EARLY GEOBIOCHEMICAL EVOLUTION OF THE EARTH

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ABSTRACT Important constraints on the nature of the early lithosphere come from estimated temperatures in the Earth during accretion/core formation, and experimental rock melting studies. For minimum and maximum temperature estimates, only a thin outer zone would have melted and cooling and fractionation should have produced a predominantly mafic proto-crust grading down into olivine-rich cumulates and depleted peridotitic mantle; the volume of granitic rock produced would have been much smaller than in the present crust. As a consequence of high geothermal gradients, and the impacting of giant projectiles pre-3.9 Ga, ultramafic to felsic igneous rocks, and exhalative sedimentary strata, would have been added to protocrust through the pre-Archean (Hadean). The main processes involved in transformation from a predominantly mafic proto-crust to a granite-rich crust were partial melting in the primitive lithosphere and sinking of dense residual mafic crust as geothermal gradients decreased.

Recent stable isotope studies, together with various geological features, imply: 1) the Archean hydrosphere was probably warmer, less saline, and contained relatively high proportions of juvenile components; 2) photosynthesis was established locally by 3.5 Ga, the age of the oldest widely accepted microfossils, but bacterial sulfate reduction was not a significant process until ≤ 2.8 Ga; 3) sulfate was not generally abundant in the Archean hydrosphere and hence, the atmosphere of this era is very unlikely to have been oxygenated.

INTRODUCTION In recent years, there has been a proliferation of studies aimed at constraining interpretation of the processes involved in the formation and early evolution of the Earth. Relevant data have come from a wide variety of field and laboratory based investigations of ancient terrains, experimental petrological studies, geophysical calculations, microbiological and astronomical considerations (cf. reviews by Lambert and Groves, 1981; McCall, 1981).

This paper considers aspects of the early geobiochemical evolution of the Earth, integrating data available from these diverse sources. It amplifies and updates a number of the conclusions reached by Lambert and Groves (1981). The first section covers the formation of the primordial crust and the changes it underwent during the Archean. The next section considers the early hydrosphere/atmosphere system, and the third speculates about the evolution of life on Earth.

PRIMITIVE LITHOSPHERE Thermal regime in newly formed Earth

Core formation must have occurred during, or within a few hundred million years after accretion of the Earth (Oversby and Ringwood, 1971; Ringwood, 1977a, 1979; Vollmer, 1977). Heating during accretion/core formation would have caused melting, and the primordial crust would have formed as cooling by convection and surface radiation led to solidification of the melt. There are no known relics of this early lithosphere, so its nature has to be deduced from considerations of estimated thermal gradients and experimental petrological data. It will be shown below that these lines of evidence imply that only a thin outer zone of the Earth would have been melted, contrary to some earlier suppositions of a largely or wholly molten Earth (e.g. Shaw, 1972, 1976).

The thermal effects of core segregation have been assessed by Ringwood (1977a, b; 1979). He concluded that if this process took a million years or more, the temperatures in the mantle would not be much different from those generat-

ed by accretion; in the outer Earth these temperatures are likely to have been no greater than 1 600 °C (Fig. 1; Ringwood, *op. cit.*; Hanks and Anderson, 1969). For catastrophic formation of the core, in a period of around a thousand years, temperatures should have been elevated to around 2,000 °C near the surface and 3,500 °C at the mantle-core boundary (Fig. 1).

Figure 1 — Beginning of melting (solidus) curves and complete melting (liquidus) curves for peridotitic mantle and estimated temperature distributions in the early Earth (adapted from Ringwood 1975, 1977a, 1979). 1 = Maximum temperature distribution post core formation (adiabat); 2 = post-accretion temperature distribution, which approximates minimum possible temperature distribution following core formation; 3 = temperature distribution in newly accreted Earth, after Hanks and Anderson (1969); 4 = zone of melting after catastrophic core formation; 5 = zone of melting for core formation at a time scale of 10^6 years

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Salient experimental data on rock melting To assess the degree of melting of the Earth, the estimates of minimum and maximum temperatures have to be considered in the light of experimentally determined melting reactions for mantle peridotite. It is apparent from Fig. 1 that the lowest and highest estimated thermal gradients both move out of the zone of melting at shallow mantle depths. The minimum gradient would have caused partial melting to a depth of only 120 km or so under dry conditions, or around 200 km if there was a minor amount of water present. The maximum gradient would have caused complete melting to depths of around 120 km, and partial melting from there to around 400 km, under wet or dry conditions (Fig. 1).

In considering the products of the outer Earth melting, it is necessary to take account of the following conclusions from experimental studies (cf. reviews by Wyllie, 1971; Nicholls and Ringwood, 1972; Ringwood, 1975; Green, 1976a, b):

(i) Partial melting of peridotite under a wide range of conditions yields basaltic magmas; ultramafic melts require very high degrees of melting, or sequential melting of peridotitic source rock.

(ii) Magmas of intermediate (basaltic andesite) composition can form directly from peridotite by wet melting only at pressures < 10 kbar (depths of < 30 km). Mysen and Boettcher (1972) reported andesitic glasses in experiments with hydrous peridotite at 20 kbar, but Nicholls and Ringwood (1974) argued that these quenched from the vapour phase and are much more silicic than melts produced under these conditions.

(iii) Silicic magmas (> 60% SiO₂) cannot be the direct melting product of peridotite, or the fractionation product of peridotitic liquids, but they can form by partial melting of basic to intermediate rocks in the crust; they can also form in minor proportions by high-level fractionation of mafic melts, as evidenced by the granophyre components of large layered mafic intrusives and by uncommon plagioclase granitoids in oceanic crust.

Composition of primitive crust and upper mantle

The above constraints imply that the main products of fractional crystallisation of melts produced in the outer Earth by both the minimum and maximum thermal gradients in Fig. 1, would have been ultramafic cumulates and mafic rocks, with the former beneath the latter in general. The constraints on the formation of granitic and anorthositic rocks from a peridotite source imply that the volume of sialic rocks in the first-formed crust must have been considerably less than in the present continental crust; if the primordial granitic material accumulated in a surficial layer, this layer could not have been more than 2-3 km thick. Mafic rocks would have formed a crust extending to roughly 30 km for the lowest temperature estimate, and 100 km for the highest temperatures. Beneath this should have been ultramafic cumulates and depleted peridotitic mantle, probably with entrapped melt, overlying unmelted mantle peridotite.

It is likely that mega-impact events markedly influenced the early (> 3.9 Ga) evolution of the outer regions of the Earth (e.g. Green, 1972; Glikson, 1976; Goodwin, 1976; Smith, 1976), causing major brecciation and fracturing, melting, degassing and addition of significant amounts of material from planetesimal bodies. Mafic and ultramafic

melts should have ascended from the mantle, whilst partial melting of mafic crust and high level fractionation of mafic melts should have generated granitic components, and degassing should have yielded exhalative sediments in addition to adding components to the atmosphere.

ASPECTS OF ARCHEAN CRUST-MANTLE EVOLUTION Early Archean crust

The oldest well-documented Archean terrain, in the North Atlantic Craton, formed 3.65-3.8 Ga ago (e.g. Moorbath *et al.*, 1977; Hamilton *et al.*, 1978; O'Nions and Pankhurst, 1978). This ancient crust comprises mainly gneisses formed by deformation of intrusive tonalitic to granodioritic rocks (e.g. McGregor, 1973). These intrude metamorphosed and deformed supracrustals (Allaart, 1976) comprising rocks which appear to have been originally ultramafic to felsic volcanics and intrusives, and sedimentary strata with major exhalative components. Evidently the surface had cooled sufficiently by 3.8 Ga for accumulation of liquid water.

Available evidence strongly implies that the amount of granite in the earliest Archean crust was still much less than in the present crust. Whilst there are some examples of reworking of the ancient sialic rocks in the North Atlantic Craton during younger thermal events (e.g. Collerson *et al.*, 1981), the least contrived interpretation of most of the radiometric age and initial ratio data world-wide is that major volumes of granitic material were added to the crust through the Archean (e.g. O'Nions and Pankhurst, 1978). Commonly, greenstone sequences yield ages slightly older than spatially associated granitoids, implying that mantle melting episodes led to crustal anatexis. Major addition of sialic material to the crust during the Archean is further evidenced by rare earth element (REE) patterns (Taylor and McLennan, 1981) and other geochemical features (Cameron and Garrels, 1980) of sedimentary rocks of that era, which indicate more mafic sources than for post-Archean sediments.

Based on regional metamorphic grades in thick greenstone sequences, average thermal gradients in the Archean are unlikely to have exceeded 40 °C/km (Glikson and Lambert, 1976).

Generation of ultramafic lavas Green (1972) concluded that Archean quench-textured ultramafic volcanics formed by very high degrees of melting (up to 80%) of mantle peridotite, with rapid upwelling of the little fractionated melt and extrusion temperatures of at least 1600 °C. This would require melting of superheated mantle rising adiabatically from considerable depths. Impact events are unlikely to have been the main triggering mechanism for komatiite generation, as proposed by Green (*op. cit.*), in view of the abundance of high-Mg peridotite lavas in late Archean sequences.

Generation of ultramafic melts by smaller degrees of partial melting of residues from previous mantle melting events has been suggested from considerations of melt viscosities and crystal settling velocities (Arndt, 1977), and from geochemical features of komatiites, particularly the light REE depletions in many of them (Arth *et al.*, 1977; Bickle *et al.*, 1976; Sun and Nesbitt, 1978). Arndt (*op. cit.*) envisaged that about 20% melting in ascending mantle diapirs produced (low-Mg) olivine tholeiite magmas. These separated from the diapirs which continued to rise, melting

at a reduced rate until a second batch of magma separated, this being of high-Mg basaltic composition. Continuation of the ascent and melting process would ultimately lead to formation of magmas of komatiitic peridotite composition by relatively low degrees of melting of crystalline residue enriched in refractory components.

The conclusion was reached above that outer Earth melting generated olivine-rich cumulates and depleted peridotite in the upper mantle. These could have yielded komatiitic magmas by less protracted sequential melting than underlying, undepleted peridotite. Another important feature of the upper mantle could have been a magma-mantle density inversion, beneath which the density of the relatively compressible melt exceeded that of the crystal residue (N. Arndt and E. Nisbet, *per. comm.*, 1982). This could have constrained high proportions of melt within ascending diapirs until they ascended above the density inversion depth.

Variations in the chemistry of komatiitic volcanics probably reflect the depths from which the mantle diapirs ascended, and high-level fractionation processes. The deeper source should have been undepleted, garnetiferous peridotite, which could have generated komatiites with high Ca/Al and heavy REE depletions, like the predominant type in the ca. 3.6 Ga Barberton greenstone sequence (e.g. Sun and Nesbitt, 1978; A. Glikson, *per. comm.*, 1982). Melts generated largely from cumulates and depleted peridotite in the upper mantle should have had lower Ca/Al and light REE depletions like a minority of the Barberton komatiites and many younger komatiites elsewhere (Sun and Nesbitt, 1978; A. Glikson, *per. comm.*, 1982).

Generation of granitoids There would have been considerable melting of the primordial, simatic crust, particularly as a result of ascent of hot mantle material. Tonalitic and trondhjemitic magmas would have been the major products (e.g. Lambert and Wyllie, 1972; Glikson and Lambert, 1976), in accord with the abundance of intrusives and gneisses of such compositions in Archean shields. Further destruction of primordial simatic crust probably occurred by ultimate sinking of dense residual rocks from the extensive partial melting events.

The Archean K-rich granitoids, generally post-date the more plagioclase-rich granitoids, and geochemical and experimental data imply that anatexis of tonalitic-trondhjemitic crust was a major source of the younger granites (Lambert and Wyllie, 1974; Glikson and Lambert, 1976; Condie, 1981).

By the end of the Archean, the transformation to a stable sialic crust appears to have been essentially completed.

EARLY ATMOSPHERE AND HYDROSPHERE

The origin and evolution of the atmosphere has been considered in numerous publications including Brown (1952), Cloud (1974, 1976), Fanale (1971) and Walker (1976a, b); the hydrosphere has been discussed in particular by Rubey (1951), Holland (1972, 1976), and Veizer *et al.* (1982).

Composition of primitive atmosphere There are extreme depletions of non-radiogenic inert gases in the Earth's atmosphere relative to cosmic abundances, indicating that primordial gases were not retained. Mass balance considerations, the abundance of radiogenic argon, and other arguments imply that the atmosphere-hydrosphere system formed largely from juvenile components degassed from

the Earth's interior, and was subsequently modified by physical, chemical and biological processes.

Rubey (1951) proposed that degassing has been a continuous or recurrent process which is still occurring. However, Fanale (1971), Walker (1976a, b) and others argued that degassing was essentially completed at a very early stage in Earth history. The answer is probably closer to the latter viewpoint as the rate of degassing must have been in proportion to the amount of igneous activity and the frequency of major impacts. Furthermore, Taylor (e.g. 1977) concluded from oxygen-deuterium isotope studies on igneous rocks that there has been little degassing of juvenile water in the past 2.5-3.0 Ga.

There are two general schools of thought on the composition of the early atmosphere. The concept of a highly reducing atmosphere received impetus from the classic Miller-Urey synthesis of amino-acids, the building blocks of life, by spark discharges in an atmosphere of NH_3 , (N_2) , CH_4 , H_2 and H_2O (Miller, 1953). On the other hand, geochemical arguments based on the oxidation state of the Earth's mantle, supported by observations of the compositions of fluid inclusions in mantle materials and modern volcanic gases, strongly imply a less-reduced atmosphere comprising mainly H_2O and CO_2 , with lesser CO , N_2 , H_2S , SO_2 , HCl and little if any NH_3 and CH_4 . The experiments of Abelson (1966) and Hubbard *et al.* (1971) imply that amino-acids could also have been synthesised from such an atmosphere. The absence of a juvenile O_2 source, and the failure of attempts to synthesise amino-acids abiotically in the presence of O_2 , strongly imply that this gas was not a stable component of the early atmosphere, but was generated by secondary processes. This point will be taken up again in the section on Archean life.

Composition of Archean hydrosphere Initially, temperatures at the surface of the Earth would have been too high for the existence of liquid water, resulting in a very H_2O -rich atmosphere. However, the presence of surface water by 3.8 Ga is indicated by the evidence for sub-aqueous sedimentation in the Isua supracrustals (e.g. Allaart, 1976) and it has been suggested that hydrosphere development was a prerequisite for preservation of crust (e.g. Costa *et al.*, 1981).

It is likely that the main controls on the chemistry of the Archean hydrosphere were reactions with hot igneous rocks, juvenile additions and seafloor "weathering", with minor input from fluvial systems. Oxygen isotope studies of Archean hydrothermal talc-bearing sediments by Costa *et al.* (1980, 1981) imply the existence of fluids isotopically similar to modern seawater. This observation, together with the lower $\delta^{18}\text{O}$ values for Archean cherts (e.g. Knauth and Lowe, 1978) and carbonates (e.g. Veizer and Hoefs, 1976), suggests that Archean hydrosphere temperatures were higher, probably around 70 °C on average.

Dolomite is the dominant carbonate mineral in Precambrian (particularly Proterozoic) sedimentary sequences, in contrast with the predominance of calcite in Phanerozoic strata. Tucker (1982) proposed that petrographic evidence suggests a lot of Precambrian dolomite is primary, and he provided some stable isotopic data which support this contention. The formation of dolomite by direct precipitation or early diagenetic reactions would probably require higher temperatures, higher Mg/Ca, higher CO_2 partial pressures and lower SO_4^{2-} than in most younger carbonate-forming environments.

Reduced sulfur species were important constituents of Archean exhalations, but in most environments the sulfur was largely precipitated as pyrite and other sulfides. There are local examples of bedded barite in *ca.* 3.45 Ga shallow water sedimentary sequences in the North Pole area of the Pilbara Block, Western Australia (*e.g.* Dunlop, 1978; Lambert *et al.*, 1978), and the Barberton area of South Africa (Perry *et al.*, 1971; Heinrichs and Reimer, 1977). The form of the barite, including interfacial angle measurements, implies that these deposits formed at least partly by baritisation of original evaporitic gypsum (Dunlop, 1978; Dunlop and Groves, 1978). Furthermore, the restricted range of isotope compositions for these barite occurrences ($\delta^{34}\text{S}$ values concentrated around $+3\text{‰}$), imply that the sulfate formed mainly by surficial oxidation of reduced sulfur (Perry *et al.*, 1971; Lambert *et al.*, 1978), but this does not indicate that the contemporaneous atmosphere was oxygenated because of the various oxygen "sinks" in the hydrosphere atmosphere (*cf.* Archean life section).

The Big Stubby deposit, though only 40 km from the North Pole and of similar age, presents an interesting contrast. Big Stubby is a small baritic-sulfide body with geological, mineralogical and textural features resembling those of Kuroko-type volcanogenic deposits; it has $\delta^{34}\text{S}$ values averaging $+12\text{‰}$ and -3‰ for barite and sulfides, respectively (Lambert *et al.*, 1978). These features are consistent with its precipitation from sulfate-bearing waters of the type which gave rise to the North Pole deposits. These waters would have had to have circulated into the volcanic pile and been extensively reduced at elevated temperatures, as is envisaged in the generation of post-Archean volcanogenic mineralisation from seawater-rich fluids (*e.g.* Ohmoto and Rye, 1979). However, the geological evidence favours a restricted basin for the North Pole sequence (*e.g.* Groves *et al.*, 1981) so, there is no evidence for the world-wide abundance of sulfate at this early stage of Earth history. Outside the east Pilbara and Barberton regions the only indications of Archean sedimentary or exhalative sulfate minerals known to the author are ankerite, which may be pseudomorphing gypsum in the *ca.* 2.7 Ga Black Flag Beds at Kalgoorlie, Western Australia (Golding and Walter, 1979), barite mineralization in the Peninsular Gneiss Complex of India (Radhakrishna and Vasudev, 1977), and minor barite in the Kidd Creek deposit of Canada (W. Brook, *per. comm.* 1978). Sulfates in metasomatised carbonates in the Aldan Shield (*e.g.* Vinogradov *et al.*, 1976) may have formed from sedimentary sulfates.

The isotopic fractionations between oxidised and reduced sulfur species in hydrothermal and biological systems (*e.g.* Ohmoto and Rye, 1979) mean that the $\delta^{34}\text{S}$ values for sedimentary and volcanogenic sulfides should have concentrated around 0‰ only as long as there was no significant concentration of SO_4^{2-} in the hydrosphere as a whole. Therefore, the observation that the great bulk of the $\delta^{34}\text{S}$ results for such sulfides from various Archean sequences are in the range $0 \pm 4\text{‰}$, is evidence against moderate to high concentrations of SO_4^{2-} in the hydrosphere (*e.g.* Lambert, 1978; Cameron, 1982; Skyring and Donnelly, 1982). A small proportion of the $\delta^{34}\text{S}$ results for Archean sulfides are outside this range, in accord with the presence of minor SO_4^{2-} ; these are best documented from some *ca.* 2.7 Ga Canadian iron formations (Goodwin *et al.*, 1976), and also reported from some volcanogenic deposits (Secombe, 1977; Menon *et al.*, 1982). In a study of sulfides in sedimentary strata from a variety of stratigraphic levels

in Archean and Proterozoic sequences of South Africa, Cameron (1982) found a $\delta^{34}\text{S}$ transition from near 0‰ in strata older than about 2.35 Ga, to significantly negative and positive values in younger rocks. Further evidence for a major increase in the concentrations of SO_4^{2-} in the hydrosphere in the Lower Proterozoic is provided by pseudomorphed sulfate-evaporite deposits in the Great Slave Lake area of Canada (Badham and Stanworth, 1977) and the Pine Creek Geosyncline (Crick and Muir, 1980).

The Great Slave Lake sequence also contains pseudomorphs after bedded halite (Badham and Stanworth, 1977). There are no reports of older halite deposits than this, suggesting that the chloride concentrations of the hydrosphere built up slowly during the Archean.

ARCHEAN LIFE Following the pioneering experiments of Miller (1953), there have been many laboratory syntheses of amino-acids and other simple organic compounds, driven by a variety of energy sources (*e.g.* Calvin, 1969). A further step in the sequence of events leading to life was achieved with the laboratory synthesis of "primitive protein" (high molecular weight organic polymers) and "protocells" (primitive organized structures) using thermal energy (Fox, 1971).

Hoyle and Wickramasinghe (1977) speculated that the low molecular weight organic compounds and radicals found in interstellar clouds are the result of radiation degradation of much more complex organic molecules, which they believe could have been added to the primitive Earth. The addition of extraterrestrial organic compounds, after solidification of the proto-crust, may have complemented terrestrial abiotic syntheses of the building blocks of life.

The main environments have been proposed for evolution of prebiotic compounds to living systems:

(i) Solar energy acting on a marine dilute organic "soup" (Haldane, 1929; Oparin, 1957).

(ii) Alternation of hot, dry conditions and cold damp conditions in desert environments (Orgel, 1974).

(iii) Terrestrial energy (heat) in active volcanic areas (Sylvester-Bradley, 1975; Degens, 1977; Corliss *et al.*, 1981).

Of these, the third seems most appropriate to the early Archean record. Corliss *et al.* (1981) consider that various reduced gases and organic molecules were generated by reactions in seawater which extracted heat and CO_2 from magmas entering the submarine crust, with saponite-coated fracture surfaces catalysing the reactions. With the prolific igneous activity in the early Earth, "protocells" could have been generated in many submarine volcanic environments, and, by chance, life forms could have evolved in a small number of them. Abiotic synthesis of organisms probably occurred locally at different places, with multiple origins, evolutions and extinctions of primitive forms.

In the past decade, there has been a concentrated effort put into locating evidence of life in ancient rocks. The two main approaches have been searches for microfossils stromatolites and stable isotopic studies.

Pflug and Jaeschke-Boyer (1979) described "yeast-like microfossils" in amphibolite facies metaquartzites from the 3.8 Ga Isua supracrustals, Schidlowski *et al.* (1979) found average $\delta^{13}\text{C}$ values of -2.5‰ for carbonate and -15.3‰ for carbonate and graphitic carbon in the Isua metasediments, with the results displaying considerable scatter. They interpreted these data in terms of metamorphic modifica-

tion of the "modern" biologically-controlled partitioning of carbon between reduced and oxidised species, which typically yields $\delta^{13}\text{C}$ values of close to 0‰ and -25‰ for carbonate and reduced carbon, respectively. This led them to conclude that there was an extremely early (pre-3.8 Ga) origin of life and photosynthetic activity on Earth, and that the terrestrial carbon cycle was virtually stabilised at the time of accumulation of the Isua strata.

However, these conclusions are disputable. The considerable metamorphism and deformation render it unlikely that microfossils would be preserved in the Isua rocks, and the "microfossil-like" objects of Pflug and Jaeschke-Boyer (*op. cit.*) have been reinterpreted as limonite-stained fluid inclusions by Bridgwater *et al.* (1981), and iron-oxide stained weathering pits after small siderite crystals by E. Roedder (*per. comm.* 1982). Amino-acids and hydrocarbons in the Isua rocks have been shown by Nagy *et al.* (1981) to include geologically unstable compounds, implying recent diffusion of biochemicals from encrusting lichens. Finally, the carbon isotopic compositions of the Isua rocks could have formed by inorganic processes in hydrothermal systems, with varying degrees of conversion of methane to carbon. Therefore, there is no compelling evidence for the existence of life at the time the Isua supracrustals were formed.

Putative microfossils have been reported from sub-green-schist facies, 3.5 Ga cherts interbedded with barite at North Pole, Western Australia (Dunlop *et al.*, 1978; Awramik *et al.*, 1982), and from the Onverwacht Group of South Africa (Muir and Grant, 1976); furthermore, Lowe (1980) and Walter *et al.* (1980) have described stromatolites in cherts from the North Pole region. Schopf and Walter (1982) have assessed the authenticity of these and other reports of Archean "fossils". They concluded that only two geological units in the Archean — the bedded stromatolitic cherts at North Pole, and cherty stromatolitic limestones of the ca. 2.8 Ga Fortescue Group of the Hamersley Basin, also in Western Australia — contain well established Archean microbios. They categorise the microstructures described from the Onverwacht and Fig Tree Groups of South Africa as possible microfossils ("dubio-microfossils"). Thus the Archean fossil record remains very poorly known. In contrast, stromatolites were an abundant component of the sedimentary environment at least as early as 2.8 Ga (Walter, 1982).

The most detailed studies by far have been conducted on the North Pole microfossils. Their morphologies, distribution and physical organisation, and kerogen geochemistry led Schopf and Walter (*op. cit.*) to infer that some of the organisms there were photo-responsive, at least some were anaerobes, some were autotrophs (organisms that used CO_2 as their immediate source of cellular carbon), and that organic carbon was probably recycled within the microbial mats by heterotrophic microorganisms (dependent on organic nutrients); there are no data indicating whether the presumed photo-autotrophs were oxygen producing. The Archean stromatolite record (Walter, 1982) provides further evidence for autotrophy, response to light, and gliding.

Schidlowski *et al.* (1982) considered the isotopic inferences of ancient biochemistries. They concluded that the carbon isotopic compositions of kerogen and carbonate in sedimentary strata ≤ 3.5 Ga are essentially constant and indicate biological (photosynthetic) activity. They believe local excursions of $\delta^{13}\text{C}$ values for kerogens to very low values (-40‰ to 50‰) are suggestive of methane utilising pathways in the formation of the kerogen precursors.

It was concluded in the previous section that sulfur isotopic and mineralogical data currently available do not favour the build up of SO_4^{2-} levels in the hydrosphere as a whole, until the Lower Proterozoic. As sulphurous exhalation must have been entering the hydrosphere in abundance throughout the Archean, it is difficult to see how an oxygenous atmosphere could have developed without a preceding period of major oxidation of reduced sulfur species in the hydrosphere. Therefore, I consider that the sulfur-isotope data, complement the various lines of evidence put forward by Cloud (*e.g.* 1974, 1976) which, although not unequivocal (*e.g.* Clemmey and Badham, 1982) are all consistent with the advent of an oxygenous atmosphere in the Lower Proterozoic. This in no way precludes oxygen production during the Archean, either by photosynthesis in at least local environments or by photodissociation. Such oxygen could have been used up in oxidising reactions within the hydrosphere/atmosphere system. It was possibly important in producing high sulfate concentrations at North Pole and the South African barite forming environments, but these could also have been achieved by the actions of photosynthetic sulfur bacteria; where iron was available any free oxygen should have reacted with it to form iron oxides.

A general build up of SO_4^{2-} is likely to have preceded the proliferation of sulfate-reducing bacteria. The wide range of $\delta^{34}\text{S}$ values in sulfide facies iron-formation in southern Canada has been cited as the earliest evidence for bacterial sulfate reduction (Goodwin *et al.*, 1976; Schidlowski *et al.*, 1982). Whilst this may be so, it is not yet proven because these deposits could well have formed as a result of hydrothermal activity, which can also lead to major sulfur isotope fractions if SO_4^{2-} is a component of the fluids (*e.g.* Ohmoto and Rye, 1979). Skyring and Donnelly (1982) speculated that sulfite from minor proportions of ^{34}S -enriched SO_2 in exhalations was the most readily available S-source to evolving organisms, and that bacterial sulfite reduction preceded dissimilatory sulfate reduction, which they consider to have become an important process in the S-cycle in the Lower Proterozoic.

SUMMARY AND CONCLUSIONS Even the maximum temperatures estimated to have been generated in the Earth during accretion and core formation would have caused melting only above a depth of ca. 400 km. Cooling and fractionation of the outer melted zone should have formed a predominantly simatic proto-crust, some 30 to 100 km thick which contained much less granitic material than the present crust. Major impacting events probably caused brecciation, fracturing, more melting and exhalative activity before ca. 3.9 Ga. The proto-mantle would have comprised olivine-rich cumulates and depleted peridotite, grading into undepleted peridotite.

Sialic components were added to the crust during the Archean; tonalitic and trondhjemitic granitoids would have formed largely by anatexis of simatic proto-crust, and potassic granites from anatexis involving earlier-formed, plagioclase-rich granitoids. Archean greenstone sequences reflect major mantle melting events at various times during the Archean, and they probably accumulated in different environments at different stages of crustal evolution. Dense residual rocks from simatic anatexis probably sank into the mantle, effectively completing the transformation from a predominantly simatic proto-crust to a granitoid-rich stable crust.

The primitive atmosphere/hydrosphere system developed largely as a result of degassing of the Earth. The earliest atmosphere probably consisted mainly of H_2O , CO_2 , with lesser amounts of CO , N_2 , H_2 , H_2S , SO_2 , HCl , and possibly some NH_3 and CH_4 . There was no juvenile source of O_2 , and sulfur isotope data support other lines of evidence that an oxygenated atmosphere did not evolve until the Lower Proterozoic. The Archean hydrosphere probably had a low $NaCl$ content, but degassing probably resulted in it being enriched in iron, silica and carbonate species. Abiotic synthesis of organic compounds leading eventually to life probably occurred before 3.5 Ga, on the basis of microfossil, stromatolite and carbon isotope data. Microbial photosynthesis was probably widespread in Archean marginal

marine environments, but there is no compelling evidence that dissimilatory sulphate reducing bacteria proliferated before the Lower Proterozoic.

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