8. Concluding Synthesis

Due to a dearth of preserved evidence, questions about Early Archaean biogeochemical cycling are highly under-determined (Chapter 1). This has two consequences. The first is that the diversity of explanatory models admissible into the scientific arena is large. The second is that new discoveries of Early Archaean meta-sedimentary outcrop potentially carry greater significance than do those of younger rocks deposited under conditions that are better understood.

Three hitherto unreported settings of Early Archaean marine sedimentation carrying potential geobiological significance were described in this thesis: ~3.7 – 3.8 Ga deep-marine metaturbidites from the Isua Supracrustal Belt in southwest Greenland, ~3.52 Ga deep-marine micritic banded-iron formation from the Coonterunah Subgroup in the Pilbara's Pilgangoora Belt in northwest Australia, and ~3.45 Ga shallow marine and intermittently sub-aerially exposed neptunian fissures cutting the Kelly-Warrawoona Group erosional unconformity, also in the Pilgangoora Belt. All three environments contain appreciable quantities of syn-sedimentary reduced carbon compounds with isotopic fractionations outside the range of equilibrium processes, but similar to those associated with autotrophic metabolism (Chapter 2).

1. Fischer-Tropsch-Type Synthesis

The origin of ancient of reduced carbon need not necessarily be biological. Hydrocarbons of an impressively complex and diverse nature can be produced abiologically through chemical processes known as Fischer-Tropsch-type ('FTT') reactions (Figure 1). FTT synthesis, *sensu strictu*, is the process whereby CO is converted to hydrocarbon gas by reaction with H_2 (compare Fischer, 1935):

$$n\,CO + (2n+1)\,H_2 \rightarrow C_nH_{(2n+2)} + n\,H_2O$$

Industrial FTT synthesis is performed under H_2O-free conditions to maximize CH_4 production, whereas geologically relevant experiments generally include an aqueous phase. The presence of a vapour phase significantly enhances the potential for

organic synthesis of chain hydrocarbons (McCollom et al., 1999). FTT synthesis has yielded a wide range of compounds in the laboratory (Lancet and Anders, 1970; Yuen et al., 1990; McCollom et al., 1999; Rushdi and Simoneit, 2001; Voglesonger et al., 2001; McCollom, 2003; McCollom and Seewald, 2003a, b; Foustoukos and Seyfried, 2004; McCollom, 2004; Rushdi and Simoneit, 2004; McCollom and Seewald, 2006). As a result, it has been suggested as a potential non-biological mechanism for the formation of simple organics in various (astro-)geological environments, including hydrothermal vents (Sherwood-Lollar et al., 1993; Berndt et al., 1996; Shock and Schulte, 1998; Horita and Berndt, 1999; Holm and Charlou, 2001; Riedel et al., 2001; Brasier et al., 2002; Charlou et al., 2002; Kennedy et al., 2002; Sherwood-Lollar et al., 2002; Ueno et al., 2003; van Kranendonk et al., 2003; Foustoukos and Seyfried, 2004; Simoneit, 2004; Simoneit et al., 2004; Ueno et al., 2004; Bjonnes and Lindsay, 2005; Brasier et al., 2005; Lindsay et al., 2005a; van Kranendonk, 2006), cooling volcanic gases (Zolotov and Shock, 1999), igneous rocks (Salvi and Williams-Jones, 1997; Potter et al., 2004), serpentinizing systems (Szatmari, 1989; Abrajano et al., 1990; Charlou et al., 1998; Kelley and Fruh-Green, 1999; Fruh-Green et al., 2003; Sleep et al., 2004; Kelley et al., 2005; Schulte et al., 2006), interplanetary dust particles (Llorca and Casanova, 1998; Zolotov and Shock, 2001) and carbonaceous chondrites (Hartman et al., 1993; Zolotov and Shock, 2001).

Despite this, empirical evidence for the non-biological formation of hydrocarbons (discounting simple C_1 compounds such as methane) through FTT synthesis in geological systems on Earth remains scarce. Theoretical calculations (Shock, 1990) suggest that n-alkanes and PAHs can form metastably under ~ 250 °C. Both the possible temperature range and energetic drive for hydrocarbon formation increase with a lower fO_2 and higher CO/CO_2 ratios (Zolotov and Shock, 2000; Rushdi and Simoneit, 2001). The rate of FTT synthesis is greatly accelerated by, or requires, the presence of a metal catalyst. Mineral phases that catalyze FTT reactions include Co, ThO_2, ZnO, Ru and Rh (Roper, 1983), magnetite (Fe_3O_4), brucite ($Mg(OH)_2$), Ni-Fe alloys such as awaruite ($Ni_{2-3}Fe$), Cr- and Fe- bearing chromite minerals (Foustoukos and Seyfried, 2004), and montmorillonite (McCollom et al., 1999) (Figure 1). The

extreme sensitivity of successful FTT experimentation to *P, T, fO_2* and catalyst conditions suggests that the ability of a given geological environment to support FTT synthesis would be largely controlled by the host rock composition.

Experiments on the isotopic signature imparted on the reaction produces of FTT reactions exhibit widely differing results. Some laboratory experiments indicate a modest fractionation of 11 - 35 ‰ depletion in ^{12}C relative to precursor CO (Yuen et al., 1990), whereas others (e.g. McCollom and Seewald, 2006) report a higher and narrower range of ^{12}C depletion on the order of 30 - 36 ‰. For both alkanes and alkenes ($C_1 < C_n < C_4$), a fractionation between 40 and 48 ‰ was recently reported in both open-system and steady-state experiments (Taran et al., 2007). Fractionations relative to CH_4 fell well under 12 ‰ for most synthesized compounds, with the majority of hydrocarbons depleted by 0 to 5 ‰ relative to methane.

As an open-system process, it is difficult to place constraints on the occurrence of FTT reactions using geological criteria. What's more, potential FTT reactions occur in the very same kinds of environments in which evidence for early metabolism may be sought, as both processes are associated with the dissipation of energy in the presence of steady flows of COH-fluids and thermochemical discontinuities. However, if Early Archaean kerogen is of microbial origin, systematic variations in isotopic behaviour may be expected to follow changes in microbial ecology in different depositional environments, which should not accompany abiotic kerogen.

2. Metamorphism and $\delta^{13}C_{org}$

Reduced carbon did not maintain isotopic closure during metamorphism, and no appreciable differences in the thermal maturation behaviour of organic matter from fluvial, shallow and deep-marine environments could be discerned (Figure 2). Schistose graphitic black meta-chert horizons from lower amphibolite-facies sub-aqueously deposited felsic schists (Kohler and Anhaeusser, 2002) collected from the Kaapvaal Craton's Bien Venue Formation, Fig Tree Group give $\delta^{13}C_{org} = -18.8 \pm 0.1$ ‰, while a value of $\delta^{13}C_{org} = -28.8 \pm 0.1$ ‰ from a sample of black chert interstratified with terrigenous clastic sediments in sub-greenschist facies rocks from

the Central Domain is probably representative of protolithic Fig Tree kerogen (Walsh and Lowe (1999) give $\delta^{13}C_{org}$ = -33.6, -26.0 and -30.3 ‰ for three Fig Tree samples).

Early Archaean marine kerogen behaved similarly under metamorphism. Lower amphibolite-facies graphite from the marine Coonterunah Subgroup's Coucal Formation gives a rather uniform $\delta^{13}C_{org}$ = -16.5 ± 0.5 ‰, with lowest grade kerogen at lower greenschist facies showing $\delta^{13}C$ = -23.8 ± 0.2 ‰. A similar fractionation appears to have accompanied metamorphism of kerogen associated with Chert VII and Chert VIII in the Euro Basalt Formation, which taken together show a range of $\delta^{13}C$ = -19.7 to -23.2 ‰ in the highest grade (lower amphibolite-facies at western Pilgangoora Belt closure) rocks from which kerogen could be isolated, systematically approaching and reaching SPC-like values of $\delta^{13}C$ = -29.5 to -32.9 ‰ eastward along strike, and maintaining this ratio for the remaining third of the strike-length of the belt at and below talc-forming metamorphic grade. Two highly recrystallized kerogenous black meta-cherts analyzed from a shallow (~ 25 m) dyke-like structure underneath Chert VII in the upper greenschist facies zone of the belt both give $\delta^{13}C$ = -17.0 ± 0.2 ‰.

All in all, Early Archaean kerogen appears to display little variation in its isotopic evolution during metamorphism, ranging from isotopically light ($\delta^{13}C$ = -29.5 to -37.1 ‰, see below) in all environments at lowest grades to < -20 ‰ at the highest (Figure 2). This is not what would be expected from kerogen of abiotic origin, which would be expected to vary greatly in different environments. Furthermore, meteorite studies suggest that FTT kerogen undergoes highly variable stepwise pyrolysis of labile fractions (Shimoyama, 1997; Kitajima et al., 2002; Septhon et al., 2004; Busemann et al., 2007), although this carbonaceous matter may present an imperfect analogue to Early Archaean kerogen.

3. Carbon Cycling

$\delta^{13}C_{carb\text{-}org}$ correlations between shallow-water and pelagic deep carbonate provide a powerful palaeo-oceanographical tool (Magaritz and Issar, 1973; Weisset et al., 1998; Immenhauser et al., 2002; Immenhauser et al., 2003; Panchuk et al., 2005). Like today, Early Archaean marine sedimentary $\delta^{13}C_{carb}$ would have depended on

temperature-dependent carbonate-DIC isotopic equilibria and DIC availability, the latter controlled by reservoir size and autotrophic production (Hayes, 1993). Carbonate-DIC isotopic equilibria also depend on the type of carbonate precipitated and the dissolved carbonate concentration. Under modern surface ocean conditions, calcite and aragonite precipitate with enrichments over seawater DIC of about +1.0 and +2.7 ‰, respectively (Romanek et al., 1992). Higher $[CO_3^{2-}]$ solutions precipitate isotopically lighter carbonates, through the linear relationship: -0.060 ± 0.015 ‰ (μmol $[CO_3^{2-}]$ $kg^{-1})^{-1}$ (McCrea, 1950; Spero et al., 1997).

Two mechanisms produce opposing effects on the isotopic differential, $\Delta^{13}C_{n\text{-}o} = \delta^{13}C_{\text{nearshore DIC}} - \delta^{13}C_{\text{open ocean DIC}}$, between partially restricted shallow water masses (e.g. on submerged platforms) and the open ocean. On the one hand, cellular $\delta^{12}C$ uptake during vigorous primary production leads to relative enrichment in near-shore surface $\delta^{13}C_{DIC}$ (Swart and Eberli, 2005). Consequently, organic matter removal affects precipitated $\delta^{13}C_{carb}$ (Magaritz, 1989) such that increases in organic matter export are accompanied by increases in $\delta^{13}C_{carb}$ (Shackleton, 1985).

On the other hand, $\delta^{12}C_{CO_2}$ input from the respiration of marine and terrestrial organic matter during water-mass residence can have the opposing effect of reducing $\delta^{13}C_{DIC}$ and $\delta^{13}C_{carb}$ (Patterson and Walter, 1994). Near-shore $\delta^{13}C_{DIC}$ depletions are also observed to result from the disequilibrium influx of atmospheric CO_2 into highly alkaline waters (Herczeg and Fairbanks, 1987; Lazar and Erez, 1992).

3.1. A Eulittoral to Basinal Trend

A compilation of pertinent Early Archaean and Proterozoic carbonate isotope compositions is shown in Chapter 5, Figure 29. Early Archean shallow marine sedimentary laminated carbonates from the ~3.45 Ga Strelley Pool Chert (from several belts across the eastern Pilbara) and Barberton's ~3.47 Ga (Armstrong et al., 1991) Onverwacht Group have similar isotopic compositions, and show linear positive correlations in their carbon and oxygen isotopes, with values ranging from $(\delta^{13}C, \delta^{18}O)_{carb}$ = (+3.0 ‰, -11.0 ‰) to (+1.0 ‰, -17.0 ‰), with a few lower outlying $\delta^{13}C_{carb}$

values obtained from the SPC in the Pilgangoora Belt. This linear trend can be attributed to isotopic equilibration with pore-waters during progressive diagenesis, although high evaporation rates may very well have played a role in increasing $\delta^{18}O_{carb}$ (Adlis et al., 1988) in the Strelley Pool Chert palaeoreef.

Compared to these shallow marine carbonates, the slightly older 3.52 Ga deep-marine carbonates from the Coonterunah Subgroup, interpreted in Chapter 5 as likely pelagic surface precipitates, are much more isotopically depleted, clustering at ($\delta^{13}C$, $\delta^{18}O)_{carb}$ = (-3.0 ± 1.0 ‰, -17.8 ± 0.2 ‰). These $\delta^{13}C_{carb}$ values are similar to the most depleted samples of Palaeoproterozoic basinal fine-laminated Ca-Mg carbonates in banded-iron formation, which likely formed in the same way, but in equilibrium with higher Palaeozoic $\delta^{18}O_{seawater}$. Partially silicified dolomitic spar in chert from Double Bar Formation drillcore shows values intermediate ($\delta^{13}C_{carb}$ = -0.9 to +0.1 ‰) between these shallow and deep marine end-members, perhaps reflecting transitional water depths and/or intermediate productivity. These values suggest significant differences in DIC compositions between Early Archaean littoral environments, with $\Delta^{13}C_{n\text{-}o}$ = $\delta^{13}C_{nearshore\ DIC}$ - $\delta^{13}C_{open\ ocean\ DIC}$ ≈ +4.0 to +6.0 ‰. (The exact figure depends on details of Early Archaean carbonate diagenesis, which could be ascertained through a comprehensive fluid-inclusion study).

Like today, Archaean primary productivity probably would have been higher in near-shore environments than in the surface waters overlying basins such as that into which the Coonturunah micrite-BIF settled. This assumption is born out by evidence for greater C_{org} sequestration in the form of higher TOC (wt.%) kerogenous bedded cherts and cementing matrix cherts deposited in shallower environments of the Barberton's Hooggenoeg Formation and the Pilbara's Strelley Pool Chert, compared with the C_{org}-poor carbonates and cherts of the deep-water Coonterunah Subgroup and Isua meta-turbidites.

The least metamorphosed concordant metachert- and carbonate-hosted kerogen from the Strelley Pool Chert (from both fresh outcrop and drillcore samples) and the upper reaches of neptunian fissures ranges isotopically between $\delta^{13}C_{org}$ ≈ - 29 and - 32 ‰, similar to analytical results obtained by other workers (Lindsay et al., 2005b).

More depleted values of $\delta^{13}C_{org}$ = - 34.7 to -37.1 ‰ are obtained from less metamorphosed (prehnite-pumpellyite facies) sedimentary kerogen in black metachert from the Barberton Hoogenoeg H_4C Member, which appears to be representative of Hoogenoeg kerogen generally (e.g. Walsh and Lowe, 1999). (On the basis of field evidence, very depleted kerogen ($\delta^{13}C_{org}$ = -37.1 to -39.1 ‰) in black and white banded chert from the H_2C Member was inferred to be of post-sedimentary origin (cross-cutting relationships are shown in Chapter 2C, Figure 4 (d, e)), as also concluded by Hofmann and Bolhar (2007)).

In contrast to this light matrix carbon in shallow-marine cherts, kerogenous oncolite breccia from the H_3C Member is distinctly enriched at $\delta^{13}C_{org}$ = - 24.0 to -26.4 ‰. Textural evidence for continuous tumbling and rapid cementation (Chapter 7) is compatible with the interpretation of this range as representative of minimally processed Early Archaean photoautotrophy. Indeed, oncolite kerogen is isotopically similar to kerogen from both black chert ($\delta^{13}C_{org}$ = -23.8 ± 0.2 ‰) and pelagic carbonate precipitate ($\delta^{13}C$ = -26.1 ± 2.4 ‰) in the deep-marine Coucal Formation, both of which may have sequestered surface ocean particulate organic matter with only a minimal contribution from more isotopically depleted benthic biota. Black chert from the Coonterunah Subgroup's uppermost Double Bar Formation contains kerogen in the range $\delta^{13}C_{org}$ = -27.3 to -30.2 ‰, intermediate between shallow and deep-marine kerogen.

The pre-metamorphic isotopic signature of ~lower-amphibolite facies graphite, $\delta^{13}C_{org}$ = -17.5, in deep-water Isua metaturbidites is harder to extrapolate. This value is similar to analyses from the only other pre-3.8 Ga meta-turbidite outcrop (Rosing, 1999), and is distinctly more fractionated than metasomatically-derived carbon from a graphitic vein ($\delta^{13}C_{org}$ = -12.6 ± 0.1 ‰) cross-cutting leached banded-iron formation immediately overlying the meta-turbidite rocks. In addition to graphite, most Isua meta-turbidites contain small amounts of recrystallized siderite, ferroan calcite and/or ankerite. This carbonate is not texturally associated with graphite, and there are no relationships between TOC (wt.%), $\delta^{13}C_{carb}$ and carbonate (wt.%) (Figure 3). Thus, meta-turbidite graphite was likely not derived from fluids evolved from siderite

decarbonation reactions (van Zuilen et al., 2002; van Zuilen et al., 2003). Organic matter may have been delivered together with clastic material from shallower benthic settings, however.

The picture that emerges is one of organic export, rather than respiratory remineralization, control on surface-ocean $\delta^{13}C_{DIC}$. The low availability of soluble electron acceptors, notably oxygen, nitrate/nitrite and sulphate, at least in the sub-photic zones, can account for the lack of a water column remineralization flux. In the absence of insuperable competition from denitrifiers and sulphate-reducers (Lovley et al., 1982), sub-photic benthic remineralization would have been dominated by metabolic processes in which organic compounds serve as electron acceptors, namely fermentation and methanogenesis. Early Archaean organic matter degradation by consortia of fermenting and methanogenic prokaryotes (see below, Figure 5) would have resulted in higher fluxes of isotopically depleted CH_4 (and H_2) and lower fluxes of relatively isotopically enriched CO_2 than in the more familiar benthic systems that were to arise later.

4. Life in Ancient Seafloor Cracks and Degradation of Organic Matter

No single anaerobic microorganism has the capability to completely break down organic polymers into C_1 compounds, and highly specific substrate requirements are the microbiological rule (Fenchel et al., 1995). Step-wise organic matter degradation is performed by syntrophic consortia of prokaryotes, each of which are typically adapted to energy yields close to the theoretical thermodynamic threshold (~ 20 kJ mol^{-1}) allowing metabolism (Valentine, 2001). As a result, variations in micronutrient availability and other environmental conditions may greatly alter the fate of organic matter in sediments.

Kerogen in Pilgangoora neptunian fissures – at least one of which contains microstromatolitic oncoids - ranges from Strelley Pool Chert-like values of $\delta^{13}C_{org} \approx$ -29 to – 31 ‰ at shallow depths, to $\delta^{13}C_{org} \approx$ -34 to –36 ‰ at depth, the latter thereby representing the most isotopically depleted kerogen sampled in the Pilgangoora Belt. Less highly metamorphosed kerogen from similar structures at North Pole Dome gives

$\delta^{13}C_{org} \approx$ -38.6 ‰, similar to 'hydrothermal dyke' kerogen from the same structures analyzed by Ueno et al. (2003). Neptunian organic matter occasionally shows an intimate association with disseminated magnetite of highly variable grain-size (<1 to ~10 μm), hinting at the operation of metabolic pathways using ferric iron. Like the magnetite in the basal Strelley Pool Chert conglomerate-sandstone, neptunian magnetite is likely derived from the erosion of Coonterunah Subgroup material, such as sedimentary magnetite-metachert. Minerals with ferric iron are otherwise rare in the Strelley Pool Chert lithofacies assemblages, particularly when compared to basinal Coonterunah sediments.

A texturally similar association between kerogen and sulphide minerals is commonly encountered in shallow-marine bedded black cherts of the Kelly Group, raising the possibility that oxidized species of sulphur acted as electron acceptors during chemoheterotrophy. Abundant diagenetic gypsum pseudomorphs in silicified lutites of the uppermost beds of the Strelley Pool Chert and in overlying Euro Basalt Formation cherts are compatible with the presence of some SO_4^{2-} in contemporary seawater, and disseminated pyrite of likely diagenetic origin is also common in some of the same rocks. The oxidized metabolic precursor(s) to pyrite may have formed through photosynthetic oxidation of volcanically-derived sulphur compounds.

The ~ 6 ‰ ^{12}C depletion of deep neptunian kerogen over that in bedded cherts requires a mechanism for both isotopic fractionation and carbon fixation (compare Hayes et al., 1987). The most natural explanation for the observed isotopic shift is the enhanced metabolic processing of SPC-derived seafloor organic detritus through coupled fermentation, acetogenesis and methanogenesis. Biomass $\delta^{13}C$ of methylotrophic (Summons et al., 1998) and methanogenic (Londry et al., 2008) Archaea can exhibit significant (up to $\Delta^{13}C \approx$ -20.9 and -24.8 ‰, respectively) depletions with respect to their carbon source, with the degree of fractionation strongly dependent on substrate type and increasing markedly with substrate availability. In addition to providing for efficient entrapment of organic matter through protection from hydraulic stirring, neptunian fissures would have acted as conduits for concentrated granitoid weathering products, heated fluids, and substrates (CO_2, CH_4,

H_2, methanol, acetate) released through organic matter degradation. Highly insoluble H_2 ($K_{H_2} \approx 7.8 \cdot 10^{-4}$ atm^{-1}), in particular, may have been a rate-limiting electron donor in bedded sediments compared to fissure environments. In comparison, vertically oriented neptunian fissures offered a relatively nutritive environment that would have sustained a larger, and more isotopicaly depleted, methanogenic biomass. This inference is also supported by apparently isotopically lighter organic matter being sequestered in shallow- compared to deep- marine Early Archaean environments (Figure 2). An opposite trend to this is observed in modern systems, where CO_2 draw-down from a smaller Phanerozoic atmospheric reservoir leads to dis-equilibrium fractionation and thus isotopically enriched POC in more shallow and productive environments (Hollander and McKenzie, 1991).

The lack of very depleted biomass ($\delta^{13}C < 50$ ‰) shows that little or none of the methane produced through these processes was recycled through the anaerobic oxidation of methane ('AOM'), suggesting that the inorganic terminal electron acceptors sulphate (Orphan et al., 2001) and ferrihydrite (Beal et al., 2009) were absent from deeper sites of methane genesis. Key metabolic steps would have followed the sequence (Figure 5):

- Hydrolysis of polymers;
- Primary fermentation of monomers into low molecular weight products such as alcohols and volatile fatty acids;
- Limited anaerobic hetrotrophy using inorganic terminal electron acceptors sulphate and ferric iron minerals such as magnetite;
- Secondary fermentation of smaller volatile fatty acids;
- Primary fermentation products mineralized to CH_4 and CO_2;
- Use of secondary fermentation products for acetogenesis;
- Acetotrophic and hydrogenotrophic methanogenesis to produce isotopically light biomass, CO_2 and CH_4.

Most non-fermenting prokaryotes are incapable of using typical monomers released during polymer hydrolysis, as a result of which fermenters dominate even

modern high-SO_4^{2-} sediments (Devereux et al., 1996). Fermenters are remarkably versatile, and can degrade sugars, amino acids, purines, pyrimidines, acetylene, many aromatic hydrocarbons, and organic acids with up to C_{18} chain lengths (Schink and Stams, 2002). All branched-chain, aromatic and $>C_2$ fatty acids require secondary fermentation prior to becoming accessible to methanogenic bacteria (Schmitz et al., 2001). Acetogens comprise a diverse group of obligately anaerobic bacteria that make use of the acetyl-CoA pathway both as a terminal electron acceptor in energy conservation and reductive synthesis (Drake, 1994), and like fermenters display a wide range of catabolic capabilities.

Methanogenesis completes catabolism of organic detritus in the absence of electron acceptors. Early Archaean methanogenesis would have benefited from high atmospheric H_2 concentrations inferred by some for the early Earth (Tian et al., 2005; but see Catling, 2006). In addition to hydrogen, methanogens require a unique suite of micronutrients that includes Co, Fe, Na, Ni, V and Zn (Jarrell and Kalmokoff, 1988), all of which appear to have been present in high concentrations in the Early Archaean surface marine environment (see Chapter 5, micrite geochemistry). Acetotrophic methanogenesis yields methane with $\delta^{13}C$ = -65 to -50 ‰, compared to extremely depleted $\delta^{13}C$ = -110 to -60 ‰ by hydrogenotrophic methanogenesis (Whiticar et al., 1986), although methane produced under conditions of substrate limitation is far less fractionated (Fuchs et al., 1979). The former process tends to occur at shallower depths, progressively transitioning to the latter (Hornibrook et al., 1997; Chasar et al., 2000; Hornibrook et al., 2000).

5. A Stratified Archaean Ocean?

High overall sedimentary Fe/Al abundances, widespread ferruginous chemical precipitates, and the chamosite- and stilpnomelane-dominated mineralogy of metamorphosed deep-sea feldspar-weathering clays all suggest high bottom-water Fe^{2+} concentrations. Evidence for the mobility of iron in solution is conspicuously absent from Early Archaean peri-tidal sediments, however, lending credence to the Eh- and pH- stratified model explored in Chapter 5.

High volcanic outgassing rates almost certainly ensured an early high-pCO_2 atmosphere, continually equilibrating with surface oceans consequently high in dissolved inorganic carbon ($\sum$DIC). In the presence of high inorganic carbon concentrations, CO_2 remineralized from organic matter consequently seems to have represented an insignificant source of isotopically light carbon. For such an ocean to have its surface chemistry controlled by organic export rates implies a large standing biomass pool and efficient nutrient cycling.

6. Conclusion

At the time of the earliest recorded sedimentation, a diverse and abundant biosphere was already well established in a variety of environmental settings. If evolution was able to gain a foothold on and within these fragmented and volcanically active slivers of greenstone belt crust, then there exists every reason to anticipate the ubiquity of life in habitable zones elsewhere.

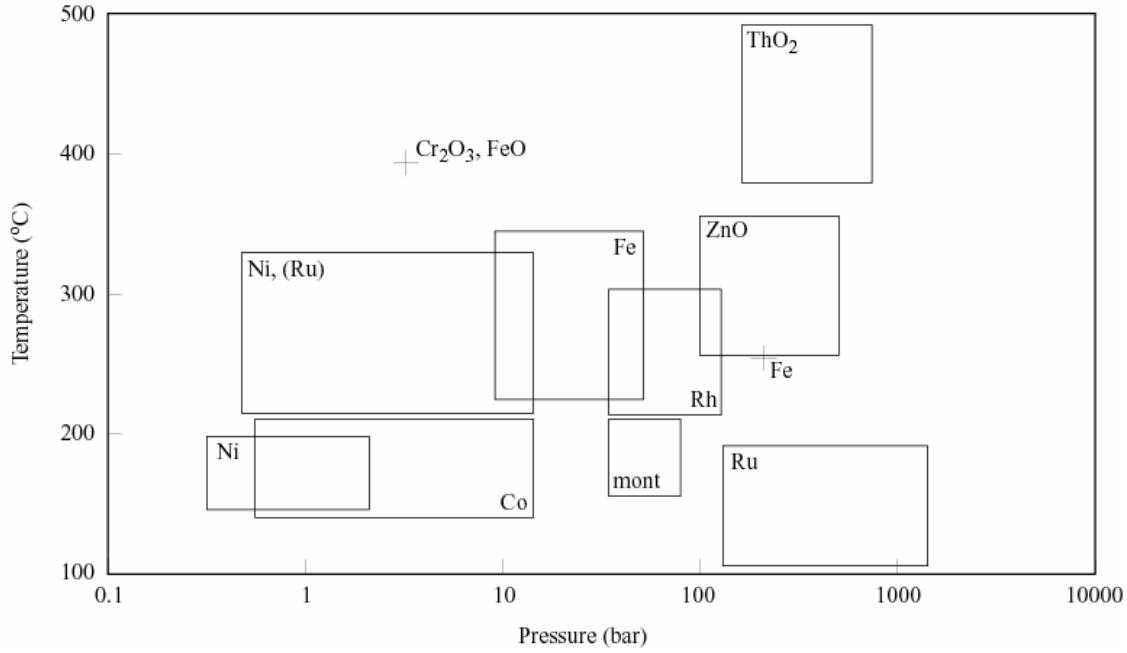

Figure 1: Selected P-T ranges of catalysts successfully applied in industrial FTT synthesis (after Roper, 1983 and references therein).

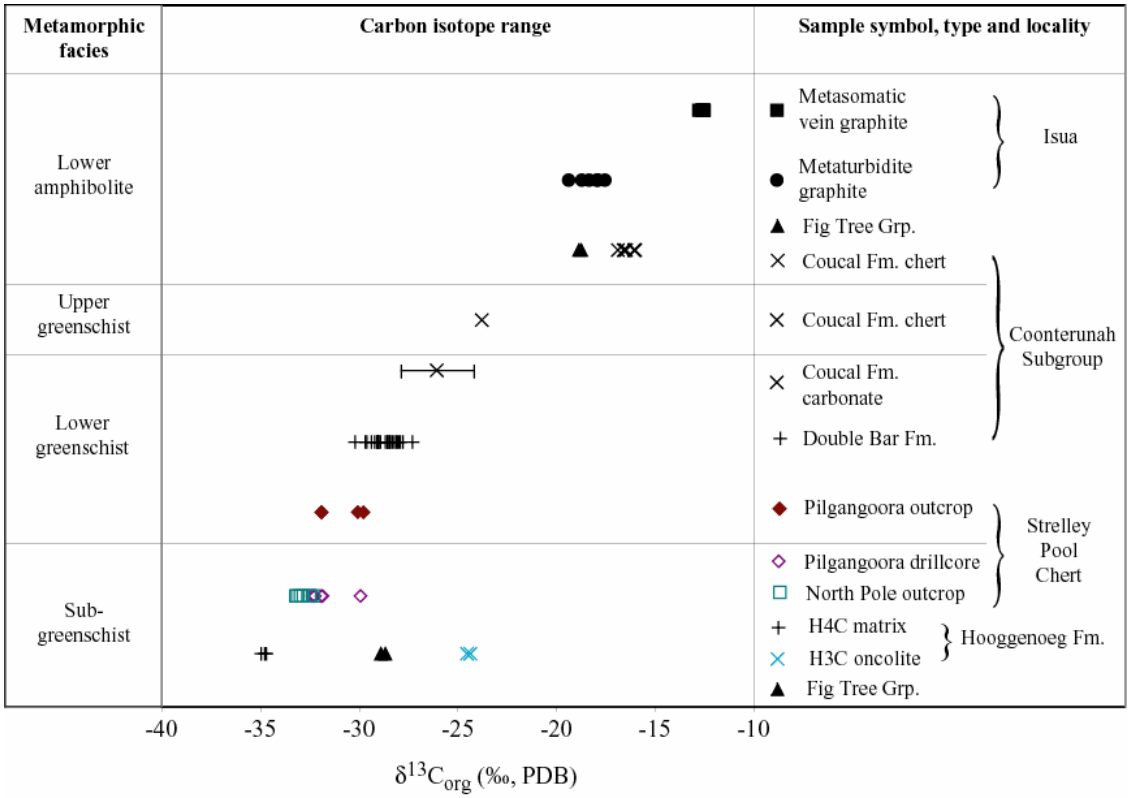

Figure 2: Carbon isotopes of kerogen and graphite from Early Archaean rocks at different metamorphic grade.

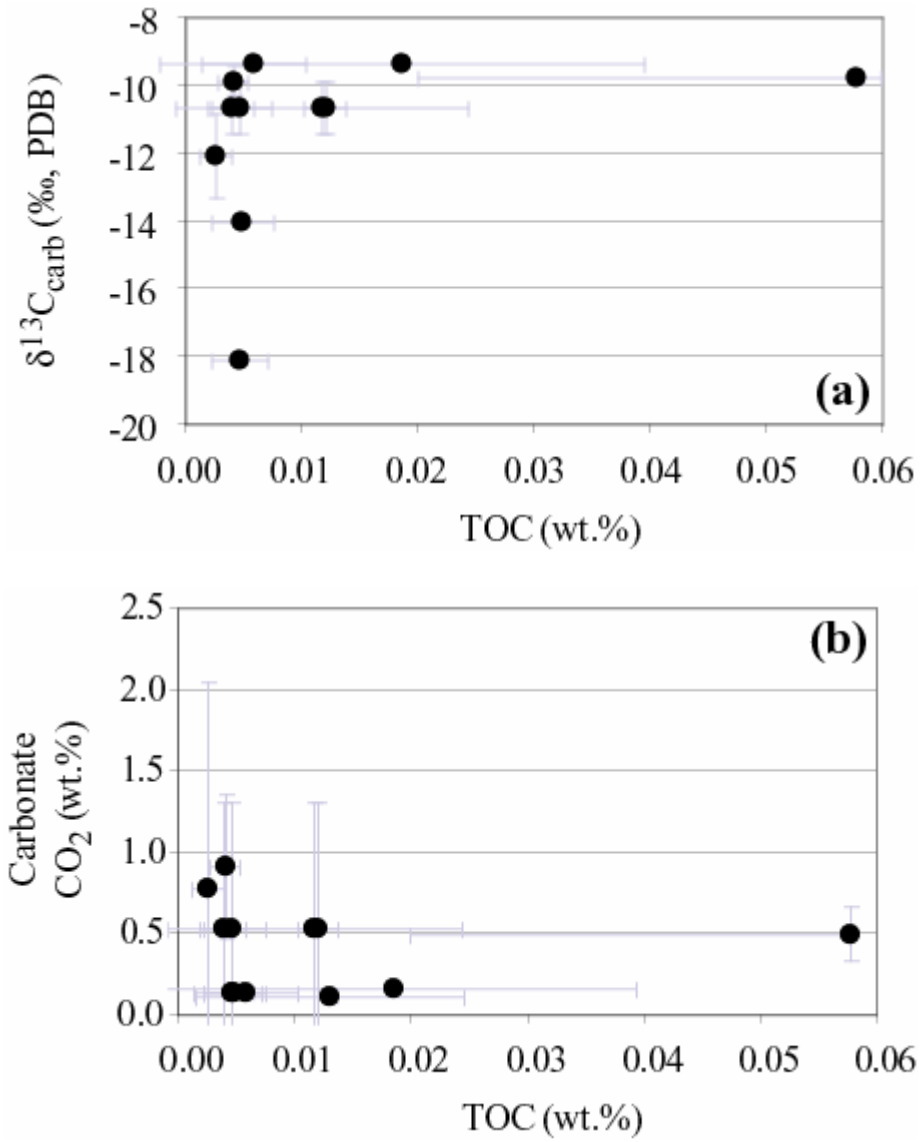

Figure 3: Isua metaturbidite graphite and carbonate are unrelated.

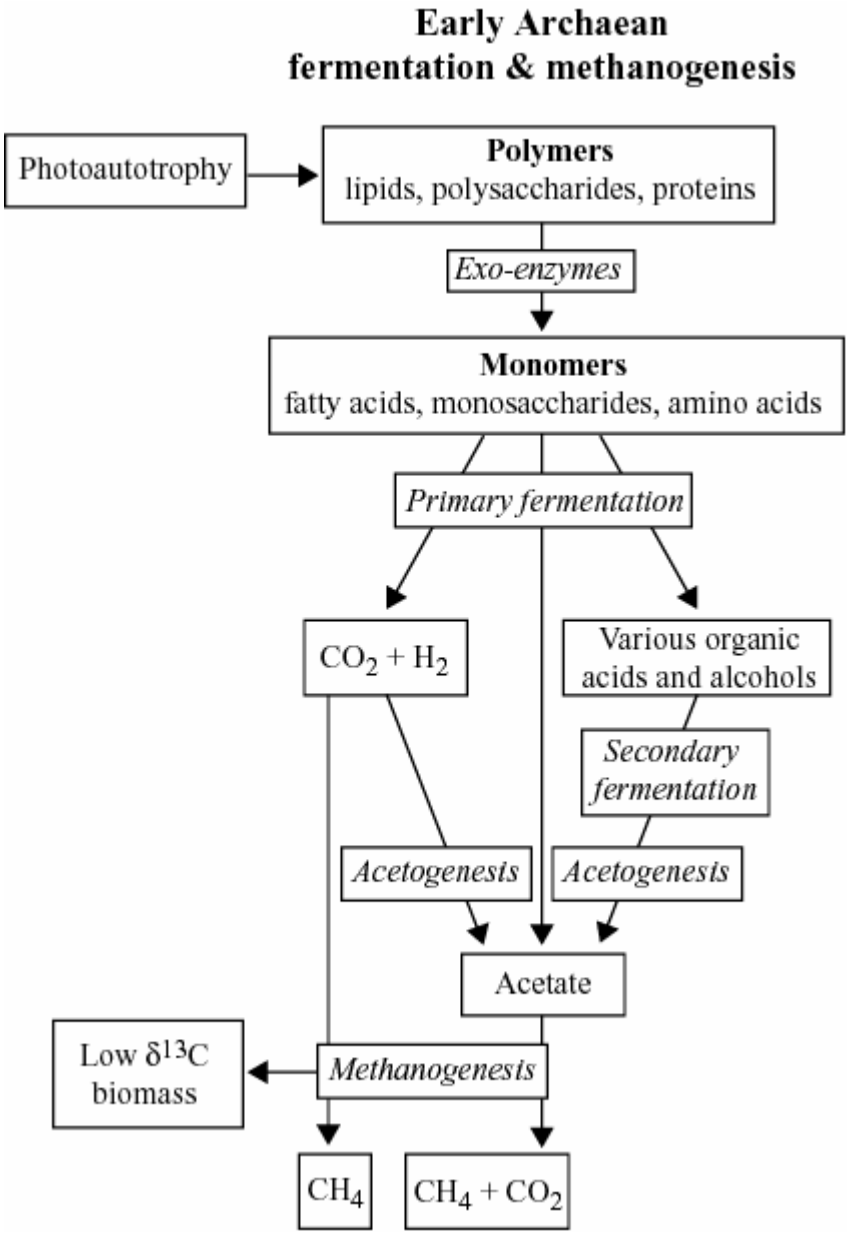

Figure 4: Flow diagram of inferred metabolic reactions in Early Archaean sediments.

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