

2A. Carbon Metabolism and Biogeochemical Cycling

This introduction serves to explain core concepts pertinent to Archaeal metabolism and biogeochemical cycling.

1. Metabolism: The Basic Framework

1.1. Metabolic Classification

The validity of using carbon isotopes in the search for early life hinges on two simple assumptions, both of which are unconditionally true for all known forms of life:

- (i) Early life was carbon-based; and
- (ii) Early life employed metabolic processes that exerted a fractionation effect on isotopes of carbon.

The unique properties of carbon which make it a suitable building-block for life are not shared by any other element. In any event, it is safe to assume that carbon-based life today must also have evolved from a carbon-based ancestor. The second assumption is perhaps harder to justify. It is first important to distinguish between *anabolic* and *catabolic* processes, which together form the keystones of metabolism. *Anabolism* is the biological process whereby the functional and structural materials of life, such as cell components, are biosynthesized. *Catabolism*, on the other hand, involves the transformation of energy from outside sources - such as sunlight, heat or chemical bonds in molecules absorbed from the environment - into a compact and transportable form that life-sustaining reactions can use. Organisms can be categorized on the basis of catabolic and anabolic processes, as shown schematically in Figure 1.

An all-encompassing classification scheme is needed as a framework for discussion on microbial diversity. In addition to requiring energy, all known forms of life are carbon-based and require carbon as their primary macronutrient. It is for this reason that life is commonly categorized on the basis of both energy and carbon sources (Figure 1). *Phototrophs* obtain their energy from light and convert this to chemical energy as part of a process called photosynthesis. *Chemotrophs* obtain their energy from chemical compounds. The compounds used by chemotrophs may be either

organic or inorganic. In these two distinct cases the organisms are said to be *chemoorganotrophs* or *chemolithotrophs*, respectively.

Carbon is derived from CO₂ in *autotrophs* and from pre-formed reduced organic compounds such as sugars in *heterotrophs*. What would be called ‘chemoheterotrophs’ are called ‘mixotrophs’ instead.

1.2. Basic Biochemical Energetics

The release and conservation of metabolic energy in living cells occurs as the result of reduction-oxidation reactions. Biological systems are thus governed by couples of electron acceptors and donors. The amount of energy released during such a redox reaction can be quantified by the ‘reduction potential’ (E_0') of a couple. Couples with a high (positive) E_0' have a greater tendency to accept electrons, and vice versa. A range of important biological couples, with their corresponding reduction potentials and number of electrons transferred (ne^-) is tabulated in Table 1. By way of example: in the couple $2H^+ / H_2$, which has a potential of -0.42 Volts, H_2 has a relatively large tendency to donate electrons while $2H^+$ does not easily accept them.

The role of electron and proton (H^+) flow is paramount in microbial energetics. In fact, oxidation-reduction reactions may be considered as chains of events resulting in just such a flow: (i) the removal of electrons from an electron donor; (ii) the transfer of electrons through electron carrier(s); and (iii) the addition of electrons to an electron acceptor. Examples of common biological electron carriers are the coenzymes nicotinamide-adenine dinucleotides NAD^+ and $NADP^+$, and the flavin-adenine di- and mono- nucleotides FAD^+ and FMD^+ . The type of electron carrier used is not really relevant here – of interest is the nature of the electron donor and acceptor. The major types of catabolism known are summarized on the basis of their electron –donor and –acceptor in Table 2.

Much of the transfer of electrons from donors to acceptors serves the purpose of relaying energy in a compact, transportable form. Energy can then later be released to carry out biological processes. More often than not the function of energy storage itself is performed by high energy phosphate bonds, in molecules such as adenosine

triphosphate (ATP). In some cases, sulfoanhydride (thioester) bonds (found, for example, in derivatives of coenzyme A) serve a similar purpose.

Cellular energy may also be stored in an electrochemical form called the Proton Motive Force (PMF), which results from a potential difference between the intra- and extra-cellular environments. The PMF is perhaps best visualized as analogous to the potential energy present in a charged battery. Conversion between PMF-derived and ATP-derived energy occurs through the action of a membrane-associated enzyme known as ATPase. ATPase functions as a reversible proton channel between the cell exterior and cytoplasm; as protons enter, the dissipation of the PMF drives ATP synthesis from $\text{ADP} + \text{P}_i$ – and *vice versa*.

The different metabolic strategies employed by living organisms are now compared.

2. Metabolic Diversity

2.1. Chemotrophy

2.1.1. Chemoorganotrophy

Chemotrophs derive their energy from chemical compounds, be they of organic or inorganic origin. The oxidation of organic electron donors for energy generation is known as ‘respiration’. In *aerobic respiration*, oxygen acts as the terminal electron donor. In *anaerobic respiration*, some molecule other than oxygen has to function as the terminal electron acceptor. *Fermentation* is a special type of anaerobic respiration in which an internal substrate acts as the electron acceptor.

The use of pre-formed organic fuels requires complex metabolic machinery whose operation serves the purposes of both catabolism and anabolism. That is, the oxidation of organic electron donors by chemoorganotrophs not only adds to the ATP and PMF pool but also manufactures the building blocks of life. A total of twelve essential precursor building blocks can be identified from which life can make further macromolecules. Figure 2 shows how the central pathways of metabolism responsible for chemoorganotrophy concurrently lead to the manufacture of these twelve precursor molecules. The three pathways shown are (i) the Embden-Meyerhof (‘Parnas’,

‘glycolysis’) pathway; (ii) the pentose phosphate pathway; and (iii) the tricarboxylic acid (TCA) cycle. All three pathways are operational during aerobic respiration. The TCA cycle in particular has major biosynthetic as well as energetic functions, and for this reason the complete cycle or major portions of it are nearly universal to life. Accordingly, it is not surprising that many organisms are able to use some of the acids produced as electron donors and carbon sources.

In the case of anaerobically respiring organisms the lack of oxygen prevents formation of certain TCA-cycle enzymes, thereby compromising the amount of reducing power generated. Manufacture of the twelve precursor molecules is still made possible through the use of *anapleurotic pathways*: enzymatic reactions or set of chemical reactions that link metabolic pathways, thereby allowing bypass of certain parts of that pathway or allowing the reversal of carbon flow. A noteworthy example of such an anapleurotic pathway is the glyoxylate cycle, which replenishes acids essential to the function of the TCA cycle using the twin enzymes isocitrate lyase and malate synthase.

Aerobic respiration allows for the continued metabolism of glucose through re-oxidation of the reduced forms of NADH and FADH produced by the central metabolic pathways. This occurs along the so-called ‘electron transport chain’, with oxygen as the terminal electron acceptor. The key intermediates in the electron transport chain differ from species to species, and usually include a variety of flavin enzymes, quinones and cytochrome complexes. The universal net result, however, is the generation of a PMF as protons (H^+) and hydroxyl ions (OH^-) accumulate on opposite sides of the cell membrane.

The major difference between aerobic and anaerobic respiration lies in the terminal electron acceptor used in the electron transport chain, as the electron carriers are similar in the two groups. Terminal electron acceptors used during anaerobic respiration include Fe^{3+} , SO_4^{2-} , CO_2 and NO_3^{2-} , all of which have a less favorable oxidation-reduction potential – and hence produce less ATP - than does O_2 .

While it lies outside the scope of this introduction to examine in detail all assimilative and dissimilative mechanisms of anaerobic respiration, it is instructive to

study one example. The use of nitrogen-based substances in metabolism is illustrative of how anabolism and catabolism can rarely be viewed as separate processes. Figure 3 contrasts assimilative and dissimilative respiratory pathways. While both use nitrogen as a terminal electron acceptor in respiration, the former incorporates the end-product into biosynthetic matter while the latter releases the end-products as waste into the atmosphere.

2.1.2. Chemolithotrophy

As an alternative to aerobic and anaerobic respiration, many microorganisms use inorganic electron donors of geological, biological or anthropogenic origin. Examples of such electron donors include hydrogen sulfide (H₂S), hydrogen gas (H₂), ferrous iron (Fe²⁺) and ammonia (NH₃). Hydrogen bacteria, for example, phosphorylate three molecules of ATP for every molecule of H₂ ‘respired’ using the hydrogenase-mediated reaction:



Other examples are the nitrifying bacteria, which generate ATP through oxidization of ammonia (NH₃) to nitrite (NO₂⁻) or nitrite to nitrate (NO₃⁻).

These chemolithotrophs rely on aerobic respiratory processes similar to those found in the electron transport chain of most chemoorganotrophs. However, while chemoorganotrophs generally rely on organic compounds such as glucose for both carbon and energy, chemolithotrophs often have to acquire their carbon elsewhere – usually from atmospheric CO₂ or (more rarely) from CH₄.

2.2. Phototrophy

The term ‘photosynthesis’ refers first and foremost to the conversion of energy in electromagnetic radiation (light) into chemical energy. Additionally, ‘photosynthesis’ implies an anabolic function; namely, the use of aforementioned chemical energy to ‘fix’ carbon into structural and functional cell components. The vast majority of photosynthetic organisms use CO₂ as their sole carbon source.

Photoheterotrophs, insignificant on a global scale, use organic compounds as a carbon source. Today, CO₂ is readily available in most environments and was probably never a limiting metabolic agent during the Earth's history.

In addition to carbon and energy, photoautotrophs require input of electrons from a donor (or 'reducing power') in order to fix CO₂. Care should be taken to distinguish this *anabolic* energy-tapping electron flow for the purpose of carbon fixation from that involved in *catabolic* energy generation discussed previously. Commonly, reducing power is generated by the oxidation of water to oxygen in the presence of light. This type of photosynthesis is called **oxygenic** photosynthesis. The production of reducing power in **anoxygenic** photosynthesis, on the other hand, rarely requires light and involves an oxidative reaction (but not oxygen production) such as H₂S → S⁰ and S⁰ → SO₄²⁻.

Photosynthesis can be categorized into distinct catabolic and anabolic phases. During the 'light reaction' phase ATP and NADPH are synthesized, while fixation of CO₂ into cellular carbon takes place during the 'dark reaction' phase. Two structural types of light-harvesting pigments are commonly used (Allen, 2002):

- (i) Isoprenoids, such as the carotenoid β-carotene;
- (ii) Tetrapyrroles, which are classed as:
 - Bile pigments such as phycobiliproteins used by cyanobacteria and red algal chloroplasts;
 - Porphyrins such as chlorophylls and bacteriochlorophylls.

It is important to distinguish between oxygenic and anoxygenic photosynthesis on the level of biochemical processes within the cell. All known oxygenic photosynthesizers make use of a cyclic, anoxygenic pathway called Photosystem I. A similar system is used by anoxygenic photosynthesizers, such as green sulfur bacteria, purple bacteria and *Heliobacterium*. Although the carriers associated with light-induced electron and energy flow in these systems are often species-specific, a general flow summary is instructive:

- Electromagnetic radiation provides the excitation energy needed to activate the *photoreaction center*, turning it into a strong electron donor;
- Subsequent electron flow drives the formation of ATP through phosphorylation of ADP;
- Electron flow through a *quinone* pool leads to charging of NAD(P)H from NAD(P)⁺;
- Specific *cytochrome* complexes, with the aid of an external electron donor, help energize another photoreaction center;
- Cyclic phosphorylation through electron flow proceeds.

Oxygenic photosynthesizers make use of an additional pathway called Photosystem II, giving rise to the ‘Z scheme’. This pathway entails the light-driven breakdown of water into oxygen and hydrogen through *non-cyclic* phosphorylation: the electrons released are used to excite a Photosystem II reaction center before passing into and thus linking the Photosystem I cycle described above. A summary of the main types of photosynthesis is presented in Table 3.

2.3. Auto- and methano- trophy

Having briefly discussed how both phototrophs and chemotrophs make energy and electrons available for carbon fixation, carbon fixation itself can now be examined. Several pathways of biological carbon fixation in which CO₂ or CH₄ are converted into living biomass are known, and tabulated in Table 4.

As implied by the table, the majority of autotrophs make use of the Calvin Benson Cycle, also known as the C₃ pathway or reductive pentose cycle (Allen, 2002), in order to fix CO₂ into cellular carbon. This occurs during the ‘dark reaction’ phase of photosynthesis. Two other less commonly used mechanisms are the reverse tricarboxylate cycle and the carbon monoxide pathway (Levin et al., 2002).

2.4. Summary of Metabolism

The large array of metabolic types known may, at first, seem overwhelming to the astrobiologist aspiring to understand the range of plausible extraterrestrial biochemistries. However, our preceding discussion reveals several dominant conceptual trends underlying the process of metabolism. These trends prevail irrespective of metabolic type, and may be summarized as shown in Figure 4. The living world shows a rich diversity in metabolic processes. However, perhaps just as remarkable is the ubiquity of key features inherent to metabolism, such as:

- An electron -donor, -carrier and -acceptor responsible for dissimilatory energy conversion using reduction-oxidation reactions. (The electron donor or acceptor may be internal, as is the case in phototrophism and fermentative chemotrophism respectively);
- The use of phosphate bonds for energy storage, transport and release;
- The creation and maintenance of a structural boundary isolating the site of metabolism from the environment;
- The reliance on this boundary for the storage of electrochemical energy, precursor metabolites and carbon-based building blocks.

3. Sources, Sequestration, and Preservation of Organic Matter

Marine, rather than terrestrial, settings dominate both the Early Archaean rock record and contemporary carbon burial alike. Today, only a minor fraction of dead organic matter is preserved in the rock record. Modern oceanic productivity and sediment burial rates of $50 \cdot 10^{15}$ and $0.16 \cdot 10^{15}$ gC yr⁻¹ respectively imply average marine preservation efficiencies under 0.5% (Hedges and Keil, 1995). The vast majority (99.0 – 99.9% according to Ronov, 1990) of organic matter that sinks towards the sediment-water interface is recycled back into the biosphere and atmosphere through decomposition. Most (~ 94%) of modern carbon burial occurs in deep-water continental-margin sediments, while only ~ 6% is buried seaward of continental rises (Berner, 1989). Despite their geographical extent, only ~ 4% of burial occurs beneath low-productivity pelagic zones.

Meanwhile, it has long been argued (e.g. Veizer and Hoefs, 1976; Perry and Ahmad, 1977; Schidlowski, 2001) that the lack of long-term variation exhibited by the marine sedimentary organic carbon record, contended by some to hold fast to a steady mean value of 0.5 wt.% organic matter, attests to the persistence of autotrophy since 3.8 Ga (Figure 5). However, several factors control the relative amounts and proportions of organic carbon buried in marine sediments. Today, these include the sedimentation rate (Stein, 1990; Betts and Holland, 1991), overlying primary productivity (Calvert and Pederson, 1992b), organic carbon rain- (or ‘irrigation-’) rate (Jahnke, 1990), organic carbon degradation rate (Emerson, 1985), bottom-water oxygen concentration (Paropkari et al., 1992; Hartnett and Devol, 2003), and oxygen exposure time (Hartnett et al., 1998).

Now, if widespread Early Archaean-onward autotrophy is assumed (Chapters 4, 5, 6) along with a steady organic carbon preservation rate, continuous complex heterotrophic biology may need to be invoked to account for the persistently low particulate PNC_{org} (‘PNC’: phosphate – nitrogen – carbon) influx into the lithospheric reservoir. Alternatively, the Archaean may have presented a radically different environment for carbon deposition and preservation. The three major potential differences that may be expected to have affected Archaean carbon cycling are (i) the chemistry of the ocean-atmosphere system; (ii) the ecology and metabolic characteristics of the Archaean biota; and (iii) greater influence of hydrothermal activity on Archaean seawater.

3.1. The pre-eminence of electron acceptors

Relative respiratory contributions of the dominant electron acceptors in contemporary marine sedimentary environments are $17 \pm 15\%$, $18 \pm 10\%$ and $62 \pm 15\%$ respectively for oxygen, ferric iron and sulphate (Thamdrup and Canfield, 2000). Within the sediment column, bacterial cell densities are highest in the oxic zone (Rusch et al., 2003). These observations may hold little implications for Archaean biogeochemistry, however, as the ultimate oxidizing agent for Fe(III), SO_4^{2-} and other potent anaerobic electron acceptors (Mn(IV), NO_x^-) is photosynthesis-derived O_2 , in

which the Archaean ocean was largely deficient (Holland, 2002; Canfield, 2005), with the possible exception of transiently oxygenated surface waters (see discussion in Chapter 5).

The importance of oxygen in organic matter preservation has been a topic of intense debate (Froelich et al., 1979; Reimers and Jr., 1986; Reimers et al., 1986; Archer et al., 1989; Archer and Devol, 1992; Hales et al., 1994). Two schools of thought may be distinguished. One school argues that preservation is largely independent of bottom water oxygen concentration, and depends primarily on the carbon supply, or 'rain rate' (Henrichs and Reeburgh, 1987; Pedersen and Calvert, 1990; Calvert et al., 1992; Calvert and Pederson, 1992a; Ganeshram et al., 1999). The second school recognizes a dominant role for oxygen (Pratt, 1984; Canfield, 1989; Paropkari et al., 1992; Canfield, 1993; Hedges and Keil, 1995; Hartnett, 1998; Hartnett et al., 1998; Hedges et al., 1999; Hoefs et al., 2002; Hartnett and Devol, 2003). More recently, members of the former group have attempted reconciliation by proposing a partial role of oxygen (Cowie et al., 1999), while a threshold O₂ concentration was put forward by adherents of the latter group (Canfield, 1994).

In aerobic environments the concentration of oxygen in sediments drops exponentially from a maximum level at the sediment/water interface, where the value is determined by the overlying O₂ concentration at the base of the water column (Figure 7). In areas that are carbon-limited, such as large parts of the deep ocean, the O₂ concentration levels off to some minimum value at a sediment depth where all metabolizable carbon has been oxidized (Grundmanis and Murray, 1982; Murray and Kuivila, 1990). In slope and shelf environments, which are typically oxygen-limited, the O₂ concentration falls under detection limits below the so-called 'oxygen penetration depth'. Typical penetration depths for O₂ in modern shallow-marine environments are in the range of millimeters.

The following modern suboxic and anoxic environments may provide insight into Archaean processes: (i) extensive stretches of sea floor exposed to permanent and severe oxygen depletion, such as where mid-water oxygen minima intercept continental margins (along much of the eastern Pacific Ocean, off west Africa, and in

the Arabian Sea and Bay of Bengal (Helly and Levin, 2004); (ii) anoxic stratified marine and lacustrine basins such as the Black Sea (Murray et al., 1995; Wakeham et al., 2004; Hiscock and Millero, 2006; Yakushev et al., 2006; Wakeham et al., 2007), the Cariaco Trench (Galimov, 2004; Wakeham et al., 2004) and Kyllaren fjord (van Breugel et al., 2005); and (iii) lakes where chemistry is constrained to an Archaean-like state by local geology. These low-oxygen settings suffer from variably from the effects of bioturbation and irrigation, which are not to be underestimated when seeking Archaean analogies (Martin and Banta, 1992). The major problem with this actualistic uniformitarian approach is that aquatic biogeochemical cycling is strongly coupled to the atmosphere, and there are obviously no terrestrial analogies to high Archaean $p\text{CO}_2$ (and perhaps $p\text{CH}_4$) systems.

3.2. Microbial Ecology

The amount of carbon sequestered within prokaryotic biomass in the open ocean and oceanic subsurface is globally significant, and has been estimated at ~11 and ~310 PgC respectively (Whitman et al., 1998). The bulk of organic matter in aquatic environments is macromolecular in nature and not ready for direct incorporation into bacterial or archaeal cells. Instead, this material has to be ‘preconditioned’ by extracellular enzymes (i.e. those found outside the cytoplasmic membrane, as defined by Priest (1984) before becoming available for growth and nutrient cycles (Hoppe, 1993). Such enzymes are produced almost exclusively by prokaryotes (Hollibaugh and Azam, 1983).

4. Conclusion

In addition to sourcing both insoluble and soluble electron acceptors, overlying productivity is also the ultimate driving force behind organic carbon production in today’s oceans. Although hydrothermal systems may have played an appreciable role in the latter (Baross and Hoffman, 1985), they are thermodynamically precluded from the former. However, no Archaean mid-ocean-ridge hydrothermal vent systems appear to have been preserved. For these reasons, Archaean benthic environments sampling

the surface ocean provide the best available environment to examine geological evidence for ancient biogeochemical cycling. The following chapters present findings from the three oldest preserved benthic environments on Earth: the ~3.7 Ga Isua Supracrustal Belt in southwest Greenland, the ~3.52 Ga Counterunah Subgroup in northwest Australia, and the ~3.45 Hooggenoeg Formation in South Africa. Shallow marine sediments of the ~3.45 Ga Strelley Pool Chert formation, meanwhile, hold crucial insights allowing direct comparison between the Archaean surface and benthic biogeochemical environments.

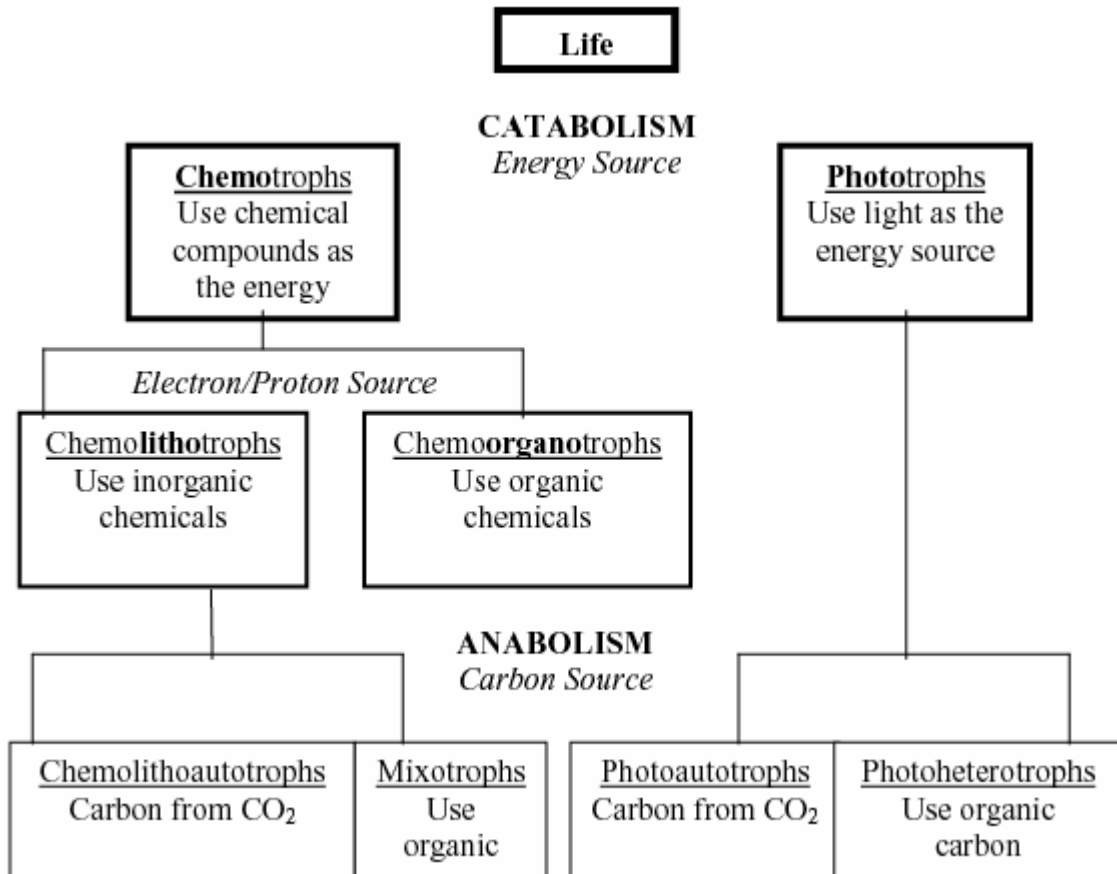


Figure 1: Classification of life in terms of metabolic energy- and carbon sources.

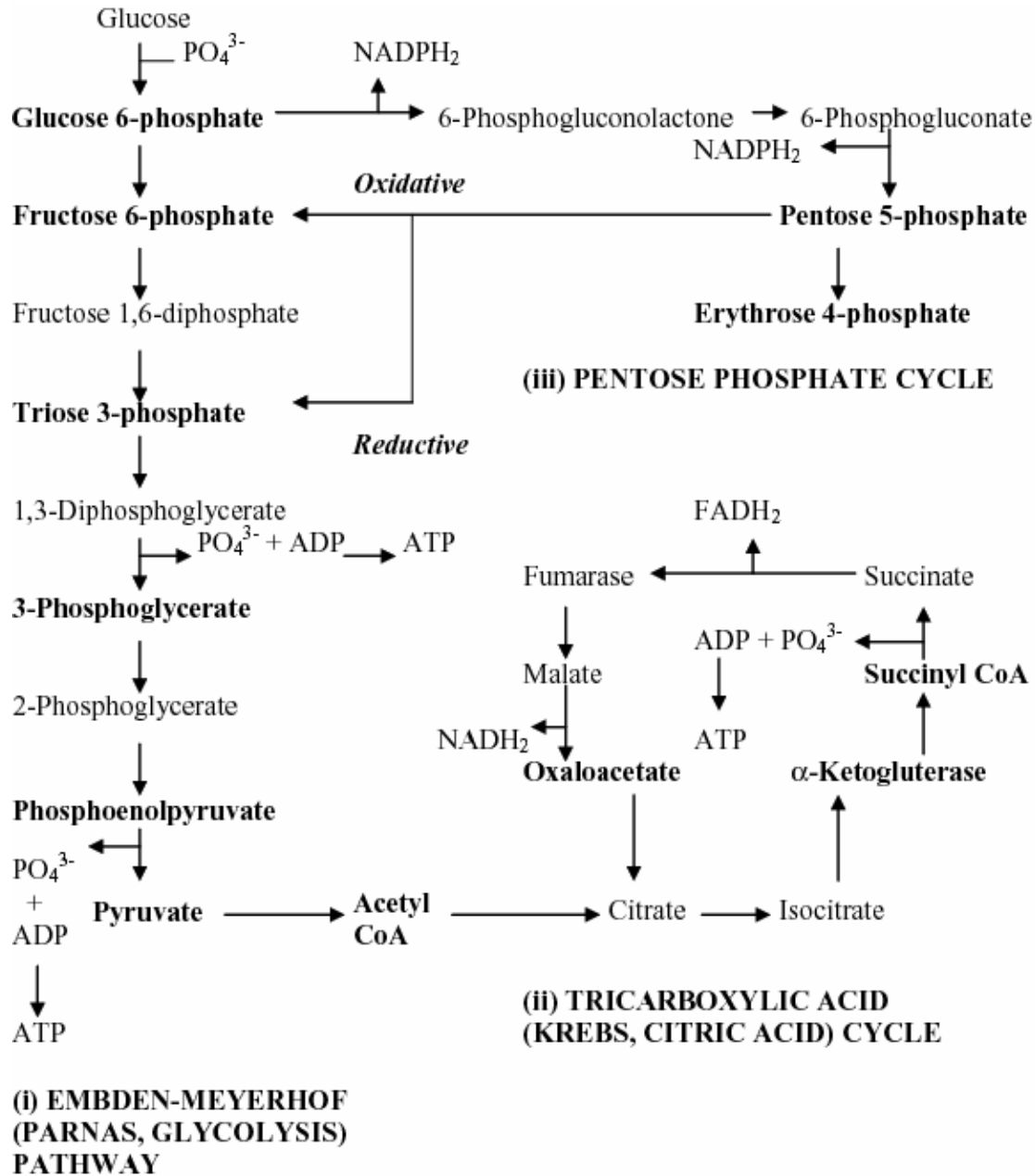


Figure 2: Central fueling and biosynthetic pathways aerobic heterotrophy: (i) The Embden-Meyerhof Pathway; (ii) The tricarboxylic acid cycle; and (iii) The pentose phosphate cycle. The oxidative and reductive branches of the pentose phosphate cycle are shown in **boldface italics**. Anapleurotic reactions and peripheral pathways (including fermentative and respiratory pathways) are not shown. The 12 precursor metabolites are shown in **boldface**.

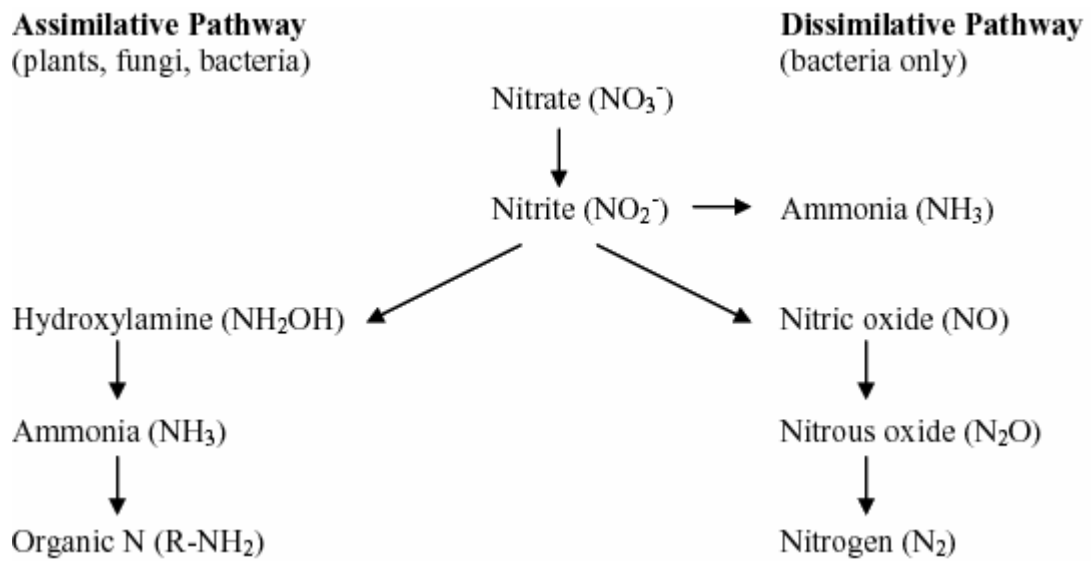


Figure 3: Assimilatory and dissimilatory pathways involving nitrogenous terminal electron acceptors.

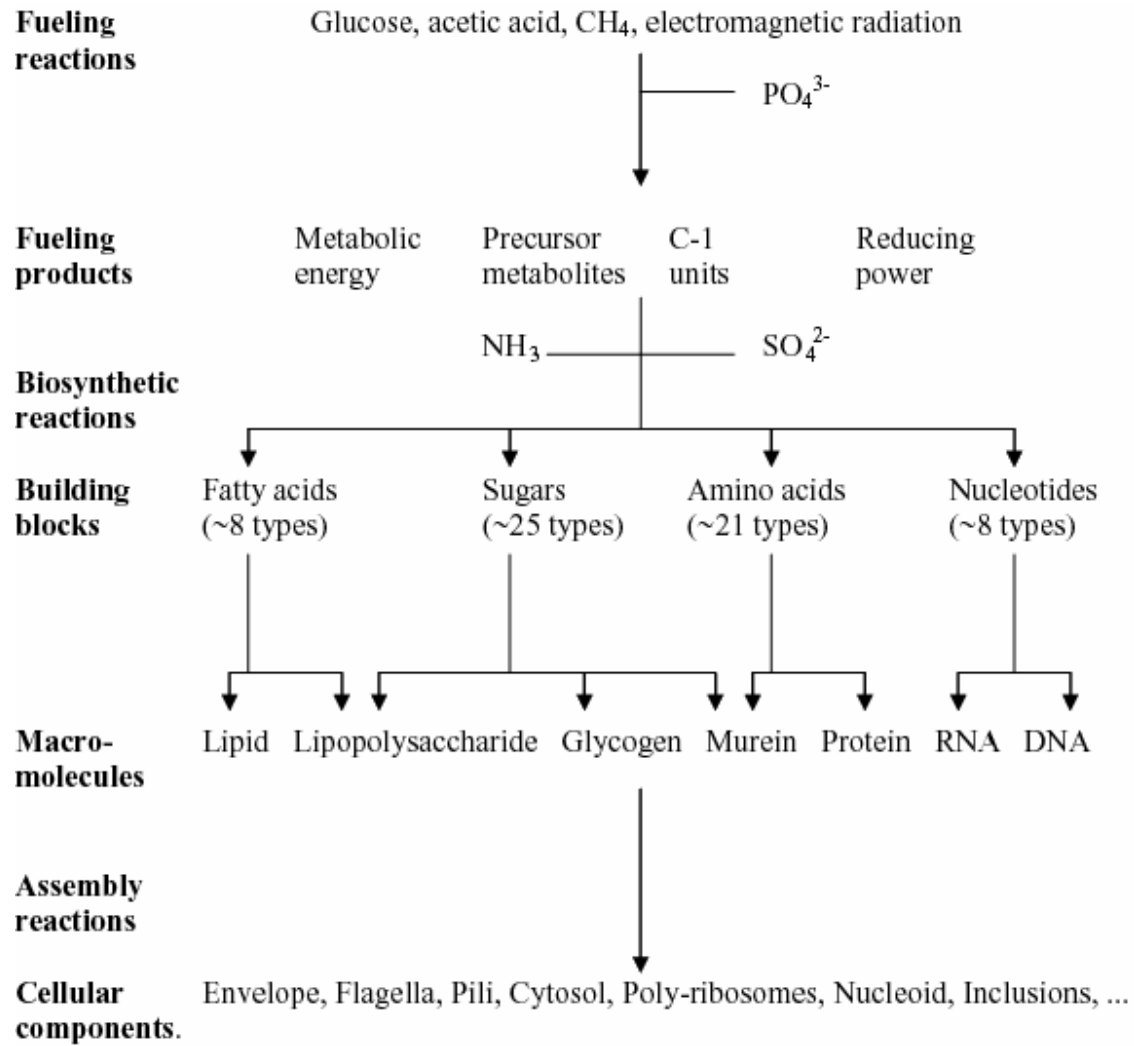


Figure 4: Schematic overview of metabolism.

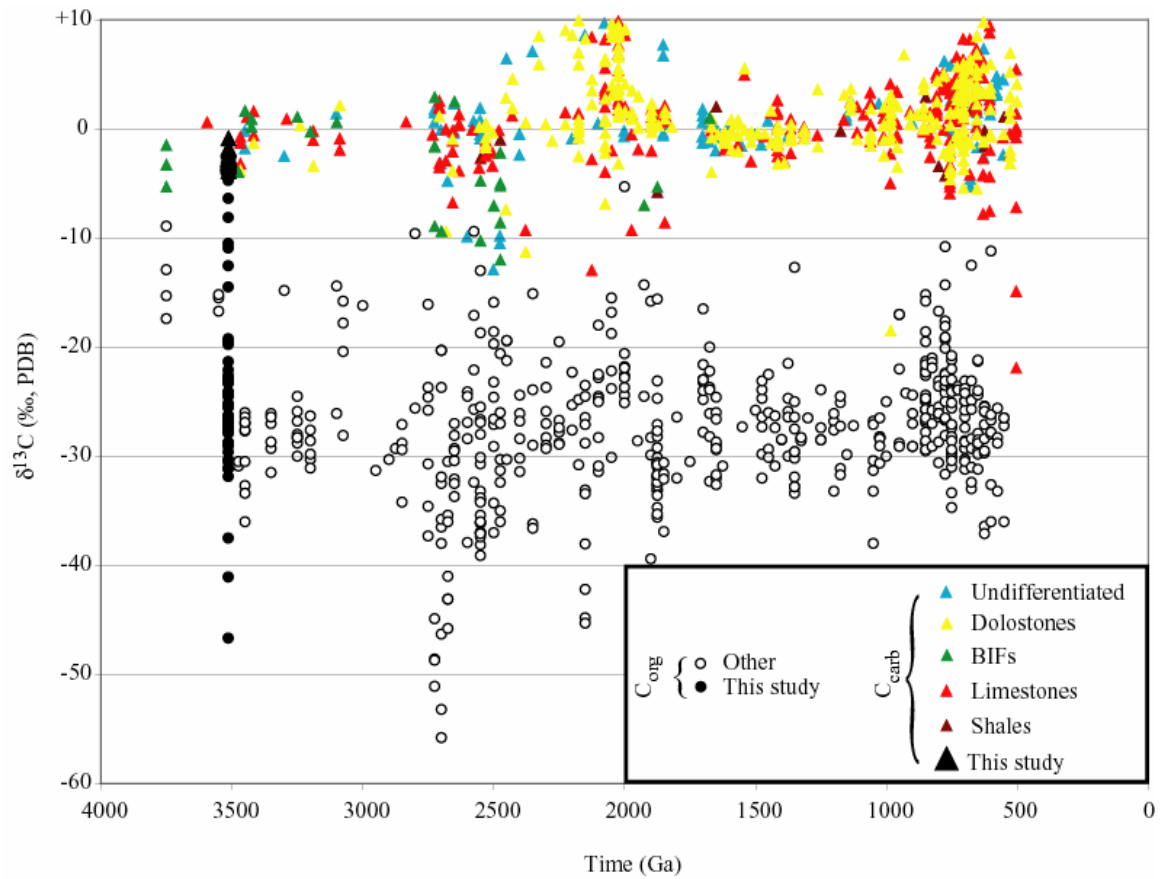


Figure 5: The carbon isotope record over time.

Table 1: Redox couples important to biological systems. Reduction potential given at standard conditions of temperature, pressure, concentration and pH (after Thauer et al., 1977).

e⁻ acceptor (oxidant)	e⁻ donor (reductant)	Reduction potential [E₀'] (V)	ne⁻
CO ₂	Glucose	-0.43	24
2H ⁺	H ₂	-0.42	2
CO ₂	Methanol	-0.38	6
NAD ⁺	NADH	-0.32	2
CO ₂	Acetate	-0.28	8
S ⁰	H ₂ S	-0.28	2
SO ₄ ²⁻	H ₂ S	-0.22	8
Pyruvate	Lactate	-0.19	2
S ₄ O ₆ ²⁻	S ₂ O ₃ ²⁻	+0.024	2
Fumarate	Succinate	+0.03	2
Cytochrome b _{ox}	Cytochrome b _{red}	+0.035	1
Ubiquinone _{ox}	Ubiquinone _{red}	+0.11	2
Cytochrome c _{ox}	Cytochrome c _{red}	+0.25	1
Cytochrome a _{ox}	Cytochrome a _{red}	+0.39	1
NO ₃ ⁻	NO ₂ ⁻	+0.42	2
NO ₃ ⁻	N ₂	+0.74	5
Fe ³⁺	Fe ²⁺	+0.76	1
½O ₂	H ₂ O	+0.82	2

Table 2: Major types of catabolism, with their corresponding electron –donor and –acceptor. Organic e⁻ donors (carbohydrates) denoted by (CH₂O)_n (after Hardie, 2000).

Process	Organism	Electron Donor(s)	Electron Acceptor(s)
Respiration	Methanogen	H ₂ , (CH ₂ O) _n	CO ₂
	Acetogen	H ₂ , (CH ₂ O) _n	CO ₂
	Sulfate reducer	H ₂ S, CH ₃ SH	Sulfate, SO ₄ ²⁻
	Sulfur reducer	H ₂ S, CH ₃ SH	Sulfur, S ⁰
	Iron reducer	H ₂ , (CH ₂ O) _n	Ferric Iron, Fe ³⁺
	Denitrifier	N ₂ , N ₂ O, NO, NO ₂ ⁻	Nitrate, NO ₃ ⁻
	Aerobe	(CH ₂ O) _n	Oxygen, O ₂
Photosynthesis	Photosynthesizer	Light-driven complexes	Cytochrome, Ubiquinone
Fermentation	Fermenter	(CH ₂ O) _n	Internal: Lactate

Table 3: Major types of photosynthesis.

	Eukaryotes	Prokaryotes		
		Cyanobacteria	Purple bacteria	Green bacteria
Electron donors	H ₂ O	H ₂ O, some can use H ₂ S	H ₂ S, S ⁰ , H ₂ , S ₂ O ₃ , organic compounds	H ₂ S, S ⁰ , H ₂ , S ₂ O ₃ , organic compounds
Site of photosynthesis	Thylakoids	Thylakoids	Cell membrane	Cytochromes
Oxygenic	Yes	Yes	No	No
Chlorophyll type	Chlorophyll a	Chlorophyll a	Bacteria-chlorophyll a and b	Bacteria-chlorophyll a and c, d, or e
Photosystem I	Present	Present	Similar	Similar
Photosystem II	Present	Present	Absent	Absent

Table 4: Anabolic pathways used to convert CO₂ and CH₄ into biosynthetic end-products (after Schidlowski, 2001).

- (1) CO₂ + ribulose-1,5-biphosphate → phosphoglycerate
 - Green plants [Green plants relying on reaction (1) exclusively are termed C3 plants]
 - Eukaryotic algae
 - Cyanobacteria
 - Purple photosynthetic bacteria (Chromatiaceae)
 - Purple nonsulfur bacteria (Rhodospirillaceae)
 - Chemoautotrophic bacteria

- (2) CO₂/HCO₃⁻ + phosphoenolpyruvate/pyruvate → oxaloacetate
 - Green plants [C4 and CAM plants combine reactions (2) and (1)]
 - Anaerobic bacteria
 - Facultatively aerobic bacteria

- (3) CO₂ + CO₂ → acetyl coenzyme A/acetate
 - Green photosynthetic bacteria (Chlorobiaceae) [via succinyl coenzyme A and α-ketoglutarate]
 - Anaerobic bacteria (Acetobacterium woodii, Clostridium acidurici)
 - Methanogenic bacteria [via C1 acceptors]

- (4) CO₂ + acetyl coenzyme A → pyruvate/phosphoenolpyruvate
 - Green photosynthetic bacteria (Chlorobiaceae) [combine reactions (2), (3) and (4)]
 - Clostridium kluyveri
 - Autotrophic sulfate reducing bacteria
 - Methanogenic bacteria

- (5) CH₄ → formaldehyde (HCHO)
 HCHO + ribulose monophosphate → hexulose monophosphate
 - Type I methanotrophic bacteria

- (6) CH₄ → formaldehyde (HCHO)
 HCHO + glycine → serine
 - Type II methanotrophic bacteria

Table 5: Major reservoirs of inorganic and organic carbon on the modern Earth (modified after a compilation in Hedges and Keil, 1995).

Reservoir		Size (x 10 ¹⁸ gC)	Reference
<i>Sedimentary rocks</i>			
Inorganic	Carbonates	60 000	Berner and Lasaga (1989)
Organic	Kerogen, coal, etc.	15 000	
<i>Active (surficial) pools</i>			
Inorganic	Marine DIC ¹	38	Olsen et al. (1985)
	Soil carbonate	1.1	
	Atmospheric CO ₂	0.66	
Organic	Soil humus	1.6	
	Land plant tissue	0.95	
	Marine DOC ²	0.60	Williams and Druffel (1987)
	Surface marine sediments	0.15	Emerson and Hedges (1988)

¹DIC (Dissolved Inorganic Carbon) refers to the combined water-soluble components CO₂ + CO₃²⁻ + HCO₃⁻ + H₂CO₃.

²DOC (Dissolved Organic Carbon) refers to biologically derived water-soluble carbon-containing molecules.

Table 6: Absolute ($\times 10^{12}$ gC yr⁻¹) and relative (% of total burial) organic carbon burial rates in different aquatic environments (modified after Hedges and Keil, 1995).

Sediment type	<i>Depositional environment</i>				
	Deltaic	Shelf	Slope	Pelagic	Total
<i>Deltaic sediments</i>	70 (44%)	-	-	-	70 (44%)
<i>Shelf- and upper slope sediments</i>	-	68 (42%)	-	-	68 (42%)
<i>High-productivity, biogenous sediments</i>	-	-	7 (4%)	3 (2%)	10 (6%)
<i>Shallow-water carbonates</i>	-	6 (4%)	-	-	6 (4%)
<i>Low-productivity, pelagic sediments</i>	-	-	-	5 (3%)	5 (3%)
<i>Anoxic basins (e.g. Black Sea)</i>	-	1 (0.5%)	-	-	1 (0.5%)
<i>All types</i>	70 (44%)	75 (46.5%)	7 (4%)	8 (5%)	160 (~100%)

References

- Allen, J. F., 2002. Photosynthesis of ATP - electrons, proton pumps, rotors and poise. *Cell* **110**, 349-360.
- Archer, D. and Devol, A., 1992. Benthic Oxygen Fluxes on the Washington Shelf and Slope - a Comparison of Insitu Microelectrode and Chamber Flux Measurements. *Limnol. Oceanogr.* **37**, 614-629.
- Archer, D., Emerson, S., and Smith, C. R., 1989. Direct Measurement of the Diffusive Sublayer at the Deep-Sea Floor Using Oxygen Microelectrodes. *Nature* **340**, 623-626.
- Baross, J. A. and Hoffman, S. E., 1985. Submarine Hydrothermal Vents and Associated Gradient Environments as Sites for the Origin and Evolution of Life. *Origins Life Evol. Biosph.* **15**, 327-345.
- Berner, R. A., 1989. Biogeochemical cycles of carbon and sulfur and their effect on atmospheric oxygen over Phanerozoic time. *Palaeogeography, Palaeoclimatology and Palaeoecology* **73**, 97-122.
- Berner, R. A. and Lasaga, A. C., 1989. Modeling the Geochemical Carbon-Cycle. *Sci. Am.* **260**, 74-81.
- Betts, J. N. and Holland, H. D., 1991. The oxygen content of ocean bottom waters, the burial efficiency of organic carbon, and the regulation of atmospheric oxygen. *Palaeogeography; Palaeoclimatology; Palaeoecology* **97**, 5-18.
- Calvert, S. E., Bustin, R. M., and Pedersen, T. F., 1992. Lack of Evidence for Enhanced Preservation of Sedimentary Organic-Matter in the Oxygen Minimum of the Gulf of California. *Geology* **20**, 757-760.
- Calvert, S. E. and Pederson, T. F., 1992a. Organic matter accumulation , remineralization and burial in an anoxic coastal sediment. In: Whelan, J. and Farrington, J. W. Eds.), *Organic carbon accumulation and preservation in marine sediments: How important is Anoxia*. Columbia University Press, New York.

- Calvert, S. E. and Pederson, T. F., 1992b. Organic matter accumulation, remineralization and burial in an anoxic coastal sediment. In: Whelan, J. and Farrington, J. W. Eds.), *Organic carbon accumulation and preservation in marine sediments: How important is Anoxia*. Columbia University Press, New York.
- Canfield, D., 2005. The early history of atmospheric oxygen. *Annual Review of Earth and Planetary Sciences* **33**, 1-36.
- Canfield, D. E., 1989. Sulfate reduction and oxic respiration in marine sediments: implications for organic carbon preservation in euxinic environments. *Deep-Sea Res.* **36**, 121-138.
- Canfield, D. E., 1993. Organic matter oxidation in marine sediments. In: Wollast, R., Chou, L., and Mackenzie, F. Eds.), *Interactions of C,N,P, and S biogeochemical cycles*. NATO-ARW.
- Canfield, D. E., 1994. Factors influencing organic carbon preservation in marine sediments. *Chem. Geol.* **114**, 315-329.
- Cowie, G. L., Calvert, S. E., Pedersen, T. F., Schulz, H., and von Rad, U., 1999. Organic content and preservational controls in surficial shelf and slope sediments from the Arabian Sea (Pakistan margin). *Mar Geol* **161**, 23-38.
- Emerson, S. E. and Hedges, J. H., 1988. Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography* **3**, 621-634.
- Emerson, S. R., 1985. Organic carbon preservation in marine sediments. In: Sundquist, E. T. and Broecker, W. S. Eds.), *The Carbon Cycle and Atmospheric CO₂: Natural Variations Archean to Present*. Amer. Geophys. Union., Washington, D.C.
- Froelich, P. N., Klinkhammer, G. P., Bender, M. L., Luedtke, N. A., Heath, G. R., Cullen, D., Dauphin, P., Hammond, D., Hartman, B., and Maynard, V., 1979. Early Oxidation of Organic-Matter in Pelagic Sediments of the Eastern Equatorial Atlantic - Suboxic Diagenesis. *Geochim. Cosmochim. Acta* **43**, 1075-1090.

- Galimov, E. M., 2004. The pattern of delta C-13(org) versus HI/OI relation in recent sediments as an indicator of geochemical regime in marine basins: comparison of the Black Sea, Kara Sea, and Cariaco trench. *Chem. Geol.* **204**, 287-301.
- Ganeshram, R. S., Calvert, S. E., Pedersen, T. F., and Cowie, G. L., 1999. Factors controlling the burial of organic carbon in laminated and bioturbated sediments off NW Mexico: Implications for hydrocarbon preservation. *Geochim. Cosmochim. Acta* **63**, 1723-1734.
- Grundmanis, V. and Murray, J. W., 1982. Aerobic respiration in pelagic marine sediments. *Geochim. Cosmochim. Acta* **46**, 1101-1120.
- Hales, B., Emerson, S. E., and Archer, D., 1994. Respiration and dissolution in the sediments of the western North Atlantic: estimates from models of *in situ* microelectrode measurements of porewater oxygen and pH. *Deep-Sea Res.* **41**, 695-719.
- Hardie, D. G., 2000. Metabolic control: a new solution to an old problem. *Curr. Biol.* **10**, 757-759.
- Harnmeijer, J., Orcutt, B., Devol, A., and Joye, S., 2005. Quantifying the role of manganese in biotic and abiotic nitrogen cycling. *Geochim. Cosmochim. Acta* **69**, A581-A581.
- Hartnett, H. E., 1998. Organic carbon input, degradation and preservation in continental margin sediments: an assesment of the role of a strong oxygen deficient zone. Ph.D., University of Washington.
- Hartnett, H. E. and Devol, A. H., 2003. The role of a strong oxygen deficient zone in the preservation and degradation of organic matter: a carbon budget for the continental margins of NW Mexico and Washington. *Geochim. Cosmochim. Acta* **67**, 247-264.
- Hartnett, H. E., Keil, R. G., Hedges, J. I., and Devol, A. H., 1998. Influence of oxygen exposure time on organic carbon preservation in continental margin sediments. *Nature* **391**, 572-536.

- Hedges, J. I., Hu, F. S., Devol, A. H., Hartnett, H. E., Tsamakis, E., and Keil, R. G., 1999. Sedimentary organic matter preservation: A test for selective degradation under oxic conditions. *Am. J. Sci.* **299**, 529-555.
- Hedges, J. I. and Keil, R. G., 1995. Sedimentary organic matter preservation: an assessment and speculative synthesis. *Mar. Chem.* **49**, 81-115.
- Helly, J. J. and Levin, L. A., 2004. Global distribution of naturally occurring marine hypoxia on continental margins. *Deep-Sea Res. Part I Oceanogr. Res. Pap.* **51**, 1159-1168.
- Henrichs, S. M. and Reeburgh, W., 1987. Anaerobic mineralization of marine sediment organic matter: Rates and the role of anaerobic processes in the oceanic carbon economy. *Geomicrobiology J.* **5**, 191-237.
- Hiscock, W. T. and Millero, F. J., 2006. Alkalinity of the anoxic waters in the Western Black Sea. *Deep-Sea Res Pt Ii* **53**, 1787-1801.
- Hoefs, M. J. L., Rijpstra, W. I. C., and Damste, J. S. S., 2002. The influence of oxic degradation on the sedimentary biomarker record I: Evidence from Madeira Abyssal Plain turbidites. *Geochim. Cosmochim. Acta* **66**, 2719-2735.
- Holland, H. D., 2002. Volcanic gases, black smokers, and the Great Oxidation Event. *Geochemica et Cosmochimica Acta* **66**, 3811-3826.
- Hollibaugh, J. T. and Azam, F., 1983. Microbial-Degradation of Dissolved Proteins in Seawater. *Limnol. Oceanogr.* **28**, 1104-1116.
- Hoppe, H. G., 1993. Use of Fluorogenic Model Substrates for Extracellular Enzyme Activity (EEA) Measurement of Bacteria. In: Kemp, A. E., Shen, Y., Sherr, B., and Cole, D. R. Eds.), *Handbook of Methods in Aquatic Microbial Ecology*. Lewis.
- Jahnke, R. A., 1990. Early diagenesis and recycling of biogenic debris at the seafloor, Santa Monica Basin, California. *J. Mar. Res.* **48**, 413-436.
- Levin, M., Thorlin, R., Kenneth, R. R., Taisaku, N., and Mercola, M., 2002. Asymmetries in H⁺/K⁺-ATPase and cell membrane potentials comprise a very early step in left-right patterning. *Cell* **111**, 77-89.

- Martin, W. R. and Banta, G. T., 1992. The measurement of sediment irrigation rates: A comparison of the Br⁻ tracer and ²²²Rn/²²⁶Ra disequilibrium techniques. *Journal of Marine Research* **50**, 125-154.
- Murray, J. W., Codispoti, L. A., and Friederich, G. E., 1995. Oxidation-Reduction Environments: The suboxic Zone in the Black Sea. In: Huang, C. P., O'Melia, C. R., and Morgan, J. J. Eds.), *Aquatic Chemistry: Interfacial and Interspecies Processes*. American Chemical Society, Washington, D.C.
- Murray, J. W. and Kuivila, K. M., 1990. Organic matter diagenesis in the Northeast Pacific: Transition from aerobic red clay to sub-oxic hemipelagic sediments. *Deep-Sea Res.* **37**, 59-80.
- Olson, D., Garrels, R. M., Berner, R. A., Armentano, T. V., Dyer, M. I., and Taalon, D. H., 1985. The natural carbon cycle. In: Trabalka, J. R. (Ed.), *Atmospheric Carbon Dioxide and the Global Carbon Cycle*. US Dep. Energy, Washington, D.C.
- Paropkari, A. L., Babu, C. P., and Mascarenhas, A., 1992. A critical evaluation of depositional parameters controlling variability of organic carbon in Arabian Sea sediments. *Mar. Geol.* **107**, 213-226.
- Pedersen, T. F. and Calvert, S. E., 1990. What controls the formation of organic-carbon-rich sediments and sedimentary rocks? *Amer. Assoc. Petrol. Geol. Bull.* **74**, 454-466.
- Perry, E. C. and Ahmad, S. N., 1977. Carbon isotope composition of graphite and carbonate minerals from 3.8-Ga metamorphosed sediments, Isukasia, Greenland. *Earth Planet. Sci. Lett.* **36**, 280-284.
- Pratt, L. M., 1984. Influence of Paleoenvironmental Factors on Preservation of Organic-Matter in Middle Cretaceous Greenhorn Formation, Pueblo, Colorado. *Aapg Bulletin-American Association of Petroleum Geologists* **68**, 1146-1159.
- Priest, F. G., 1984. Extracellular enzymes. *Aspects of Microbiology* **9**, 1-79.
- Reimers, C. E. and Jr., K. L. S., 1986. Reconciling measured and predicted fluxes of oxygen across the deep sea sediment-water interface. *Limnol. Oceanogr* **31**, 305-318.

- Reimers, C. E., K.M. Fischer, R. Merewether, K.L. Smith, J., and Jahnke., R. A., 1986. Oxygen microprofiles measured in situ in deep ocean sediments.
- Ronov, A. B., 1990. *Chemical Structure of the Earth's Crust and Chemical Balance of Major Elements*. Izdatel'stvo, Moscow.
- Rusch, A., Huettel, M., Reimers, C. E., Taghon, G. L., and Fuller, C. M., 2003. Activity and distribution of bacterial populations in Middle Atlantic Bight shelf sands. *FEMS Microbiol. Ecol.* **44**, 89-100.
- Schidlowski, M., 2001. Carbon isotopes as biogeochemical recorders of life over 3.8 Ga of Earth history: evolution of a concept. *Precamb. Res.* **106**, 117-134.
- Stein, R., 1990. Organic-Carbon Content Sedimentation-Rate Relationship and Its Paleoenvironmental Significance for Marine-Sediments. *Geo-Marine Letters* **10**, 37-44.
- Thamdrup, B. and Canfield, D., 2000. Benthic respiration in aquatic sediments. In: Sala, O. E., Jackson, R. B., Mooney, H. A., and Howarth, R. W. Eds.), *Methods in Ecosystem Science*. Springer, New York.
- Thauer, R. K., Jungermann, K., and Decker, K., 1977. Energy conservation in anaerobic chemotrophic bacteria. *Bacteriological Review* **41**, 100-180.
- van Breugel, Y., Schouten, S., Paetzel, M., Nordeide, R., and Damste, J. S. S., 2005. The impact of recycling of organic carbon on the stable carbon isotopic composition of dissolved inorganic carbon in a stratified marine system (Kyllaren fjord, Norway). *Org. Geochem.* **36**, 1163-1173.
- Veizer, J. and Hoefs, J., 1976. The nature of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ secular trends in sedimentary carbonate rocks. *Geochim. Cosmochim. Acta* **40**, 1387-1395.
- Wakeham, S. G., Amann, R., Freeman, K. H., Hopmans, E. C., Jorgensen, B. B., Putnam, I. F., Schouten, S., Damste, J. S. S., Talbot, H. M., and Woebken, D., 2007. Microbial ecology of the stratified water column of the Black Sea as revealed by a comprehensive biomarker study. *Org. Geochem.* **38**, 2070-2097.
- Wakeham, S. G., Hopmans, E. C., Schouten, S., and Damste, J. S. S., 2004. Archaeal lipids and anaerobic oxidation of methane in euxinic water columns: a

comparative study of the Black Sea and Cariaco Basin. *Chem. Geol.* **205**, 427-442.

Whitman, W. B., Coleman, D. C., and Wiebe, W. J., 1998. Prokaryotes: The unseen majority. *Proc. Natl. Acad. Sci. U. S. A.* **95**, 6578-6583.

Williams, P. M. and Druffel, E. R. M., 1987. Radiocarbon in Dissolved Organic-Matter in the Central North Pacific-Ocean. *Nature* **330**, 246-248.

Yakushev, E. V., Chasovnikov, V. K., Debolskaya, E. I., Egorov, A. V., Makkaveev, P. N., Pakhomova, S. V., Podymov, O. I., and Yakubenko, V. G., 2006. The northeastern Black Sea redox zone: Hydrochemical structure and its temporal variability. *Deep-Sea Res Pt II* **53**, 1769-1786.