13}C = \left[\frac{(^{13}C/^{12}C)_{sa}}{(^{13}C/^{12}C)_{st}} - 1\right] \times 10^3 \text{ (‰, PDB)}.$$

Positive values of $\delta^{13}C$ stand, accordingly, for an enrichment in the sample of heavy carbon (^{13}C) relative to the standard while negative values indicate a ^{13}C depletion, respectively.

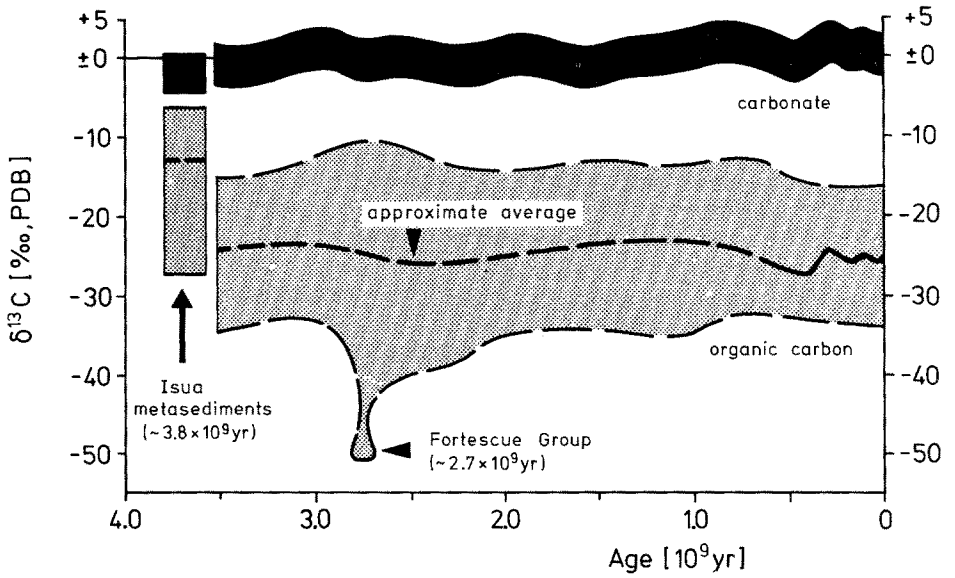

Fig. 2. Isotopic composition of sedimentary carbonate and organic carbon ('kerogen') through geologic time. The envelope shown for organic carbon covers the data base given by Schidlowski *et al.* (1983, Figure 7–3) and represents, in essence, the geochemical manifestation of the isotope-discriminating properties of the key enzyme of the Calvin cycle (ribulose-1,5-bisphosphate carboxylase); extremely negative values at the lower fringe suggest the involvement of methanotrophic pathways in the formation of the respective kerogen precursors. The discontinuity at $t \cong 3.5$ Ga can be best explained by the amphibolite-grade metamorphism of the Isua suite entailing an isotopic reequilibration of both sedimentary carbon species with a concomitant decrease in average fractionation.

(1971) who had obtained $\delta^{13}C$ values between -14 and $-18\,‰$; other surveys of both naturally occurring and cultured cyanobacteria (Calder and Parker, 1973; Seckbach and Kaplan, 1973; Pardue *et al.*, 1976; Barghoorn *et al.*, 1977; Peters *et al.*, 1981; Estep, 1982; and others) have likewise recorded a consistent (though variable) trend of $\delta^{13}C$ toward more positive readings. A synopsis of the presently known isotope spreads of potentially mat-building cyanobacteria and non-oxygenic photosynthetic bacteria is presented in Figure 3A. It is obvious from this compilation that the average isotopic composition of naturally occurring cyanobacterial communities ($\delta^{13}C \cong -16\,‰$) is markedly slanted toward isotopically heavy carbon as compared to respective compositions of C3 plants and eukaryotic algae that account for the bulk of the Earth's standing biomass. The $\delta^{13}C$ mean of the average global biomass (between about -24 and $-28\,‰$) is, in turn, closely approximated by the isotopic composition of organic matter entering present-day sediments (see Figure 3B).

Although this isotopic discrepancy between ancient and modern stromatolites had constituted a mild embarrassment for the profession right from the beginning (with occasional eruptions of more acute controversy, e.g., Towe, 1982; Schoell and Wellmer, 1982), the more inspired students of the stromatolite record had probably never been in doubt about the ultimate biogenicity of the isotopically anomalous

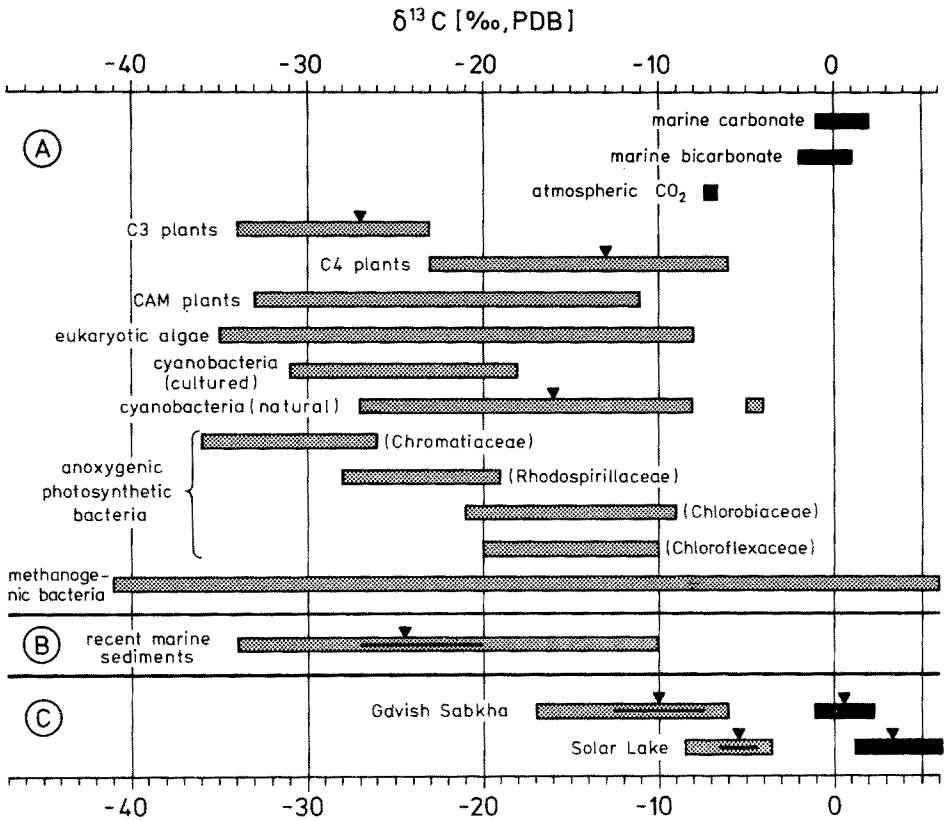

Fig. 3. (A) Carbon isotope spreads of major groups of higher plants and autotrophic microorganisms (approximate means indicated by triangles) as compared to respective compositions of the principal forms of inorganic carbon (carbonate, bicarbonate, carbon dioxide). Note that $\delta^{13}C$ values of average organic matter are between 20 and 30‰ more negative than those of marine bicarbonate (HCO_3^-), the most abundant inorganic carbon species of our environment. (B) Isotopic composition of organic matter from recent marine sediments based on some 1.600 samples; > 90% of the data points lie on inserted bar (adapted from Deines, 1980). (C) Isotopic composition of microbial mats from hypersaline pools of the Sinai coast (Schidlowski *et al.*, 1985). Triangles indicate means, inserted bars give ranges of standard deviation. Black bands on the right are corresponding spreads for coexisting carbonates.

organic carbon, let alone our current interpretation of Precambrian stromatolites as fossil microbial mats. The only conclusion one could justifiably draw from this apparent anomaly was that there were some biochemical or environmental factors involved that were as yet poorly understood. In any case, these findings were unlikely to introduce basic uncertainties into our current concepts pertaining to the nature of ancient stromatolites as these had evolved during the last decades.

In the following, an attempt will be offered to solve this problem. The explanation proposed has emerged as a by-product of a recent isotope survey of hypersaline cyanobacterial mats from the Sinai Peninsula (Schidlowski *et al.*, 1984, 1985) that have yielded the isotopically heaviest organic carbon as yet encountered in the terrestrial biosphere (cf. Figure 3C).

2. Microbial Mats from Sinai Coastal Brine Pools: Contributing Microbiota and Carbon Isotope Composition

It is known that the coastline of the Sinai Peninsula is beset with a number of hypersaline lagoons (Gavish, 1980), the most conspicuous ones being Solar Lake south of Eilat (Krumbein and Cohen, 1974; Cohen *et al.*, 1980) and the so-called 'Gavish Sabkha' (Friedman and Krumbein, 1985) with salinities ranging up to 300‰ and more. Both brine pools host prolific and rather diversified microbial communities well adapted to hypersaline conditions. Most abundant among the primary producers of these habitats are photosynthetic prokaryotes, notably coccoid and filamentous cyanobacteria (for details see Krumbein *et al.*, 1979; Cohen *et al.*, 1980; Friedman and Krumbein, 1985); minor elements among the prokaryotic community are flexibacteria (including *Chloroflexus* sp.) as well as halobacteria. Cyanobacterial mats are often superimposed on layers of non-oxygen-evolving ('anoxygenic') prokaryotes such as purple and green sulfur bacteria. Further below follow the domains of chemoautotrophs and sulfate reducers (the latter dominated by *Desulfovibrio* sp.). Subordinate eukaryotic elements include diatoms and *Enteromorpha* sp., a green alga that was found to particularly abound in restricted low-salinity compartments of the Gavish Sabkha.

Since the predominant cyanobacterial species tend to form extended carpets at the sediment-water interface, both hypersaline pools qualify as potentially stromatolite-forming biotopes, i.e., environments capable of developing the laminated bio-sedimentary structures linked to the mat-building activities of benthic prokaryotes. Recorded rates of primary productivity in these mats are impressive and range up to 8–12 g carbon/m^2day (Krumbein amd Cohen, 1977; Cohen *et al.*, 1980). Such high productivities probably result from a eutrophication of these brine ponds brought about by a continuous influx of nutrient-enriched pore waters whose upward movement is promoted by the high evaporation rates typical of arid areas.

As may be inferred from Figure 3C and is fully detailed elsewhere (Schidlowski *et al.*, 1984, 1985), the Gavish Sabkha and Solar Lake microbial ecosystems have furnished the isotopically heaviest organic matter as yet encountered in a natural biotope (the partially heavier values for methanogens shown in Figure 3A were obtained in culture experiments under specific conditions that are unlikely to be realized in natural environments; for details see Fuchs *et al.*, 1979). In terms of $\delta^{13}C$ values, the microbial biomass of the above habitats has yielded means of -10.0 ± 2.6‰ (25 samples) and -5.4 ± 1.1‰ (14 samples), respectively. These spreads not only confirm previous findings that the biomass of extant bacterial and algal mats is generally heavy as compared to common plant matter, but represent obvious extremes (notably in the case of the Solar Lake values). As is evident from a comparative plot of the above means and the corresponding total spreads, the anomalous distribution patterns obtained for these communities clearly surpass the positive maxima of $\delta^{13}C$ yielded by common photoautotrophic organisms (Figure 3A) as well as by sedimentary organic matter (Figure 3B; see also Figure 2 for extrapolation into the geological past).

With this state of affairs, the specific problem posed by these microbial ecosystems

can be epitomized by the question: Why are the hypersaline mats from the Sinai coastal brine pools – and notably those from Solar Lake – composed of the isotopically heaviest carbon known to occur in the Earth's biosphere? To answer this question, we have to briefly review some biochemical essentials of autotrophic carbon fixation.

3. Biological Carbon Isotope Fractionation: Biochemical Background

It is known that all pathways of autotrophic carbon fixation – and notably the photosynthetic ones – discriminate against heavy carbon (^{13}C), mainly as a result of a kinetic isotope effect inherent in the first carbon-fixing carboxylation reaction (cf. Vogel, 1980; O'Leary, 1981). Consequently, biogenic substances display a marked bias in favor of ^{12}C, the degree of enrichment in light carbon varying with the type of plant or autotrophic microorganisms. On average, the $\delta^{13}C$ values of organic carbon are some 20–30‰ more negative than those of marine bicarbonate, the most abundant inorganic carbon species in our environment (Figure 3A).

The principal isotope-discriminating steps in the primary metabolism of autotrophs are (i) the uptake and intracellular diffusion of external CO_2 into the photosynthetically active tissue, and (ii) the first enzymatic carboxylation reaction by which CO_2 is incorporated into the COOH (carboxyl) group of an organic acid. Hence, the essentials of biological carbon fixation may be adequately described by the two-step model first proposed by Park and Epstein (1960),

$$CO_2(e) \rightleftarrows CO_2(i) \rightarrow R\text{–}COOH, \tag{1}$$

where $CO_2(e)$ and $CO_2(i)$ represent external and internal CO_2, respectively, and R–COOH stands for the product of the first carbon-fixing carboxylation. Naturally, the 'ideal' model conditions symbolized by Equation (1) are complicated by superimposed and ensuing processes involving the divertion of part of the assimilated CO_2 to other (generally subordinate) pathways.

While diffusion as the first step shown in Equation (1) is linked to a minor isotope effect of about −4‰, the subsequent enzymatic step entails much larger fractionations, spanning mostly the range from −20 to −40‰ in the case of the ribulose-1,5-bisphosphate (RuBP) carboxylase reaction (Winkler *et al.*, 1982) that fixes CO_2 as a C3 compound, phosphoglycerate, in so-called 'C3 photosynthesis'. A quantitatively less important carboxylation reaction fixing CO_2 via phosphoenolpyruvate (PEP) carboxylase as a C4 compound (oxaloacetate) is associated with a minor effect of −2 to −3‰ relative to bicarbonate ion (HCO_3^-) which serves as the 'active' carbon species in this pathway (O'Leary, 1982). This small fractionation, in conjunction with the utilization of isotopically heavy bicarbonate, accounts for the relative enrichment of ^{13}C in so-called 'C4 plants' (see Figure 3A). Intrinsic fractionations of ferredoxin-linked carboxylations (specifically those fixing carbon as α-ketoglutarate and acetyl coenzyme A, cf. Buchanan, 1979) still await elucidation, but discriminations displayed by green photosynthetic sulfur bacteria (Chlorobiaceae) that utilize these reactions in a

reverse Krebs cycle ('reductive carboxylic acid cycle') commonly fall into the range of C4 plants (Figure 3A).

Total isotope fractionation in carbon assimilation will be, accordingly, dependent on an interplay of the processes summarized in Equation (1) and, notably, on which of the two steps there indicated becomes rate-controlling in the specific instance. In part, retrograde (dissimilatory) reactions such as photorespiration may strongly counteract the fractionations achieved in the assimilatory pathway. With the bulk of all biosynthesized materials displaying fractionations between -20 and $-30‰$, there is little doubt that the Earth's biomass as a whole principally bears the isotopic signature of the RuBP carboxylase reaction. As this reaction (that feeds CO_2 directly into the Calvin cycle as phosphoglycerate) brings about most of the carbon transfer from the inorganic to the organic world, the isotope discriminating properties of the enzyme RuBP carboxylase certainly could not fail to leave their mark on both the extant biosphere (Figure 3A) and the huge reservoir of fossil organic carbon (Figure 2) that is stored in the Earth's sedimentary shell (Schidlowski, 1982; Schidlowski *et al.*, 1983). There is little doubt that the isotopic composition of organic matter is basically retained during incorporation in sediments (see also Hayes *et al.*, 1983) and thus encoded in the rock section of the carbon cycle back to at least 3.5 (if not 3.8) Ga ago. Incidentally, the constancy of the $\delta^{13}C$ age function of fossil organic matter (Figure 2) is likely to constitute convincing evidence of an extreme degree of evolutionary conservatism inherent in the principal pathway of autotrophic carbon fixation.

4. Isotopically Superheavy Organic Carbon: Peculiarities of the Assimilatory Pathway

The time-honored relationship between the average isotopic compositions of organic carbon and carbonate as illustrated in Figure 2 is strikingly contrasted by the isotopically anomalous carbon from the Sinai microbial mats. When compared to the respective compositions of major divisions of extant photoautotrophs, the $\delta^{13}C$ distribution patterns displayed by the biomass of these brine pools largely coincide with the positive maxima of C4 plants and selected groups of photosynthetic bacteria (Figure 3). Moreover, a significant proportion of the values – notably those from Solar Lake – exceed these maxima in positive direction (as mentioned above, the still heavier values for some methanogens are artifacts obtained in culture experiments).

The observed coincidence with C4 plant must be necessarily fortuitous since both the predominant cyanobacterial community and most other primary producers of these hypersaline ecosystems are known to sequester carbon via the RuBP carboxylase reaction and not via PEP carboxylase as do C4 plants. The only bacterial family resorting to an assimilatory pathway other than C3 photosynthesis are green photosynthetic sulfur bacteria (Chlorobiaceae) that operate a reverse Krebs cycle ("reductive carboxylic acid cycle") which pathway is apparently unique to photosynthetic prokaryotes and fixes CO_2 as acetyl coenzyme A (cf. Buchanan, 1979). The $\delta^{13}C$ spread hitherto known for this group is shown in Figure 3 A. It should be noted, however, that green photosynthetic sulfur bacteria - though present in the Gavish Sabkha and Solar

Lake microbial communities – figure as a decidedly minor component of these ecosystems.

Hence, with the overwhelming majority of primary producers from these habitats relying on C3 photosynthesis, the crucial problem posed by these microbial communities is why the sizable fractionations of the RuBP carboxylase reaction fail to become manifest in the average isotopic composition of their biomass.There is, in fact, little doubt that the intrinsic fractionations of the C3 pathway must have been suppressed here by a set of external factors that consequently came to attain complete control of the isotope economy of the microbial ecosystems in question.

A closer inspection of the isotope spread obtained for the Gavish Sabkha, and notably a comparison of its mean ($\delta^{13}C = -10.0 \pm 2.6‰$) with the respective mean of atmospheric carbon dioxide ($\delta^{13}C = -7‰$; see also Figure 3) shows that the average fractionation between the microbial carpets and their ultimate feeder substrate is on the order of $-3‰$ only. This makes it sufficiently certain that the total rate of carbon assimilation must be controlled by the inital diffusion step of Equation (1) which, when fully expressed, gives rise to a fractionation of about $-4‰$ (which is the value for *gaseous* diffusion of CO_2). Since most fractionations observed are smaller than this, liquid diffusion entailing fractionations well below this value (cf. Vogel, 1980) has obviously played the dominant role. In fact, with primary producers made up wholly of aquatic microorganisms, it is reasonable to expect that liquid diffusion has imposed the isotopic imprint of a diffusion-limited pathway on the local ecosystem. Moreover, we may safely assume that transport of CO_2 to the photosynthetically active sites was further impeded by the protective slime coatings that characteristically cover most microbial mats. It has been shown that gas diffusities in such gelatinous polysaccharide slimes are very slow (e.g., Krumbein *et al.*, 1979), this probably further accentuating the role of CO_2 diffusion as rate-limiting 'bottle-neck' of the assimilatory pathway.

On the other hand, retarded transport of CO_2 due to liquid diffusion cannot be the only explanation for the observed isotope anomaly.. All groups of microbial autotrophs whose $\delta^{13}C$ spreads are shown in Figure 3A are basically composed of aquatic species but, nevertheless, display a much wider range of fractionations. Accordingly, the processes generally responsible for the production of isotopically heavy biomass in the diffusion-limited pathway of aquatic photoautotrophs must have been further enhanced in the brine habitats investigated.

As has been proposed elsewhere (Schidlowski *et al.*, 1984, 1985), the crucial contribution to the observed reduction of the average carbon isotope fractionation in hypersaline microbial communities was probably rendered by decreasing CO_2 solubilities in response to increasing ionic strength and elevated temperature (Figure 4). While retarded diffusion of CO_2 in aqueous and other liquid media (e.g., slimes) generally sets the stage for an environmental scenario in which the CO_2 supply may become potentially rate-limiting, the dramatically decreasing CO_2 solubilities in heliothermal brines are likely to force carbon into the unusual role of a limiting nutrient. As can be inferred from the relationships summarized in Figure 4, carbon dioxide is indeed apt to become a rare commodity in hypersaline environments. Under

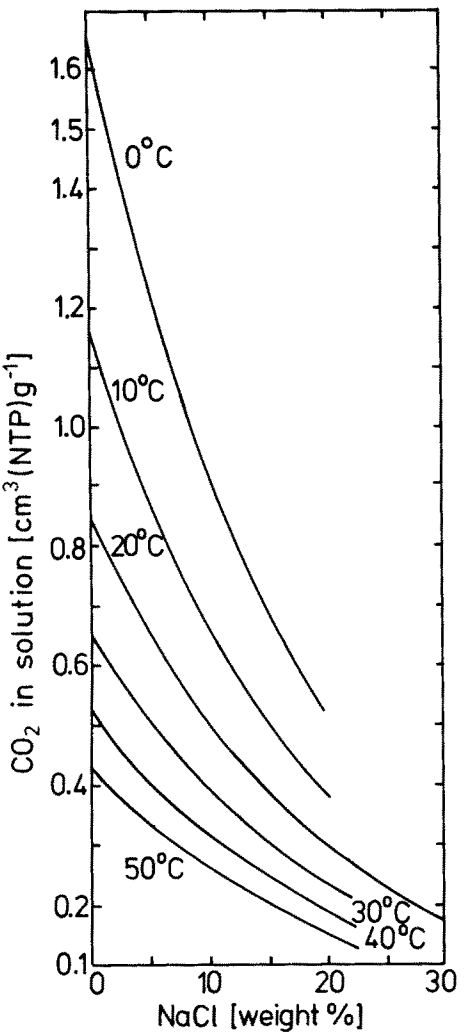

Fig. 4. Solubility of carbon dioxide in aqueous solution of sodium chloride at P_{CO_2} = 760 Torr over the temperature range 0–50 °C (Landolt-Börnstein, 1962). Although CO_2 solubilities in pure NaCl solutions only represent a model situation, it is obvious that natural waters will be depleted in carbon dioxide with increasing ionic strength and temperature of the solution.

extreme shortage of CO_2, excessive isotope fractionation apparently becomes a luxury for the biological community. Notably, in eutrophicated habitats (including sabkhas) the trend to utilize heavy carbon is proportionately enhanced by the high rates of primary productivity which can only be sustained by a largely indiscriminate assimilation of all available carbon dioxide resources. With the carbon-fixing pathway of microbial photoautotrophs from CO_2-deficient habitats consequently supply-(or diffusion-)limited, the large fractionations of the RuBP carboxylase reaction have no chance to express themselves and necessarily remain cryptic (as they do in the

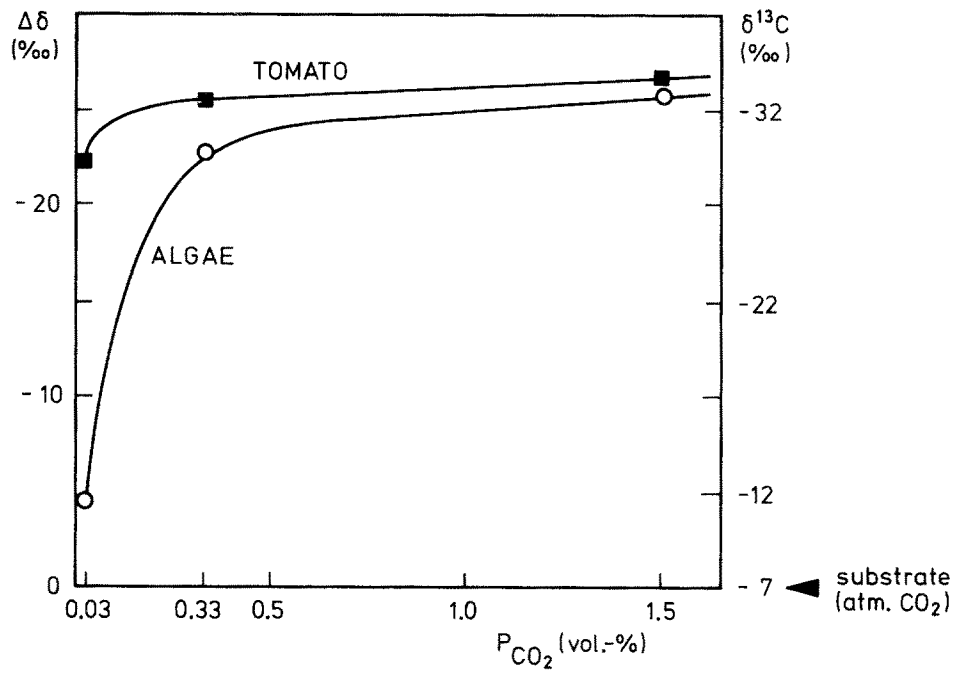

Fig. 5. Carbon isotope fractionation in a C3 plant (tomato) and in aquatic algae relying on the C3 pathway (including *Chlorella* sp.) in response to increasing partial pressures of CO_2 (adapted from Vogel, 1980). At atmospheric P_{CO_2} (0.03 %), fractionation in algae appears to be completely diffusion-controlled ($\Delta\delta$ between substrate and cell material $\lesssim 4$ ‰) while the corresponding value for higher C3 plants (tomato) reflects the sizable fractionation of the enzymatic (RuBP carboxylase) reaction. Increasing P_{CO_2} leads to but small increases of $\Delta\delta$ in tomato plants but, on the other hand, dramatically increases fractionations by algae as the diffusion barrier (cf. Equation 1) is overwhelmed and the large isotope effect of the enzymatic reaction consequently expressed.

'compartmented' biochemistry of the C4 pathway). Accordingly, the conclusion seems warranted that the exceptional enrichment of ^{13}C in the biomass of these microbial ecosystems is a habitat-specific adaption to extreme degrees of CO_2 depletion in hypersaline environments.

It should be noted, however, that in culture experiments with microbial photoautotrophs such as the green alga *Chlorella* sp. the enzymatic effect was shown to emerge with increasing environmental CO_2 pressure (Figure 5) since the rate-limiting step in the assimilatory pathway then shifted from diffusion to carboxylation. It is consistent with these findings that Estep *et al.* (1978a, b) have observed carbon isotope fractionations between -28 and -39 ‰ when conducting *in vitro* experiments with RuBP carboxylase that was isolated from both eukaryotic (diatoms) and prokaryotic microorganisms (the prokaryotes including *Agmenellum* sp., a coccoid cyanobacterium). Accordingly, the anomaly observed is certainly not due to an impairment of the isotope discriminating properties of the principal carbon-fixing enzyme, but rather derives from a lack of opportunity for these properties to express themselves in a diffusion-limited pathway.

Incidentally, mention should be made of the fact that the Solar Lake biomass is, on average, isotopically heavier ($\delta^{13}C = -5.4 \pm 1.1‰$) than atmospheric carbon dioxide which could be possibly mistaken as a perplexing case of *inverse* fractionation in biological carbon fixation. However, it has been shown that the coexisting carbonates ($\delta^{13}C = +3.5 \pm 0.4‰$) are also exceptionally heavy (Aharon *et al.*, 1977; Schidlowski *et al.*, 1985; see also Figure 3C). Dissolved carbon dioxide in equilibrium with these carbonates would be about 7 to 8 ‰ lighter (Mook *et al.*, 1974), thus ranging between -3.5 and $-4.5‰$. With such composition of the feeder substrate, a small but distinct discrimination against ^{13}C is clearly evident also in the Solar Lake biomass.

5. Implications for the Carbon Isotope Record of Precambrian Stromatolites

As can be inferred from the comparative plot of isotope data presented in Figure 3, and particularly from the $\delta^{13}C$ spread of organic matter entering present-day sediments (Figure 3B), the rare repositories of superheavy carbon excercise virtually no impact on the global carbon cycle. This is by no means surprising since hypersaline environments hosting prolific microbial communities of the type described represent quantitatively unimportant side stages of the cycle. There is, however, widespread consensus that microbial ecosystems of both the benthic and planktonic type had, in fact, monopolized all biologically hospitable environments during the first 3 billion years of recorded Earth history, with specifically the benthic variant well preserved in the form of an impressive stromatolite record as from 3.5 Ga ago (Lowe, 1980; Walter *et al.*, 1980; Orpen and Wilson, 1981).

It seems reasonable conjecture to envision for such 'primitive' (largely prokaryotic) global ecosystem a state of plenitude or 'biotic saturation', that is, a situation in which bacteria and algae had proliferated in existing aquatic habitats to ultimate limits set by the availability of environmental resources, notably phosphorus and nitrogen as crucial nutrients. With the ancient continents barren of life, there were no nutrients retained by any land biota (with the exception of perhaps a miniscule layer of endolithic life), and the Precambrian seas were most probably eutrophicated by at least a factor of two as compared to the present ocean. It would hardly strain the imagination to envision in such microbial world major local blooms that came close to those of artificially eutrophicated environments of the present world (cf. Stanley, 1981, p. 194 ff.). In fact, acceptance of the role of phosphorus as the ultimate determinant for the size of the Earth's biomass (Broecker, 1973; Junge *et al.*, 1975; Holland, 1978, p. 213) would necessarily result in the postulate of a state of global biological plenitude from the time of emergence of the oldest prokaryotic ecosystems.

With microorganisms constituting the sole sources of organic carbon in Precambrian rocks, it had been noted that organic matter from the most ancient stromatolites differed markedly in isotopic composition from that of extant microbial mats. While the $\delta^{13}C$ spreads of kerogen constituents from Precambrian (including Archaean) stromatolites fall into the mainstream of average sedimentary organics between -20 and $-30‰$ as represented in Figure 2 (Hoering, 1967; Schopf *et al.*,

1971; Eichmann and Schidlowski, 1975[2]), respective values from modern mats are markedly slanted toward negative readings (mostly between -12 and -22; see Behrens and Frishman, 1971; Smith and Epstein, 1971; Calder and Parker, 1973; Seckbach and Kaplan, 1973; Oehler, 1976; Barghoorn *et al.*, 1977; Peters *et al.*, 1981; Estep, 1982), with the Solar Lake average of $-5.4 \pm 1.1\,‰$ (Schidlowski *et al.*, 1985) representing an obvious extreme. Based on the insight into the problem gained during recent studies of the Red Sea mats, a plausible explanation may be offered for this discrepancy.

There is widespread consensus today that the emergence of Metazoan heterotrophs at the dawn of the Phanerozoic some 0.7 Ga ago (Cloud, 1976; Glaessner, 1983), and the subsequent adaptive radiation of grazing and burrowing animals, has abruptly terminated the global reign of the microbial world that had lasted over the 3 billion years of preceding Earth history. As a result of the severe grazing stress imposed since then on microbial communities in all common aquatic habitats (including the marine realm), bacterial and algal mat builders failed to develop stromatolite-type carpets at the sediment-water interface except in environments that proved hostile to potential predators. As is obvious from current global inventories of stromatolite-hosting habitats, hypersaline basins constitute the principal sanctuaries of extant benthic microbial communities (Bauld, 1981), followed by hot spring (hyperthermal) environments. Accordingly, the bulk of potentially stromatolite-forming biotopes in the present world are of the hypersaline type where reduced solubility of CO_2 holds the carbon supply at check (Figure 4) while other nutrients commonly abound. This results in an exceptional situation in which the carbon supply becomes rate-limiting for the productivity of the specific ecosystem, an immediate corollary being the largely indiscriminate metabolization of all available carbon resources with a minimum of isotopic discrimination. Consequently, the $\delta^{13}C$ values of the biomass produced under such conditions closely approach the isotopic composition of atmospheric carbon dioxide as the ultimate feeder substrate.

On the other hand, the same benthic microbial communities had been free to spread throughout the 'normal' marine environment during the Precambrian Era because of the absence of heterotrophic grazers. Accordingly, the manifestations of the CO_2 concentration effect so pronounced in their modern analogs were necessarily absent in the carbon-fixing pathway of these ancient forms. Therefore, it could not surprise that organic matter from Precambrian stromatolites displays fractionations typically linked to C3 photosynthesis that are dominated by the sizable enzymatic isotope effect of the RuBP carboxylase reaction.

In summary, there can be little doubt that an elimination of the diffusion barrier in the assimilatory pathway was the crucial prerequisite for the observed expression of the enzymatic fractionation effect in the oldest stromatolite-forming microbiota. Since, on the other hand, the $\delta^{13}C$ values of extant fresh water mats rarely go below $-22\,‰$

[2] 22 kerogen samples from Precambrian stromatolites reported by Eichmann and Schidlowski (1975) had yielded $\delta^{13}C = -28.5 \pm 3.6\,‰$ [PDB].

(Smith and Epstein, 1971; Barghoorn *et al.*, 1977), and cyanobacterial and algal cultures grown artificially at atmospheric CO_2 pressures often display pronounced fractionation deficits as compared to higher C3 plants (Calder and Parker, 1973; Seckbach and Kaplan, 1973; and others), it remains to be shown whether or not the above explanation can account for the *total* difference in isotopic composition between fossil stromatolites and the bulk of their modern counterparts. If subsequent work should confirm that fractionations typical of the RuBP carboxylase reaction are not fully expressed in freshwater mats, this could certainly point to the involvement of an additional physiological factor (most probably retarded CO_2 diffusion in the protective polysaccharide slimes). Therefore, it cannot be ruled out that higher mixing ratios of CO_2 in the Precambrian atmosphere may be a complementary requirement for obtaining the large fractionations observed in the oldest stromatolites (Mizutani and Wada, 1982).

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References

Aharon, P., Kolodny, Y., and Sass, E.: 1977, *J. Geol.* **85**, 27–48.

Awramik, S. M.: 1982, in H. D. Holland and M. Schidlowski (eds.), *Mineral Deposits and Evolution of the Biosphere* (Berlin: Springer), pp. 67–81.

Barghoorn, E. S., Knoll, A. H., Dembicki, H., and Meinschein, W. G.: 1977, *Geochim. Cosmochim. Acta* **41**, 425–430.

Bauld, J.: 1981, *Hydrobiologia* **81**, 87–111.

Behrens, E. W. and Frishman, S. A.: 1971, *J. Geol.* **79**, 94–100.

Broecker, W. S.: 1973, in C. M. Woodwell and E. V. Pecan (eds.), *Carbon and the Biosphere* (Washington, D.C.: U.S. Atomic Energy Comm.), pp. 32–50.

Buchanan, B. B.: 1979, in M. Gibbs and E. Latzko (eds.), *Encyclopedia of Plant Physiology* (New Series) **6** (Berlin: Springer), pp. 416–424.

Calder, J. A. and Parker, P. L.: 1973, *Geochim. Cosmochim. Acta* **37**, 133–140.

Cloud, P. E.: 1976, *Paleobiology* **2**, 351–387.

Cohen, Y., Aizenshtat, Z., Stoler, A., and Jørgensen, B. B.: 1980, 'The microbial geochemistry of Solar Lake, Sinai', in J. B. Ralph, P. A. Trudinger, and M. R. Walter (eds.), *Biochemistry of Ancient and Modern Environments* (Berlin: Springer), pp. 167–172.

Deines, P.: 1980, in P. Fritz and J. C. Fontes (eds.), *Handbook of Environmental Isotope Geochemistry* (Amsterdam: Elsevier), Vol. 1, pp. 329–406.

Eichmann, R. and Schidlowski, M.: 1975, *Geochim. Cosmochim. Acta* **39**, 585–595.

Estep, M. F.: 1982, Ann. Rept. Director Geophys. Lab. Carnegie Inst. Washington 1981–82, 403–410.
Estep, M. F., Tabita, F. R., and Van Baalen, C.: 1978a, *J. Phycol.* **14**, 183–188.
Estep, M. F., Tabita, F. R., Parker, P. L., and Van Baalen, C.: 1978b, *Plant. Physiol.* **61**, 680–687.
Friedman, G. M. and Krumbein, W. E. (eds.): 1985, *Hypersaline Ecosystems: The Gavish Sabkha* (Berlin: Springer), 437 pp.
Fuchs, G., Thauer, R., Ziegler, H., and Stichler, W.: 1979, *Arch. Microbiol.* **120**, 135–139.
Gavish, E.: 1980, 'Recent sabkhas marginal to the southern coasts of Sinai, Red Sea', in: A. Nissenbaum (ed.), *Hypersaline Brines and Evaporitic Environments*, Developments in Sedimentology, **28** (Amsterdam: Elsevier), pp. 233–251.
Glaessner, M. F.: 1983, 'The emergence of Metazoa in the early history of life', in B. Nagy, R. Weber, J. C.
Guerrero, and M. Schidlowski (eds.), *Developments and Interactions of the Precambrian Atmosphere, Lithosphere and Biosphere* (Amsterdam: Elsevier), pp. 319–333.
Hayes, J. M., Kaplan, I. R., and Wedeking, K. W.: 1983, 'Precambrian organic geochemistry: Preservation of the record', in J. W. Schopf (ed.), *Earth's Earliest Biosphere: Its Origin and Evolution* (Princeton, N.J.: Princeton University Press), pp. 93–134.
Hoering, T. C.: 1967, 'The organic geochemistry of Precambrian rocks', in P. H. Abelson (ed.), *Researches in Geochemistry* (New York: Wiley), pp. 89–111.
Holland, H. D.: 1978, *The Chemistry of the Atmosphere and Oceans*. New York: Wiley, 351 pp.
Junge, C. E., Schidlowski, M., Eichmann, R., and Pietrek, H.: 1975, *J. Geophys. Res.* **80**, 4542–4552.
Krumbein, W. E.: 1983, 'Stromatolites – the challenge of a term in space and time', in B. Nagy, R. Weber, J. C. Guerrero, and M. Schidlowski (eds.), *Developments and Interactions of the Precambrian Atmosphere, Lithosphere and Biosphere* (Amsterdam: Elsevier), pp. 385–423.
Krumbein, W. E. and Cohen, Y.: 1974, *Geol. Rdsch.* **63**, 1035–1065.
Krumbein, W. E. and Cohen, Y.: 1977, 'Primary production, mat formation and lithification chances of oxygenic and facultative anoxygenic cyanophytes (cyanobacteria)', in E. Flügel (ed.), *Fossil Algae* (Berlin: Springer), pp. 37–56.
Krumbein, W. E., Buchholz, H., Franke, P., Giani, D., Giele, C., and Wonneberger, K.: 1979, *Naturwiss.* **66**, 381–389.
Landolt-Börnstein: 1962, Zahlenwerte und Funktionen aus Physik, Chemie, Astronomie, Geophysik und Technik. 6. Aufl., Bd. II/2b: Gleichgewichte ausser Schmelzgleichgewichten, p. 1/175 (Berlin: Springer).
Lowe, D. R.: 1980, *Nature* **284**, 441–443.
MacGregor, A. M.: 1941, *Trans. Geol. Soc. S.Afr.* **43**, 9–15.
Mizutani, H. and Wada, E.: 1982, *Origins of Life* **12**, 377–390.
Mook, W. G., Bommerson, J. C., and Staverman, W. H.: 1974, *Earth Planet. Sci. Lett.* **22**, 169–176.
Oehler, J. H.: 1976, *Geol. Soc. Amer. Bull.* **87**, 117–129.
O'Leary, M. H.: 1981, *Phytochemistry* **20**, 553–567.
O'Leary, M. H.: 1982, *Ann. Rev. Plant Physiol.* **33**, 297–315.
Orpen, J. L. and Wilson, J. F.: 1981, *Nature* **291**, 218–220.
Pardue, J. W., Scalan, R. S., Van Baalen, C., and Parker, P. L.: 1976, *Geochim. Cosmochim. Acta* **40**, 309–312.
Park, R. and Epstein, S.: 1960, *Geochim. Cosmochim. Acta* **21**, 110–126.
Peters, K. E., Rohrback, B. G., and Kaplan, I. R.: 1981, *Amer. Ass. Petrol. Geol. Bull.* **65**, 501–508.
Schidlowski, M.: 1982, in H. D. Holland and M. Schidlowski (eds.), *Mineral Deposits and the Evolution of the Biosphere* (Berlin: Springer), pp. 103–122.
Schidlowski, M., Hayes, J. M., and Kaplan, I. R.: 1983, in J. W. Schopf (ed.), *Earth's Earliest Biosphere: Its Origin and Evolution* (Princeton, N.J.: Princeton University Press), pp. 149–186.
Schidlowski, M., Matzigkeit, U., and Krumbein, W. E.: 1984, *Naturwiss.* **71**, 303–308.
Schidlowski, M., Matzigkeit, U., Mook, W. G., and Krumbein, W. E.: 1985, in G. M. Friedman and W. E. Krumbein (eds.), *Hypersaline Ecosystems: The Gavish Sabkha* (Berlin: Springer), pp. 381–401.
Schoell, M. and Wellmer, F. W.: 1982, *Nature* **295**, 172.
Schopf, J. W., Oehler, D. Z., Horodyski, R. J., and Kvenvolden, K. A.: 1971, *J. Paleont.* **45**, 477–485.
Seckbach, J. and Kaplan, I. R.: 1973, *Chem. Geol.* **12**, 161–169.
Smith, B. N. and Epstein, S.: 1971, *Plant Physiol.* **47**, 380–384.
Stanley, S. M.: 1981, *The New Evolutionary Timetable*, New York: Basic Books Inc., 222 p.
Towe, K. M.: 1982, *Nature* **295**, 171.
Vogel, J. C.: 1980, Sitzungsber. Heidelb. Akad. Wiss., Math.-Nat. Kl., **1980** (3), 111–135.

Walter, M. R.,: 1983, in J. W. Schopf (ed.), *Earth's Earliest Biosphere: Its Origin and Evolution* (Princeton, N.J.: Princeton University Press), pp. 187–213.
Walter, M. R., Buick, R. and Dunlop, J. S. R.: 1980, *Nature* **284**, 443–445.
Winkler, F. J., Kexel, H., Kranz, C., and Schmidt, H. L.: 1982, in H. L. Schmidt, H. Förstel, and K. Heinzinger (eds.), *Stable Isotopes* (Anal. Chem. Symp. Ser. *11*), Amsterdam: Elsevier, pp. 83–89.