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REVIEW

Distribution of CO_2 fixation and acetate mineralization pathways in microorganisms from extremophilic anaerobic biotopes

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Abstract Extremophilic anaerobes are widespread in saline, acid, alkaline, and high or low temperature environments. Carbon is essential to living organisms and its fixation, degradation, or mineralization is driven by, up to now, six metabolic pathways. Organisms using these metabolisms are known as autotrophs, acetotrophs or carbon mineralizers, respectively. In anoxic and extreme environments, besides the well-studied Calvin–Benson–Bassham cycle, there are other five carbon fixation pathways responsible of autotrophy. Moreover, regarding carbon mineralization, two pathways perform this key process for carbon cycling. We might imagine that all the pathways can be found evenly distributed in microbial biotopes; however, in extreme environments, this does not occur. This manuscript reviews the most commonly reported anaerobic organisms that fix carbon and mineralize acetate in extreme anoxic habitats. Additionally, an inventory of autotrophic extremophiles by biotope is presented.

Keywords Anoxic · Anaerobe · Assimilation · Carbon · Dissimilatory metabolism

Introduction

Extreme biotopes refer to those environments that are far from normal conditions of pH, temperature, pressure, radiation or salinity, among others, being the extreme condition not transient but constant. Microorganisms that grow and carry out their metabolism under a given extreme condition are referred to as "extremophiles"; their adaptation mechanisms are diverse ranging from structural to metabolic (Gerday and Glandsdorff 2007; Pikuta et al. 2007), because they face with a number of specific stress factors. Such adaptive strategies imply an energy investment; as a consequence, mechanisms of energy conservation differ from those of non-extremophilic microorganisms or neutrophiles (Valentine 2007).

The anaerobic way of life adds another constraint in bioenergetic terms: the Gibbs free energy ($\Delta G^{\circ\prime}$) retrieved is low, compared to the Gibbs free energy retrieved in aerobic metabolism using the same substrate (Heimann et al. 2010). This difference in $\Delta G^{\circ\prime}$, which is a variable that helps to explain the zonation of heterotrophs in anaerobic biotopes in a hierarchical way (Thullner et al. 2007), is exemplified with acetate as electron donor (Table 1). In addition, the energy available for metabolism in many anoxic environments is so minimal that anaerobes can operate at conditions close to thermodynamic equilibrium (Jackson and McInerney 2002). The bioenergetic approach based on the differences in Gibbs free energy is

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useful to explain anaerobic dynamics and it is known as "thermodynamic ecology" (Valentine 2004).

Accordingly, anaerobic extremophiles constitute a group of interest to address the issue of limits of life. Although there are reviews about biological adaptations and diversity of anaerobic extremophiles (Lowe et al. 1993; Ollivier et al. 2000), their autotrophic condition has been left out of focus, despite the essential role of autotrophy in anoxic ecosystems (Hugler and Sievert 2011). Likewise, once the organic matter has been fixed, it undertakes a series of degradation processes which have been defined as "intermediary ecosystem metabolism", where different functions are involved: extracellular hydrolysis, fermentation of monomers and carbon mineralization of the volatile fatty acids (VFA) released by fermentation (Drake et al. 2009). In such intermediary ecosystem metabolism, acetate plays a key role since the metabolism of almost all organic compounds leads to the formation of acetyl-CoA which is used for biosynthesis, excreted as acetate or oxidized (Thauer et al. 1977). As a consequence, terminal mineralizers or acetotrophic microorganisms play an important ecological role by converting acetate back to CO_2 or CH_4 (Valentine 2004).

Therefore, given the importance of autotrophs and carbon mineralizers in extreme biotopes and because most reviews concerning extremophiles have been focused on the extremophilic biotope or electron acceptors and the mechanisms to adapt to extreme conditions, we have focused the present review on the inorganic carbon assimilation and carbon mineralization pathways. In addition, an inventory of autotrophic and carbon mineralizing extremophiles by biotope is presented.

Carbon fixation pathways

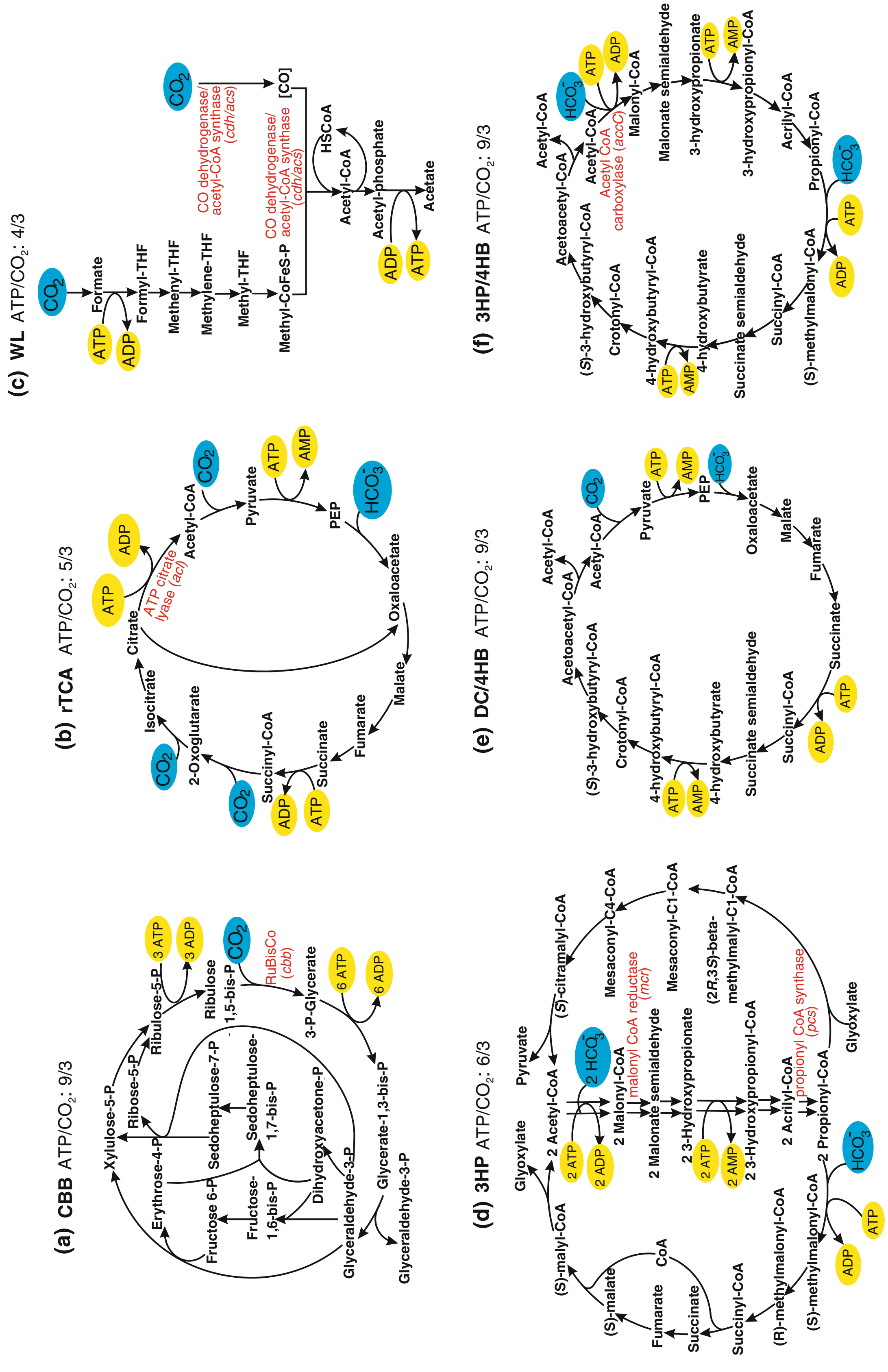
In bacteriology, autotrophy is determined by the growth media devoid of any organic compounds, while CO_2 serves as the sole source of carbon (Srinivasan et al. 2012). Other autotrophs may incorporate C_1 compounds as carbon

Fig. 1 Schematic representation of carbon fixation pathways found in prokaryotes. ATP/CO_2 ratio indicates the molecules invested in each carbon fixation pathway. *R* Reductive or carbon fixation (as presented in the figure), *O* oxidative or carbon mineralization, *M* modified pathway. Key enzymes (gene). **a** Calvin–Benson–Bassham (CBB) cycle. Key enzyme (gene): ribulose-1,5-bisphosphate carboxylase (*cbb*). Present in: plants (R), algae (R), cyanobacteria (R), some aerobic or facultative anaerobic proteobacteria (R), CO-oxidizing mycobacteria (R), representatives in gen. *Sulfobacillus* (R), *Oscillochloris* (R), purple non-sulfur bacteria (R), *Rhodobacter*, *Rhodospirillum*, purple sulfur bacteria (R), *Chromatium*, some hydrogen-oxidizers (R), *Ralstonia*, *Hydrogenovibrio*, some sulfur-oxidizers (R), *Thiobacillus*, nitrite-oxidizers (R), *Nitrobacter*, ammonia-oxidizers (R) and *Nitrosomonas*, *Nitrosococcus* (Canfield et al. 2005; Tourova et al. 2010; Boyle and Morgan 2011; Hugler and Sievert 2011). Although a functional Calvin cycle has not yet been identified in archaea, some hyperthermophilic strains harbor proteins that exhibit Rubisco activity (Atomi 2002). **b** Arnon–Buchanan cycle or reductive tricarboxylic acid (rTCA) cycle. Key enzyme (gene): ATP citrate lyase (*acl*). Present in: green sulfur bacteria (R), *Chlorobaculum tepidum* (R, O), three species in *Desulfobacteraceae* (O), aquificales (R), ε-proteobacteria (R) and autotrophic members nitrospirae (R) (Campbell et al. 2003; Canfield et al. 2005; Tang and Blankenship 2010; Boyle and Morgan 2011; Hugler and Sievert 2011). The reductive acetyl-CoA pathway is so far the only known CO_2 fixation pathway used by bacteria as well as archaea (Hugler and Sievert 2011). This and their metal clusters argue strongly in favour of its antiquity and in the view that methanogens and acetogens might represent the most ancestral autotrophs within the archaea and bacteria, respectively (Martin 2011). **c** Acetyl-CoA pathway or Wood–Ljungdahl (WL) pathway. Key enzyme (gene): CO dehydrogenase/acetyl-CoA synthase (*cdh/acs*). Present in: strictly anaerobic low G + C Gram-positive bacteria (R), *Thermoacetogenium phaeum* (R, O), anaerobic ammonia-oxidizing Planctomycetes (R), some Spirochaeta, most of *Desulfobacteraceae* (R, O), Methanococcales (M), Methanobacteriales (M), Methanomicrobiales (M), Methanosarcinales, Methanopyrales (M), autotrophic Archaeoglobales (Canfield et al. 2005; Hugler et al. 2007; Amann et al. 2010; Berg et al. 2010; Boyle and Morgan 2011; Hori et al. 2011). **d** 3-Hydroxypropionate (3HP) bicycle (Fuchs–Holo bicycle). Key enzymes (gene): malonyl-CoA reductase (*mcr*) and propionyl-CoA synthase (*pcs*). Present in: *Chloroflexaceae* (R) (Canfield et al. 2005; Boyle and Morgan 2011). This pathway has not been found elsewhere (Berg et al. 2010). **e** Dicarboxylate/4-hydroxybutyrate (DC/4HB) cycle. Up to date, no key enzyme has been identified. Present in: Thermoproteales (R) and Desulfurococcales (R) (Huber et al. 2008; Boyle and Morgan 2011; Hugler and Sievert 2011). **f** 3-Hydroxypropionate/4-hydroxybutyrate (3HP/4HB) cycle. Key enzyme (gene): acetyl CoA carboxylase (*accC*). Present in: Thermoacidophilic Sulfolobales (R) (Canfield et al. 2005; Berg et al. 2007; Auguet et al. 2008; Boyle and Morgan 2011) ▶

Table 1 Bioenergetics of common dissimilatory pathways and the aerobic acetate oxidation

Dissimilatory pathway	Summarized reaction	$\Delta G^{\circ\prime}$ (kJ/mol)[a]	Reference
Aerobic respiration	$CH_3COO^- + 2O_2 \rightarrow CO_2 + HCO_3^- + H_2O$	−848.9	Rittmann and McCarty (2001)
Sulfate reduction	$CH_3COO^- + SO_4^{2-} \rightarrow 2HCO_3^- + HS^-$	−47.7	Oude Elferink et al. (1994)
Sulfate reduction	$4H_2 + SO_4^{2-} + H^+ \rightarrow HS^- + 4H_2O$	−38.1	Oude Elferink et al. (1994)
Methanogenesis	$CH_3COO^- + H_2O \rightarrow CH_4 + HCO_3^-$	−31.0	Oude Elferink et al. (1994)
Methanogenesis	$4H_2 + HCO_3^- + H^+ \rightarrow CH_4 + 3H_2O$	−33.9	Oude Elferink et al. (1994)
Homoacetogenesis	$4H_2 + 2CO_2 \rightarrow CH_3COO^- + H^+ + 2H_2O$	−94.9	Schink (1997)
Anoxygenic photosynthesis	$CO_2 + 2H_2S \rightarrow CH_2O + H_2O + S_2$	+35.6	Stein et al. (1994)

[a] Standard Gibbs free energy


(a) CBB ATP/CO2: 9/3
Xylulose-5-P
Ribose-5-P
Ribulose-5-P
3 ATP
3 ADP
Ribulose 1,5-bis-P
CO2
RuBisCo (cbb)
3-P-Glycerate
6 ATP
6 ADP
Glycerate-1,3-bis-P
Glyceraldehyde-3-P
Dihydroxyacetone-P
Sedoheptulose-1,7-bis-P
Sedoheptulose-7-P
Erythrose-4-P
Fructose 6-P
Fructose-1,6-bis-P
Glyceraldehyde-3-P
(b) rTCA ATP/CO2: 5/3
Citrate
ATP
ADP
ATP citrate lyase (acl)
Acetyl-CoA
CO2
Pyruvate
ATP
AMP
PEP
HCO3-
Oxaloacetate
Malate
Fumarate
Succinate
ATP
ADP
CO2
Succinyl-CoA
CO2
2-Oxoglutarate
Isocitrate
(c) WL ATP/CO2: 4/3
CO2
Formate
ATP
ADP
Formyl-THF
Methenyl-THF
Methylene-THF
Methyl-THF
Methyl-CoFeS-P
CO dehydrogenase/acetyl-CoA synthase (cdh/acs)
CO2
CO dehydrogenase/acetyl-CoA synthase (cdh/acs)
[CO]
HSCoA
Acetyl-CoA
Acetyl-phosphate
ADP
ATP
Acetate
(d) 3HP ATP/CO2: 6/3
Glyoxylate
Pyruvate
(S)-citramalyl-CoA
Mesaconyl-C4-CoA
Mesaconyl-C1-CoA
(2R,3S)-beta-methylmalyl-C1-CoA
Glyoxylate
(S)-malyl-CoA
2 Acetyl-CoA
2 ATP
2 ADP
2 HCO3-
2 Malonyl-CoA
malonyl CoA reductase (mcr)
2 Malonate semialdehyde
2 3-Hydroxypropionate
2 ATP
2 AMP
2 3-Hydroxypropionyl-CoA
2 Acrilyl-CoA
propionyl CoA synthase (pcs)
2 Propionyl-CoA
HCO3-
ATP
ADP
(S)-methylmalonyl-CoA
(R)-methylmalonyl-CoA
Succinyl-CoA
Succinate
Fumarate
(S)-malate
CoA
(e) DC/4HB ATP/CO2: 9/3
Acetyl-CoA
Acetoacetyl-CoA
Acetyl-CoA
CO2
Pyruvate
ATP
AMP
PEP
HCO3-
Oxaloacetate
Malate
Fumarate
Succinate
ATP
ADP
Succinyl-CoA
Succinate semialdehyde
4-hydroxybutyrate
ATP
AMP
4-hydroxybutyryl-CoA
Crotonyl-CoA
(S)-3-hydroxybutyryl-CoA
(f) 3HP/4HB ATP/CO2: 9/3
Acetyl-CoA
Acetoacetyl-CoA
Acetyl-CoA
HCO3-
ATP
ADP
Acetyl CoA carboxylase (accC)
Malonyl-CoA
Malonate semialdehyde
3-hydroxypropionate
ATP
AMP
3-hydroxypropionyl-CoA
Acrilyl-CoA
Propionyl-CoA
HCO3-
ATP
ADP
(S)-methylmalonyl-CoA
Succinyl-CoA
Succinate semialdehyde
4-hydroxybutyrate
ATP
AMP
4-hydroxybutyryl-CoA
Crotonyl-CoA
(S)-3-hydroxybutyryl-CoA

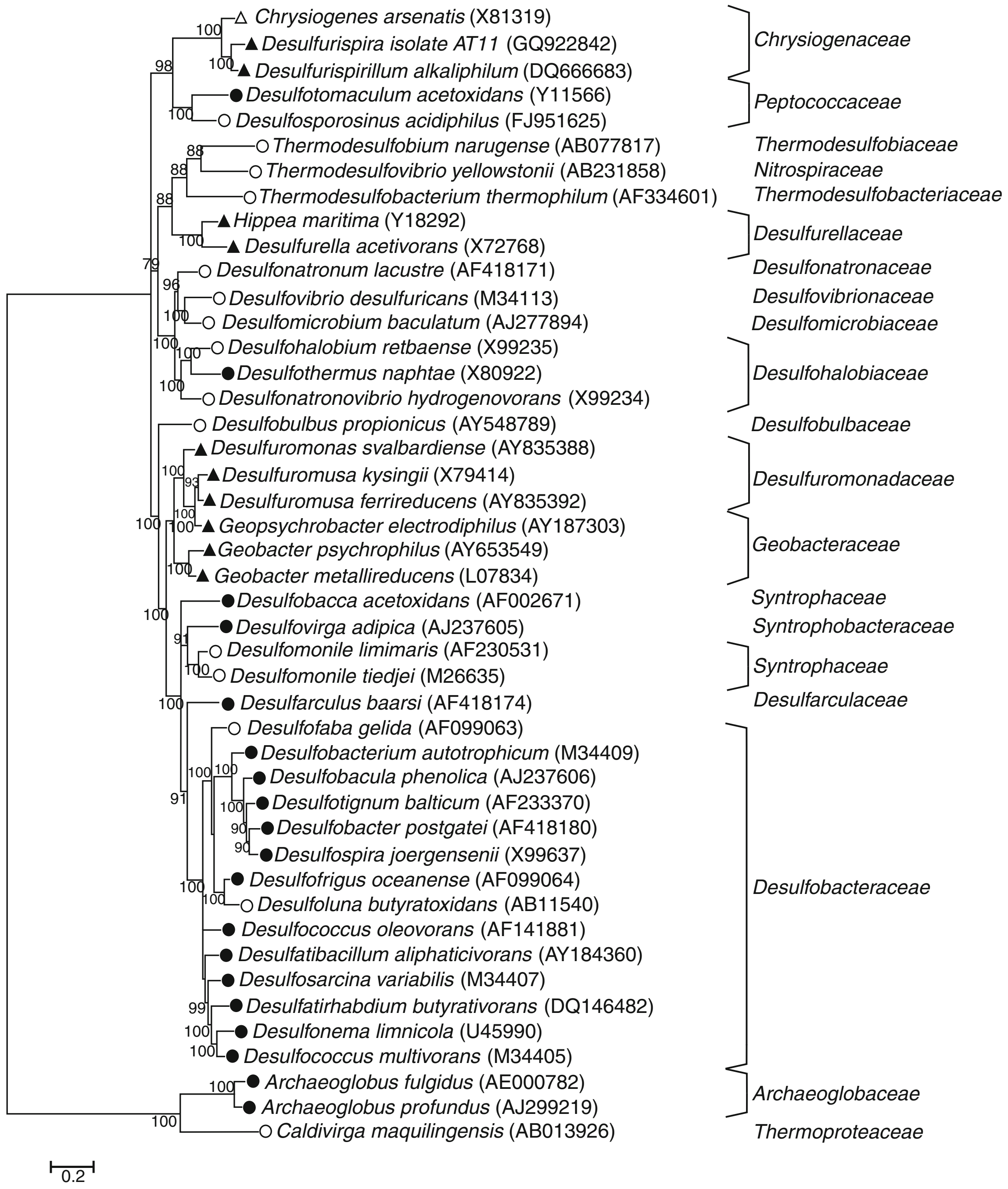


Fig. 2 Bayesian tree of prokaryotic *16S rRNA* gene sequences showing the phylogenetic position of TCA and WL acetate oxidizers or complete oxidizers (*filled symbols*) among sulfur oxidizers (*triangle*) and sulfur reducers (*circle*). Unfilled symbols denote non acetate oxidizers or incomplete mineralizers. The tree was rooted on *Caldivirga maquilingensis* (Crenarchaeota) and posterior probability values >70 % are indicated next to the branch nodes. The *bar* denotes the expected number of changes per nucleotide position

monoxide, carbon disulfide, methane and formic acid (Raymond 2005). We have focused the present inventory in the reductive fixation of CO_2. In terms of genomic content, the importance of CO_2 fixation is evident, taking into consideration that almost 5 % of the reactions annotated in the Kyoto Encyclopedia of Genes and Genomes (KEGG) database directly consume or produce CO_2 (Raymond 2005). From the bulk protein contents, the importance of CO_2 fixation is also evident; for example in the case of *Rhodospirillum*, the enzyme RuBisCO of the Calvin–Benson–Bassham (CBB) cycle may account as much as 50 % of total cell protein (Barton 2005).

To date, six major systems used by autotrophs to fix CO_2 have been described: (1) the CBB cycle, (2) the Arnon–Buchanan cycle or reductive tricarboxylic acid (rTCA) cycle, (3) the acetyl-CoA pathway or Wood–Ljungdahl (WL) pathway, (4) the 3-hydroxypropionate (3HP) bicycle or Fuchs–Holo bicycle, (5) the dicarboxylate/4-hydroxybutyrate (DC/4HB) cycle and (6) the 3-hydroxypropionate/4-hydroxybutyrate (3HP/4HB) cycle. A synthesis of these autotrophic pathways among prokaryotes is given in Fig. 1. The detailed biochemistry of these pathways is out of the scope of this review and may be found elsewhere (Berg 2011; Fuchs 2011; Hugler and Sievert 2011). Each pathway has unique features such as: (1) mechanism for CO_2 assimilation (oxidation state of +4) to generate cellular carbon (average oxidation state of 0, as in carbohydrates), (2) requirements in reducing equivalents because anaerobes often use low-potential electron donors (e.g. ferredoxin) for CO_2 fixation, whereas aerobes usually rely on NAD(P)H as reductant (Berg 2011), and (3) enzymes catalyzing critical steps, which are often regarded as key enzymes (Fig. 1). The differences between the six CO_2 assimilation pathways are so notorious that they reveal multiple origins (Barton 2005). Indeed, it has been argued after phylogenetic analysis of whole genome sequences that autotrophy was gained several times along history (Blank 2009b).

Carbon mineralization

Carbon mineralization refers to the conversion of organic carbon into inorganic carbon. In anaerobic ecosystems, non-fermentable carbon compounds such as acetate (a key volatile fatty acid) can be converted into methane and/or carbon dioxide by carbon mineralizers.

To date, it has been shown that the modified oxidative versions of the TCA and the WL pathway can mineralize acetate completely under anaerobic conditions. The distribution of the oxidative TCA cycle and the oxidative WL in carbon mineralizing microorganisms is related to the redox potential, where organisms using the oxidative TCA cycle developed at higher redox potentials than the oxidative WL-bearing organisms. In fact, it was believed that the oxidative TCA cycle operated only in aerobic organisms, denitrifiers and in phototrophic purple non-sulfur bacteria. In contrast, all WL organisms are anaerobes or strict anaerobes (Thauer 1988).

The most predominant acetotrophs in anoxic environments are the acetotrophic methanogens and acetotrophic sulfate- and sulfur-reducing microorganisms. In the first case, methanogens are common in freshwater systems and the sulfate- and sulfur-reducers are common in marine systems (Canfield et al. 2005). The phylogenetic tree (Fig. 2) shows the distribution of some carbon mineralizers linked to the sulfur cycle. All the acetotrophic methanogens run a modified version of the WL pathway. In contrast, related to sulfate- and sulfur-reducers, the distribution of pathways for carbon mineralization among species is not uniform. Among extremophiles and neutrophiles, the sulfate-reducing bacteria, which are best represented in *Desulfobacteraceae*, are dominated by WL-genera and there is only one genus, *Desulfobacter* that uses the oxidative TCA pathway (Fig. 2). *Desulfobacter hydrogenophilus* deserves special attention because it uses all the enzymes of the oxidative TCA cycle at specific activity levels that would be sufficient for autotrophic growth (Atomi 2002). In contrast to sulfate reducers, all the sulfur-reducing bacteria, grouped in Deltaproteobacteria, are capable of oxidizing acetate with the oxidative TCA cycle (Goevert and Conrad 2010). Another carbon mineralization process occurring in natural and engineered systems is the syntrophic acetate oxidation or reversal chemolithotrophic acetogenesis, which occurs with the oxidative WL pathway mediated by genera such as *Thermoacetogenium* and *Symbiobacterium* (Hori et al. 2011) (Liu and Conrad 2011).

Common pathways of carbon fixation and mineralization at neutrophilic conditions

As true autotrophs, chemo- and photo-autotrophs are primary producers and they must be present in excess to sustain the respiration and fermentation metabolisms. Oxygenic photoautotrophic microbial communities base their major primary production on cyanobacteria (which use the CBB cycle). The CBB cycle is one of the most ATP-requiring carbon fixation pathways and is by far the most abundant in the biosphere (Barton 2005). It was the first carbon fixation pathway described, tolerates oxidizing conditions and is typical of aerobic cyanobacterium and chloroplasts. Despite the ATP expenditure of the CBB cycle (Fig. 1), the CBB cycle can be found in anaerobic photosynthetic sulfide/sulfur oxidizers (purple sulfur, purple non-sulfur, and green non-sulfur bacteria) from extreme habitats, e.g. hypersaline (Tourova et al. 2010), where we might think that energy investment should be low. Anaerobic photosynthesis can be also performed by the reductive TCA route by the green sulfur bacteria, organisms commonly found below the oxygenic photosynthesizers like *Chlorobium limicola*, the type species.

Carbon fixation can occur independently of photosynthesis and under anoxic conditions by chemolithoautotrophy. Chemolithoautotrophic communities derive their metabolic energy from catalyzing inorganic chemical reactions that are out of equilibrium in the environment and driving the reactions toward equilibrium (McCollom and Amend 2005). Mesophilic chemolithoautotrophs are present in rumen and anaerobic digesters, and might have other carbon assimilation pathways. However, in the case of rumen, carbon mineralization is incomplete and most of the intermediate products formed (e.g. volatile fatty acids) are resorbed into the bloodstream serving as nutrients (Garcia et al. 2000). In these environments, the WL pathway is ecologically important, because homoacetogenic bacteria use the reductive WL to synthesize acetyl-CoA from CO_2; this pathway operates in a variant version in some autotrophic and acetoclastic methanogens (Drake et al. 2008; Liu and Whitman 2008).

But, what about extremophiles?

We propose that the distribution of carbon fixation pathways in extreme biotopes might agree with one of the following criteria:

1. Simplicity, the pathway with the lowest number of enzymes (WL) would be the most widespread in extreme biotopes.
2. Assimilation efficiency, the most efficient pathways in terms of energy expenditure during assimilation are dominant within extremophiles. In terms of energy investment, there are two computational analyses helpful to compare the carbon fixation pathways. The first analysis compared the energetic cost as ATP and NADP among pathways, and indicated that the efficiency followed the sense CBB < rTCA < WL (Bar-Even et al. 2010). The other in silico analysis focused on the energy demand for biomass synthesis as kJ/mole of CO_2, and showed that the most efficient pathway was the rTCA followed by the CBB and WL cycles (Boyle and Morgan 2011). The latter analysis is of interest in the present inventory because it considered all the pathways of carbon fixation.
3. Catalytic efficiency, catalysis varies with environmental conditions (e.g. pH, temperature and salinity), and determines the distribution of pathways within the microorganisms of extreme biotopes. An example of this view explains differences between C-fixation in oxic and anoxic conditions. The cycles DC/4HB and 3HP/4HB (pathways e and f in Fig. 1) share many common enzymes and intermediates, for example the 4-hydroxybutyryl-CoA dehydratase. However, they differ on the tolerance to oxygen given by the sensitivity of some of the enzymes and electron carriers of the DC/4HB cycle, restricting this cycle to microorganisms growing under anoxic conditions. Consequently, the 3HP/4HB cycle functions in aerobic Sulfolobales and the DC/HB cycle in mostly anaerobic–autotrophic representatives of Thermoproteales and Desulfurococcales (Berg 2011). However, there are exceptions to this trend and some 3HP/4HB-species such as *Stygiolobus azoricus* have returned to an anaerobic lifestyle (Fuchs 2011). A second example comes from *Chloroflexaceae* (3HP), because the 3HP bicycle has an optimal functioning in slightly alkaline conditions (Berg 2011).

The carbon mineralization process is also of interest for the study of anaerobic extremophiles because it is sensitive to temperature (Gudasz et al. 2010), and it is bioenergetically constrained, e.g., in the volatile fatty acid acetate, the low Gibbs free energy with sulfate as electron acceptor ($\Delta G^{\circ\prime} = -47.7$ kJ) causes a reduction in acetate turnover in some extreme conditions such as acidity and salinity (Ollivier et al. 1994). Thus, could it be that most of the anaerobic extremophiles that mineralize carbon use the oxidative WL pathway? Unfortunately there are no inventories to evaluate this. Regarding acetoclastic methanogenesis, which is a version of the WL pathway, it is unfavorable under alkaline pH (Dolfing et al. 2010) and organisms with this dissimilatory metabolism have not been documented at hypersaline conditions (Oren 2011). At thermophilic conditions, there are acetoclastic methanogens (*e.g. Methanosaeta thermophila*) growing as high as 60 °C (Liu and Whitman 2008); in addition, at low temperature, acetoclastic methanogens are still active (Kotsyurbenko 2005; Metje and Frenzel 2007).

Carbon fixation and mineralization pathways in anaerobic extremophiles

Anaerobic extremophilic autotrophs and acetotrophs are bioenergetically constrained

Growth and metabolism are clearly limited at extreme conditions (temperature, pH and salinity); therefore, life is more abundant at normal conditions. Adaptations to counteract these detrimental conditions involve energy investment; therefore, ecotypes at extreme conditions are generally energetically constrained in comparison with their neutrophilic counterparts. The following sections present a review of the reported anaerobic species capable of growth under extreme conditions; a summary of these organisms is listed in Table 2.

Salinity

Hypersaline biotopes are located in areas with dry climate conditions that facilitate evaporation (Grant 2004). Extreme halophilic microorganisms require at least 15 % NaCl and tolerate up to 35 % NaCl, and under such

Table 2 Comparative properties of representative extremophilic anaerobes

Microorganism species	Range of tolerance	Dissimilatory pathway	C-metabolism	Reference
Salinity				
Halorhodospira halophila	11–32 % NaCl	Photosynthesis	CF/CBB	Imhoff (1984); Imhoff and Suling (1996)
Desulfobacter halotolerans	1–4.5 % (optimal 1–2 %) NaCl	Sulfate reduction	CM/TCA	Brandt and Ingvorsen (1997)
Methanocalculus halotolerans	0–12 % (optimal 5 %) NaCl	Methanogenesis	CF/WLm	Ollivier et al. (1998)
Acetohalobium arabaticum	10–25 % (optimal 15–18 %) NaCl	Homoacetogenesis	CF/WL	Sikorski et al. (2010)
Acidity				
Methanosarcina sp.	pH 4.0–4.5	Methanogenesis	CF/WLm	Sanz et al. (2011)
Desulfosporosinus acidiphilus	pH 3.6–5.6 (optimal 5.2)	Sulfate reduction	CF/WL?	Alazard et al. (2010)
Styolobus azoricus	pH 1.0–5.5 (optimal 2.5–3.9)	Sulfur reduction	CF/3HP/4HB	Segerer et al. (1991)
Alkalinity				
Methanobacterium subterraneum	pH 7.8–8.8	Methanogenesis	CF/WLm	Kotelnikova et al. (1998)
Fuchsiella alkaliacetigena	pH 8.5–10.5 (optimal 8.8–9.3)	Acetogenesis	CF/WL	Zhilina et al. (2011)
Ectothiorhodospira haloalkaliphila	pH 8.5–10.0	Sulfur oxidation	CF/CBB	Sorokin and Kuenen (2005); Venkata-Ramana et al. (2010)
Desulfobacteraceae isolate APT2	pH optimal 10.0	Sulfate reduction	CM/WL?	Sorokin et al. (2011)
Desulfurispira natronophila strain AHT11	pH 8.5–10.9 (optimal 10.2)	Sulfur reduction	CM/TCA?	Sorokin et al. (2011)
High temperature				
Styolobus azoricus	Temperature 57–89 (optimal 80) °C	Sulfur reduction	CF/3HP/4HB	Segerer et al. (1991)
Archaeoglobus spp.	Temperature 60–90 (optimal 75–82) °C	Sulfate reduction	CF/WL	Ollivier et al. (2000)
Ignicoccus hospitalis	Temperature 73–98 (optimal 90) °C	Sulfur reduction	CF/DC/4HB	Paper et al. (2007)
Methanopyrus kandlery	Temperature optimal 98 °C	Methanogenesis	CF/WL	Garcia (1990)
Low temperature				
Rhodoferax antarcticus	Temperature optimal 18 °C	Photosynthesis	CF/CBB	Madigan (2003)
Methanogenium frigidum	Temperature 0 –18 (optimal 15) °C	Methanogenesis	CF/WL	Franzmann et al. (1997)
Desulfuromonas svalbardensis	Temperature −2 to 20 (optimal 14) °C	Iron (III) reduction	CM/TCA?	Vandieken et al. (2006)

CM carbon mineralization, *CF* carbon fixation, *m* modified, *CBB* Calvin–Benson–Bassham cycle, *WL* Wood–Ljungdahl pathway, *TCA* tricarboxilic acid cycle, *3HP/4HB* 3-hydroxypropionate/4-hydroxybutyrate cycle, *DC/4HB* dicarboxylate/4-hydroxybutyrate cycle

conditions, they must balance osmotically the cytoplasm with the medium. A specific range of turgor pressure must be maintained, therefore given the expenditure in osmotic balance, the ecotypes best adapted are those with highly exergonic dissimilatory metabolisms such as aerobic respiration and denitrification (Oren 2011, 2008). However, regarding autotrophy, anoxygenic photosynthetic life employs the CBB pathway by anaerobic microorganisms such as the halophilic *Rhodospirilum salinarum* and *Halorhodospira* species, the latter growing up to saturating levels of salt (Ollivier et al. 2000; Madigan 2003).

The acetoclastic and the hydrogenotrophic methanogens, running WL pathway, are excluded from extreme saline biotopes due to the low Gibbs free energy retrieved from their metabolisms (Andrei et al. 2012). On the contrary, homoacetogens using the autotrophic WL pathway, such as *Acetohalobium arabaticum* which is able to grow between 10 and 25 % NaCl, are present in hypersaline biotopes due to intracellular adaptations, i.e. the “salt in” strategy (Oren 1999). Another exclusion has been described for sulfate-reducing prokaryotes: most of acetoclastic sulfate reducers cease to tolerate high osmolarity conditions, as in *Desulfobacteraceae* species, with the exception of the halotolerant *Desulfobacter halotolerans*, which grows in the presence of up to 13 % NaCl and uses the oxidative TCA cycle (Oren 2011; Brandt and Ingvorsen 1997). Probably, the acetate turnover relies on sulfur reduction more than on sulfate reduction. An interesting study that supports this view reports the isolation of *Halobacterium* from Hummocky Lake (Kulunda Steppe Altai, Russia) with a salinity of 33 % and a pH 8.2; these isolates reduce sulfur with acetate as electron donor (Sorokin et al. 2012). Although it is uncertain which pathway the *Halobacterium* isolates employ to oxidize acetate, they might share the oxidative TCA cycle as the known sulfur-reducing bacteria do.

Acidity

The microorganisms termed acidophiles, inhabit both natural and man-made acidic biotopes such as geothermal, sulfur-rich soils, springs, sulfidic mine areas and mineral bioleaching heaps. Acidophilic organisms maintain a higher pH in the cytosol compared to that of the surroundings and this requires energy, therefore microorganisms with a low metabolic energy yield might be especially susceptible to low pH (Golyshina et al. 2006; Koschorreck 2008). The acid-loving anoxygenic phototrophs include the species *Rhodoblastus acidophilus* and *Rhodopila globiformis* with the CBB and are common in mild acidic environments showing a lower pH for growth between 3.5 and 4 (Madigan 2003). Molecular ecology data from the acidic Tinto River (Spain) indicate that the dominating obligate autotrophic chemolithotrophs are the sulfide-oxidizing *Leptospirillum ferrooxidans* using the rTCA (Goltsman et al. 2009) and *Acidithiobacillus ferrooxidans* using CBB cycle, the latter growing on sulfur with ferric iron as the oxidant (Garcia-Moyano et al. 2007; Cardenas et al. 2010). Most of the isolated anaerobic acidophilic microorganisms are heterotrophic hyperthermophiles and belong to Archaea. The use of the 3HP/4HB cycle has been reported in thermoacidophilic Sulfolobales (Hugler and Sievert 2011). *Desulfosporosinus acidiphilus* is the sulfate reducer with the lowest pH range of tolerance (between 3.6 and 5.6) using H_2 as electron donor and CO_2 as carbon source (Alazard et al. 2010). It is unknown the pathway that this species use for carbon fixation, however because of the phylogenetic proximity with *Desulfotomaculum acetoxidans,* it is probably that *D. acidiphilus* uses the reductive WL pathway to fix CO_2.

Regarding methanogenesis, it is noteworthy that pH is a significant factor determining the electron donor used; in this sense, a shift from acetoclastic to H_2-dependent methanogenesis has been reported between pH of 4.7 and 3.8 in a methanogenic community, from an acidic peat bog. The community changed from *Methanosarcinaceae* predominance to *Methanomicrobiaceae* and *Methanobacteriaceae* (Kotsyurbenko et al. 2007). This fits with the low Gibbs free energy retrieved by acetoclastic methanogenesis in comparison with the hydrogenotrophic methanogenesis (Table 1). Other evidences of enrichment of hydrogenotrophic methanogenic archaea have been reported from acid systems, e.g., Tinto River sediments with a pH of 5 in the sediment, where *Methanobacterium bryantii* has been enriched (Sanz et al. 2011). Also, there are no evidences of homoacetogenesis in acid biotopes which is congruent with bioenergetic estimates (Dolfing et al. 2010). Regarding syntrophs, no reports have been published so far. Carbon mineralizers in sulfate-reducing bacteria have not been isolated, and the described acidophilic species oxidize carbon incompletely (Koschorreck 2008; Alazard et al. 2010). The presence of the sulfur reducers has been reported, e.g., the genus *Desulfurella* in Tinto River system, which uses the oxidative TCA pathway (Sanchez-Andrea et al. 2011).

Alkalinity

Naturally occurring biotopes with a high pH and high salinity are called “soda lakes” where sodium carbonate/bicarbonate are among the dominant salts (Sorokin et al. 2011). Their ecotypes face the necessity to maintain the intracellular pH level and the bioenergetic status of their cells in a medium with a low proton concentration, recurring to Na^+/H^+ antiport systems (Pitriuk et al. 2004). A common species of these biotopes is the anaerobic alkaliphilic purple sulfur bacteria *Ectothiorhodospira* spp. that runs the CBB pathway (Sorokin and Kuenen 2005; Kovaleva et al. 2011).

Early reports describe that under extreme alkaline conditions, homoacetogens were chemoorganotrophs, e.g., *Natroniella acetigena*, which uses the reductive WL pathway for the reduction of CO_2 but does not utilize hydrogen as electron donor (Zhilina et al. 1996). They are outcompeted by sulfate-reducing-H_2 ecotypes such as the well-adapted *Desulfonatronovibrio* and *Desulfonatronum* (Sorokin et al. 2011). *Fuchsiella alkaliacetigena* (*Halobacteroidaceae*) isolated from soda lake Tanatar III (Altay, Russia) uses H_2 as electron donor, a feasible metabolism taking into account that homoacetogenesis is still exergonic at alkaliphilic conditions, thus its growth pH ranges from 8.5 to 10.5 (Dolfing et al. 2010; Zhilina et al. 2011). The adaptation of carbon fixation to alkaline conditions is more evident than under acid conditions when it is considered the case of *Chloroflexaceae.* This group of organisms uses the 3HP pathway that is optimized in slightly alkaline conditions, where bicarbonate (HCO_3^-) concentration is much higher than the concentration of dissolved CO_2; 3HP-autotrophs profit from using bicarbonate instead of CO_2 (Berg 2011).

Regarding acetate mineralization, the highest activity reported at alkaline pH comes from sulfur reducers such as *Desulfurispira natronophila.* Sulfur reduction is more favorable than sulfate reduction at alkaline conditions. This condition is determined by the stability of reactants and results in differences of the free energy change ($\Delta G^{\circ\prime}$). In sulfur reducers it ranges from −40 to −70 kJ/mol acetate and in sulfate reducers it is less favorable (−47.7 kJ/mol acetate) (Sorokin et al. 2011). Acetoclastic methanogenesis seems to be endergonic at high pH (Dolfing et al. 2010). Intriguingly, acetoclastic and methanogenic isolates have been reported in Qinghai Lake, a saline (12.5 g/L) and alkaline (pH 9.4) biotope on the Tibetan Plateau. However, the authors sustain that more work is necessary to confirm these observations (Dong et al. 2006). Syntrophic associations have been reported at alkaline conditions, an example is the one sustained by the obligate syntrophic Candidatus *Contubernalis alkalaceticum* (Clostridiales) and *Desulfonatronum coopertivum* (Desulfovibrionales), which were isolated from a sulfidogenic soda lake sediment. When *C. alkalaceticum* is cocultured with the alkaliphilic sulfate reducer *Desulfonatronum cooperativum*, it can oxidize acetate at pH 10 with the production of sulfide (McInerney et al. 2008; Sorokin et al. 2010). *C. alkalaceticum* might harbor the reverse (oxidative) WL pathway to complete acetate mineralization as Thermoanaerobacterales also in Clostridiales (Hattori 2008; Hori et al. 2011).

High temperature

Hyperthermophiles have received the most attention to date and as in acidophiles, they display alternative carbon fixation pathways. The reductive CBB cycle appears to be the dominant pathway in terrestrial and marine habitats characterized by temperatures <55 °C. This cycle operates in some thermophiles such as *Beggiatoa* in Gammaproteobacteria, but never in hyperthermophiles; indeed its upper temperature appears to be between 70 and 75 °C (Nakagawa and Takai 2008; Berg 2011). The organisms running the rTCA cycle are partitioned in Epsylonproteobacteria, dominating at temperatures 4–70 °C, and Aquificales, predominant up to 90 °C, with some members able to grow above 90 °C (Hugler et al. 2007; Hall et al. 2008; Nakagawa and Takai 2008; Hugler and Sievert 2011). The alternative at temperatures higher than 90 °C is the DC/4HB cycle. Also, among the hyperthermophiles are the autotrophic methanogens (modified WL) such as *Methanopyrus kandlery* and the sulfate reducers belonging to Archaeoglobales (modified WL). Therefore, because mainly hyperthermophilic archaea (WL and DC/4HB) grow most at temperatures above 90 °C, if not all, the biomass production at these temperatures is carried out by this domain (Hugler and Sievert 2011). It can be discarded that homoacetogenic bacteria (reductive WL) perform autotrophic growth given that this metabolism becomes less active at thermophilic conditions (Akutsu et al. 2009) and the reaction is thermodynamically unfavorable at hyperthermophilic temperature (122 °C), thus they appear to rely on heterotrophic metabolism when growing on hyperthermophilic biotopes (Lever 2012). Studies completed in bioleaching heaps within gradient temperature have shown that at mesophilic conditions, the robust but complex CBB cycle appears to be the principal CO_2 fixation process, and it has been shown that other CO_2 fixation pathways such as the reductive TCA (rTCA) cycle and the 3HP/4HB pathway address the C-cycle as bioleaching proceeds and temperature rises (Cardenas et al. 2010; Valdes et al. 2010).

Regulation of carbon mineralization is detectable at large scale and depends on temperature (among other factors). For example, a strong positive correlation between temperature and mineralization of organic carbon was reported for a wide range of boreal lake sediments in Sweden (Gudasz et al. 2010). The importance of temperature in carbon mineralization is also observed at microscale, e.g., syntrophic acetate oxidation becomes more exergonic as temperature increases (Liu and Conrad 2011). There are some acetotrophic consortia favored by thermophilic conditions, e.g. the H_2-methanogen belonging to *Methanocellales* and acetate degrading populations belonging to gen. *Thermacetogenium* (using the Wood–Ljungdahl pathway), which are active at 50 °C (McInerney et al. 2009; Rui et al. 2011). In brief, acetate degradation becomes more exergonic as temperature increases (Liu and Conrad 2011).

Low temperature

The biotopes with permanently low temperatures include the regions of the Arctic and Antarctic with polar ice sheets, glaciers and permafrost, the snow-caps and glaciers of high mountains, and the deep water and marine sediments of the oceans. According to Hugler and Sievert (Hugler and Sievert 2011), the CBB cycle and reductive WL may be the principal carbon fixation pathways at <20 °C. Anoxygenic phototrophs belong to Chloroflexus clade (3HP) or to purple non-sulfur bacteria such as *Rhodoferax antarcticus* which uses the CBB pathway (Madigan 2003). There are reports of a diverse group of methanogens (WL modified), which are among the most abundant anaerobic and autotrophic members in cold biotopes. The methanogen with the lowest known optimum growth temperature is *Methanogenium frigidum* (15 °C), which is unable to grow above 18 °C. This H_2-methanogen was isolated from Ace Lake in the Vestfold Hills region of Antarctica (Franzmann et al. 1997). The consumption of hydrogen by *Acetobacterium* (WL) populations has been reported in cold anoxic sediments (Margesin and Miteva 2011) in accordance with a competitive participation of homoacetogens in low temperature biotopes (Conrad and Wetter 1990). Up to now, all of these isolates of acetogenic bacteria have been defined as psychrotolerant and are grouped in *Acetobacterium* genera; among them, the most competitive at low temperatures are *Acetobacterium baki* and *A. tundrae* (Finster 2008). *Desulfofrigus oceanense* has the lowest optimal temperature reported for an acetotrophic sulfate-reducing bacteria but the pathway for carbon mineralization is not known (Knoblauch et al. 1999). Psychrophilic iron reducers performing acetate mineralization have also been isolated: (1) *Geobacter psychrophilus* growing between 4 and 30 °C (Nevin et al. 2005) and (2) *Desulfuromusa ferrireducens* and *Desulfuromonas svalbardiense* isolated from permanently cold Arctic marine sediments (Svalbard), both strains grew at −2 °C (Finster 2008). It is probably that iron reducers run the oxidative TCA pathway to oxidize acetate as their neutrophilic counterparts.

Conclusions

It has been accepted that in anoxic and extreme conditions, the nature of the dissimilatory metabolism plays a significant role in the survival of microorganisms (Oren 2011). Here, we attempted to bring into consideration that carbon assimilatory metabolism might also explain their distribution on extreme environments. The most elemental precondition might be that if anaerobic microorganisms are sustained by very small Gibbs free energy changes, they use the simplest and an energy saving pathway (WL) to fix and mineralize carbon as it occurs, in microorganisms living close to the thermodynamic limit, like syntrophic prokaryotes (Stams and Plugge 2009; Berg 2011). Nevertheless, given the current inventory, in extreme biotopes expensive pathways such as CBB cycle predominate in alkaliphiles and acidophiles. Therefore, the selection of carbon fixation and mineralization pathways in these organisms is probably more related to catalytic efficiency rather than assimilation efficiency or simplicity, which might be generalized to the extremophiles including the hyperthermophiles (DC/4HB, 3HP/4HB) since they do not use outstanding energy efficient pathways (Boyle and Morgan 2011). This means that other factors besides anabolic energy-cost, such as catalytic efficiency and contingency would explain why expensive and complex pathways are present under extremophilic conditions.

At this point and observing the composition of autotrophs and C-mineralizers in biotopes, it agreed that a major issue to decipher the C-biogeochemical “black boxes” would reside in Molecular Ecology to compare concrete functional-pathway activities. This perspective would be useful to explore key issues in: (1) bioengineering, e.g., acidification is a factor not fully understood in terms of diversity (Akuzawa et al. 2011); (2) geomicrobiology, increasing knowledge of pathways for fixing CO_2 would bring insight into inferences for C-biogeochemical cycles, e.g., early life was anaerobic and controversial regarding temperature (Canfield et al. 2006; Blank 2009a) and (3) astrobiology, extremophiles act as sustainable ecotypes in this field of research and guide the concept of “habitability” (Hoehler et al. 2007).

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