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Case Report

A variety of substrates for methanogenesis

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ABSTRACT

The number of methanogenesis substrates known to date has increased more than six-fold since the late 80s, bringing to 152 the number of proven substrates for methanogenesis, plus 41 putative substrates predicted on the basis of 'omic' and biochemical data. In particular, it was demonstrated that new classes of substrates, such as halogenated compounds, sulfur compounds or aromatics, enable methanogenesis. In this article, which straddles the boundary between a scientific paper and a review, we take stock of all these known and putative substrates, and calculate Gibbs free energy changes under standard biological conditions for methanogenesis. Out of all the substrates for methanogenesis, two-thirds of the $\Delta G_r^{0'}$ values calculated lie between 0 and –30 kJ mol^{-1} CH_4. We discuss the sources of these substrates, the environments in which they occur and the taxa that use them to produce energy through methanogenesis. Given the diversity of anoxic environments in which these different substrates are found, methanogens could populate a greater number of ecological niches than previously thought.

1. Introduction

Methanogenesis is one of the oldest energy metabolisms on Earth, with the most ancient evidence for microbial methanogenesis coming from fluid inclusions in hydrothermal silica dykes over 3.46 billion years old [1]. This metabolism may have played a key role in the evolution of Earth's atmosphere before the 'Great Oxygenation Event' [2]. Today, this metabolism still influences our atmosphere and climate, as methane is a strong greenhouse gas with a global warming potential 25 to 28 times that of carbon dioxide (CO_2) [3–5]. It is estimated that about 55–70 % of global annual methane emissions on Earth derives from archaeal methanogenesis [6,7]. Methanogenic *Archaea* are widespread, inhabit a great variety of anoxic natural or anthropogenic environments, including marine and freshwater sediments, wetland and permafrost soils, rice paddies, anaerobic sludges, and digestive tracts of various animals [8–10]. Thus, they are detected in all types of anoxic systems, from polar environments to high temperature systems, through acidic or alkaliphilic environments, to hypersaline or high-pressure ecosystems. When methanogenesis is based on the use of conventional competitive substrates such as H_2/ CO_2 or acetate ($CH_3CO_2^-$), this process is mainly restricted to anoxic ecological niches lacking or poorly concentrated in terminal electron acceptors such as dioxygen (O_2), nitrate (NO_3^-), ferric iron (Fe^{3+}), manganese IV (Mn^{4+}) and sulfate (SO_4^{2-}) [11,12].

Conversely, non-competitive substrates such as methylamines or methylsulfides can be converted to methane in anoxic habitats where strong oxidants are present [11,13]. Recent studies based on the measurement of biological methane production associated to metagenomic/metatranscriptomic data suggested that methanogenesis could also occur in well-oxygenated parts of wetland soils and in oxygenated parts of lake water columns [14,15]. Over the past decade, a resurgence of interest in methanogenic *Archaea* research led to the discovery of many new methanogenic lineages through culture-based approaches [16,17], augmented by other putative methanogenic lineages predicted by genome-centric metagenomic studies and single-cell genomic approaches [18–26]. By discovering almost as many new orders of putative methanogens as had been known for more than 30 years, these studies revealed that the diversity of methanogenic *Archaea* is much broader than previously thought and not limited to the single phylum *Euryarchaeota*. These studies also showed that there are other pathways of methanogenesis beyond the 3 canonical pathways – CO_2-reducing hydrogenotrophic, acetoclastic and methylotrophic – traditionally described in the literature. Concomitantly, the spectrum of substrates described for methanogenesis expand dramatically beyond the narrow range of substrates (H_2/ CO_2, formate, acetate and few C_1 compounds) reported until the 2010s. In fact, some studies reported new substrates for methanogenesis supported by physiological demonstration of the reaction (*n*-alkanes, *n*-alkylcyclohexanes, *n*-alkylbenzenes, methoxylated aromatics) and proposed new putative substrates (e.g., *n*-fatty

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acids) [18,27,28]. These findings suggest that many discoveries are still to come concerning the metabolism, ecology and evolution of methanogens.

In a context where knowledge is evolving very rapidly, no comprehensive review article, to our knowledge, addresses the great diversity of proven or putative methanogenesis substrates documented in literature and their inherent thermodynamic properties. Yet, thermodynamics could represent a first approach to posit the existence of hypothetical chemotrophic microbial reactions and to compare their standard Gibbs energy change in a hypothetical biological reference frame ($\Delta G_r^{0'}$), before calculating the actual energy of this reaction under *in situ* conditions (ΔG_r) and also demonstrating that this process can actually be catalyzed by microorganisms.

In this publication, which is on the edge between a research paper and a review article, we provide an overview of the current knowledge of demonstrated and proposed methanogenesis substrates, calculate the standard Gibbs energy change ($\Delta G_r^{0'}$) of reactions from these substrates under biological reference frame, and compile the taxa and systems where they are detected, as well as their sources in natural, anthropogenic and digestive environments.

2. Materials and Methods

2.1. Inventory of methanogenesis reactions and substrates

To undertake this work, an extensive literature review was conducted to provide as comprehensive a list as possible of the methanogenesis substrates and associated reactions. With few exceptions, the original publication providing the physiological demonstration that methane is derived from this substrate is cited. Similarly, for hypothetical substrates suggested from metagenomic or single cell genomic data, we selected publications providing indirect genetic clues to methanogenesis from a given substrate. Thus, 21 publications listing a total of 193 substrates of methanogenesis were selected [18,21,25,27–44]. Whenever possible, when values of the standard Gibbs energy of formation of chemical species were available or calculable, the standard Gibbs energy change ($\Delta G_r^{0'}$) of the reactions from the listed substrates was calculated. The stoichiometry of the reactions and of the methane produced following the complete degradation of various substrates (e.g., *n*-alkylated hydrocarbons, *n*-fatty acids) has been estimated from the Buswell equation [45,46]. The namings of the methanogenesis pathways adopted in this article are those proposed by Zhou et al. [28], Garcia et al. [47], Garcia et al. [48], and Le Mer and Roger [49], taking into account the electron donor and acceptor of the reactions.

2.2. Thermodynamics: theory and notations

The notations referring to the standard state and the standard biological state developed below are as follows: ΔG_f^0 is the standard Gibbs energy of formation of a chemical species, $\Delta G_f^{0'}$ the Gibbs energy of formation of a chemical species under biological standard conditions (see text below), ΔG_r^0 the standard Gibbs energy change of a reaction, $\Delta G_r^{0'}$ the Gibbs energy change of a reaction under biological standard conditions, and ΔG_r the standard Gibbs energy change of a reaction.

As mentioned above, a convenient way to estimate whether a biochemical reaction is feasible or not and to determine its energy yield, is to calculate the corresponding change of energy of the reaction. This value can be estimated using (Eq. (1))

$$\Delta G_r = \Delta G_r^0 + R \times T \times \ln Q_r \tag{1}$$

where ΔG_r^0 is the standard Gibbs energy change (kJ mol^{-1}) (298.15 K, 10^5 Pa, 1 M of each chemical species), R the universal gas constant ($\sim$8.314 10^{-3} kJ K^{-1} mol^{-1}), T the temperature of interest (K), and Q_r the reaction quotient (unitless) [50]. The latter takes into account the concentration of each chemical species involved in the reaction and corresponds to the ratio between the activities (a, corresponding to the effective concentration, unitless) of products (p) and reactants (r), following stoichiometric reaction coefficients ($\upsilon_{p,r}$) (Eq. (2) and (3)),

$$Q_r = \prod a_{p,r}^{\upsilon_{p,r}} \tag{2}$$

with

$$a = \frac{C}{C^0} \times \gamma \tag{3}$$

The activity of a chemical species can be defined as the ratio between the concentration (C, usually in mol kg^{-1}) and standard state concentration (C^0) multiplied by the corresponding activity coefficient (γ, unitless). Activity coefficients depend on temperature, chemical species charge and the ionic strength of chemical environment and can be calculated or taken from various publications [51–53]. When referred to the equilibrium constant K_c (unitless), Q_r allows to predict the evolution of the system of interest [50]. In fact, if $Q_r < K_c$, then the reaction tends to shift towards the products and if $Q_r > K_c$, then the reaction tends to move towards the reactants. The reaction is at chemical equilibrium when $Q_r = K_c$.

One of the key-term in Eq. (1) is ΔG_r^0, a standard Gibbs energy change in a hypothetical reference frame called standard state. A common way to calculate ΔG_r^0 is to subtract the change in standard enthalpy (ΔH_r^0, kJ mol^{-1}) from the change in standard entropy (ΔS_r^0, J mol^{-1} K^{-1}) multiplied by the temperature (K), such as (Eq. (4))

$$\Delta G_r^0 = \Delta H_r^0 - T \times \Delta S_r^0 \tag{4}$$

Another way to calculate ΔG_r^0 is to subtract the sum of the Gibbs energies of formation (ΔG_f^0, kJ mol^{-1}) of the products (p) from those of the reactants (r), ensuring the stoichiometric coefficients (ν) and the appropriate phase of matter (Eq. (5))

$$\Delta G_r^0 = \sum_p \upsilon_p \times \Delta G_f^0(p) - \sum_r \upsilon_r \times \Delta G_f^0(r) \tag{5}$$

When considering a biological system, a particular set of standard conditions were proposed by the Interunion Commission on Biothermodynamics (ICB) to account for and mimic the circumneutrality of living cells: 298.15 (or 303.15) K (i.e., 25 or 37 °C), 101.325 kPa, 1 M of each compound and pH 7 [54,55]. However, two remarks can be made about these parameters. First, the International Union of Pure and Applied Chemistry (IUPAC) has recommended to change the standard state pressure (P_0) from 101.325 to 100 kPa [56]. While this change results in a slight change in the thermodynamic values of all chemical species, it is mostly negligible for chemical species in their condensed phases (i.e., liquid and solid, denoted l and s, respectively), but can be noticeable for the standard entropy (S^0) of gaseous (g) chemical species and thus any ΔG_r^0 involving gaseous chemical species [56,57]. Nevertheless, atmospheric pressure is still widely used as the reference pressure in literature, especially in bioenergetic calculations. The second concern is the direct relation between pH and H^+ concentration. In fact, setting the pH to 7 breaks the molarity rule and thus affects the inherent value of the Gibbs energy of formation of the proton in aqueous (aq) solution. To accommodate this, its value can be calculated by following an adapted version of the Nernst equation (Eq. 6)

$$\Delta G_f^{0'}\left(H^+_{(aq)\ pH7}\right) = \Delta G_f^0\left(H^+_{(aq)\ pH0}\right) + R \times T \times \ln\left(10^{-7}\right) \approx -39.956 \text{kJ mol}^{-1} \tag{6}$$

where $\Delta G_f^0(H^+_{(aq)\ pH0})$ equals to $\log(10^0)$.

As recently pointed out by Amend and LaRowe [51], it is crucial to consider the phase (aq, g, l or s) of the chemical species of interest. In fact, since the $\Delta G_r^{0'}$ values of the same compound can differ from one

phase to another (e.g., ΔG_f^0 of methane in gaseous and aqueous phases are equal to −50.8 and −34.4 kJ mol^{-1}, respectively [50]), the application of the wrong one could affect the value of ΔG_r and thus lead to erroneous interpretations. To avoid these pitfalls, it is useful to assess the correct phase, water solubility and pK_a of each compound of interest under the conditions of interest.

2.3. Gibbs energy changes of methanogenesis reactions

For the above reasons, the Gibbs energy changes of methanogenesis reactions were calculated according to the biological standard conditions proposed by the ICB, and are denoted $\Delta G_r^{0'}$. In these calculations, chemical species considered for acetate were $CH_3CO_2^- + H^+$, formate were $HCO_2^- + H^+$, *etc*. A notable exception to consider is the main form of 'CO_2' (i.e., $CO_{2(aq)} + H_2CO_3 + HCO_3^- + CO_3^{2-}$) ($H_2CO_3$ denotes a conventional chemical species encompassing the sum of H_2O and $CO_{2(aq)}$ properties) dissolved in an aqueous system [58–60]. In fact, although HCO_3^- is the dominant (pK_{a1} (H_2CO_3/ HCO_3^-) = 6.35, and pK_{a2} (HCO_3^-/ CO_3^{2-}) = 10.3, respectively) form of 'CO_2' present under biological standard conditions, the enzyme complex (see below) that catalyzes the first step of the CO_2-reducing methanogenesis uses $CO_{2(aq)}$ rather than HCO_3^- [58–63]. We have therefore considered $CO_{2(aq)}$ – simply denoted CO_2 hereafter – in our calculations, in place of HCO_3^-.

2.4. Documentary sources for standard phases

Gibbs free energies of formation (in aq, g, l or s phase) for several chemical species mentioned in this publication have been published previously [40,41,50,54,64–71] and are listed in Table A.1 (Appendix A).

The standard phase, water solubility, and possible speciation of all chemical species of interest mined from these sources were identified and checked against articles by Lide et al. [72] and Haynes et al. [61], and/or against the online PubChem chemistry database (https://pubchem.ncbi.nlm.nih.gov/) to fulfill the conditions defined above. Selected ΔG_f^0 values for $CO_{2(aq)}$ and $CH_{4(aq)}$ were those taken from Hanselmann [50], and that for water from Thauer et al. [54].

2.5. Calculation of missing ΔG_f^0

Three different approaches were implemented to calculate the Gibbs free energies of formation of compounds not available in the literature or not given in the appropriate phase (listed in Table A1, Appendix 1), and then to calculate the corresponding standard Gibbs energy changes of methanogenesis reactions. In all cases, and in order to get more confidence, the exact value of R and a temperature of 298.15 K were used. Data expressed in 'thermochemical calories' (cal_{th}) in literature were converted to kilojoules (kJ) (1 cal_{th} = 4.184 J, exactly) [55]. The Gibbs free energy of formation of the proton in aqueous solution at pH 7 was calculated using Eq. (6).

The first approach consisted to apply thermodynamic phase-transition and dissolution relationships (Fig. 1) on chemical species retrieved in their gaseous form and for which no suitable phase was given in literature. Gibbs free energies of formation values for *n*-butane ($CH_3(CH_2)_2CH_3$), dimethylsulfide (DMS, $(CH_3)_2S$), *n*-heptanoic acid (enanthic acid, $CH_3(CH_2)_5CO_2H$), 2-hydroxyphenol (pyrocatechol, $C_6H_4(OH)_2$), 4-hydroxyphenol (hydroquinone, $C_6H_4(OH_2)$), 2-methoxyphenol (guaiacol, $C_6H_4(OH)OCH_3$), 4-methoxyphenol (mequinol, $C_6H_4OHOCH_3$), methanethiol (MT, CH_3SH), methyl-iodide (iodomethane, CH_3I), *n*-octanoic acid (caprylic acid, $CH_3(CH_2)_6CO_2H$), *n*-pentane ($CH_3(CH_2)_3CH_3$), and *n*-propane ($CH_3CH_2CH_3$) in their aqueous phases were calculated using Eq., 7 [76]:

$$\Delta G^0_{f(aq)} = \Delta G^0_{f(g)} - R \times T \times \ln(H) \quad (7)$$

where H is the Henrys law constant (mol L^{-1} atm^{-1}). Henry's law constants were taken from Sander [80] and converted from mol m^{-3} Pa^{-1} to mol L^{-1} atm^{-1} [76] (Table A.2, Appendix A). As a side note, $-R \times T \times \ln(H)$ corresponds to the standard Gibbs free energy of hydration ($\Delta_g^{aq}G^0$).

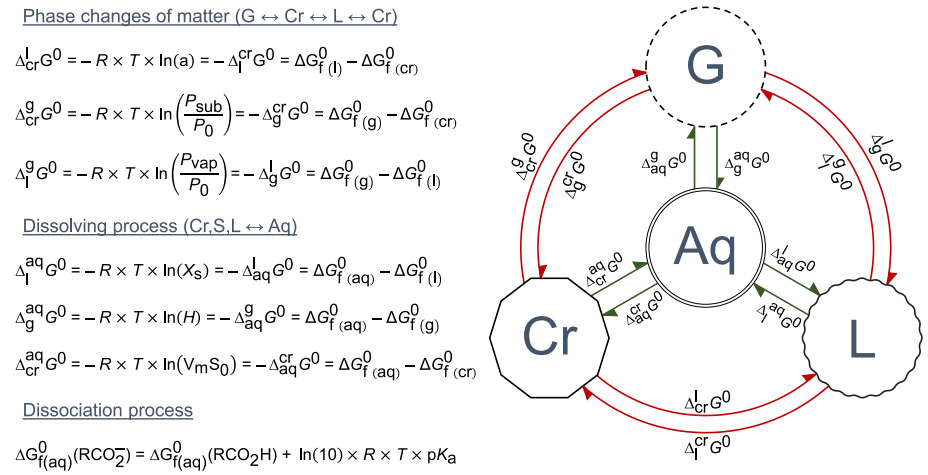

Fig. 1. Thermodynamic cycle resuming the phase-transition (red arrows) along with the dissociation process (green arrows) equations. Formula and related thermodynamic concepts were taken from various articles where they are further discussed [73–79]. At given conditions of temperature, the properties of thermodynamic processes are interrelated, such as, for example: $\Delta_l^g G^0 = \Delta_{cr}^g G^0 - \Delta_{cr}^l G^0$, $\Delta_{cr}^{aq} G^0 = \Delta_{cr}^g G^0 - \Delta_g^{aq} G^0$, and $\Delta_l^g G^0 = \Delta_l^{aq} G^0 - \Delta_g^{aq} G^0$. Standard Gibbs energies of hydration ($\Delta_g^{aq} G^0$), sublimation ($\Delta_{cr}^g G^0$) and dissociation ($\Delta_{aq}^l G^0$) expression were applied in this study to calculate a number of Gibbs free energies of formation for various chemicals, by converting them from one phase to another and/or from one form to another. Standard Gibbs free energies formula for other processes were also featured to support further investigations, i.e., $\Delta_{aq}^l G^0$, $\Delta_g^l G^0$, $\Delta_l^g G^0$, $\Delta_{aq}^g G^0$, $\Delta_l^{aq} G^0$, $\Delta_{cr}^l G^0$, $\Delta_g^{aq} G^0 \Delta_{aq}^{cr} G^0$, $\Delta_g^{cr} G^0$, and $\Delta_l^g G^0$. In these equations, a is the activity of the compound in its solid phase, H represents the Henry's law constant (mol L^{-1} atm^{-1}), m the aqueous solubility (mol L^{-1}), P_0 the reference pressure (kPa), P_{sub} the sublimation pressure (kPa), P_{vap} the vapor pressure (kPa), pK_a the common logarithm of the dissociation constant, RCO_2^- the carboxylated anion of an ionisable chemical species, RCO_2H the carboxylic acid form of an ionisable species, S_0 the intrinsic solubility of a unionized chemical species in a saturate solution (mol L^{-1}), V_m the crystalline molar volume (L mol^{-1}), X_s the mole fraction aqueous solubility, and $\Delta G^0_{f\,(aq)}$ the standard Gibbs free energy of formation in aqueous solution. Aq: aqueous, Cr: crystalline solid, G: gaseous, L: liquid.

As mentioned previously, pH is a key parameter for calculating ΔG^0_r. Adjustments based on pK_a were performed to deduce $\Delta G^0_{f(aq)}$ of caprylate and enanthoate at pH 7 based on their respective carboxylic forms [76] (Eq., 8)

$$\Delta G^0_{f(aq)}\left(RCO_2^-\right) = \Delta G^0_{f(aq)}(RCO_2H) - R \times T \times \ln(10) \times pK_a \quad (8)$$

where RCO_2^- and RCO_2H represent the anionic and carboxylated forms of an ionisable chemical species, respectively. The pK_a of these chemical species are published elsewhere [72] (Table A.2, Appendix A).

The Gibbs free energy of formation for methoxybenzene (anisole, $C_6H_5OCH_3$) in liquid phase was calculated using a relationship based on Eq., 9, assuming ideal gas-phase conditions and neglecting the volume of the condensed phases

$$\Delta G^0_{f(l)} = \Delta G^0_{f(g)} - R \times T \times \ln\left(\frac{P_{vap}}{P_0}\right) \quad (9)$$

In this reaction, P_{vap} is the vapor pressure of anisole (3.61 mmHg) and P_0 the reference pressure (here, 101.325 kPa). P_{vap} of anisole was taken from Yaws [81] and converted from mmHg to atm after checking its applicable temperature range (236–642 K) (Table A.2, Appendix A). Here, $-R \times T \times \ln\left(\frac{P_{vap}}{P_0}\right)$ corresponds to the standard Gibbs free energy of condensation ($\Delta^g_l G^0$) [75].

The Gibbs free energy of formation for 4-methoxybenzoic acid (*p*-anisic acid, $CH_3C_6H_4OCO_2H$) in solid phase was calculated by using the following reaction (Eq. (10))

$$\Delta G^0_{f(s)} = \Delta G^0_{f(g)} - \Delta^g_{cr} G^0 \quad (10)$$

where $\Delta^g_{cr} G^0$ is the standard Gibbs free energy of sublimation, which is equal to $-R \times T \times \ln\left(\frac{P_{sub}}{P_0}\right)$, with P_{sub} being the sublimation pressure of the compound in its crystalline phase [74] (see Table A.2, Appendix A). As mentioned by Amend and Plyasunov [74], the latter relation is valid only if the vapor pressure over a crystalline phase is low. $\Delta^g_{cr} G^0$ of *p*-anisic acid (46.9 kJ mol^{-1}) was retrieved from Perlovich et al. [82].

In the second approach the ΔG^0_f of 28 *n*-alkylbenzenes (*n*-alkylcyhex, C_{13-40} moieties), 27 *n*-alkylcyclohexanes (*n*-alkylbz, C_{13-39} moieties), 36 *n*-alkanes (C_{3-38} moieties) and 13 medium-to long-chain *n*-fatty acids (C_{9-21} moieties) were calculated in their gaseous, liquid, or solid forms from the second-order group-increment method developed by Domalski and Hearing [64]. Due to the nature of these linear hydrocarbons essentially characterized by fragments consisting of an increment of $-CH_2-$ groups terminated by a methyl, this approach seemed suitable.

Briefly, this method is a practical and compelling way to estimate the enthalpies of formation (ΔH^0_f, kJ mol^{-1}) and standard entropies (S^0) of a large number of organic chemical species in their gas, liquid, or solid phases, based on the known thermochemical properties of their constituent molecular substructures (groups), and the interactions between them. Following this approach, ΔG^0_f of the chemical species cited above were determined as follows (Eqs. (11) and (12)) [50,64]

$$\Delta G^0_f = \Delta H^0_f - T \times \Delta S^0_f \quad (11)$$

where

$$\Delta S^0_f = \sum S^0_{(group)} - \sum_j \upsilon_j \times S^0_{(element)} \quad (12)$$

In these reactions, ΔS^0_f (J mol^{-1} K^{-1}) is the standard entropy of formation of the chemical species, $\sum S^0_{(group)}$ is the sum of the entropies of the constituent groups of the molecule and $\sum_j \upsilon_j \times S^0_{(element)}$ is the stoichiometric (υ_j) sum of the standard entropies of the constituent elements of the molecule. In accordance with Domalski and Hearing [64], standard entropies of the elements were retrieved from Cox et al. [83] and corresponded to: $C_{(c,graphite)}$ (5.74 J mol^{-1} K^{-1}), $H_{2(g)}$ (130.571 J mol^{-1} K^{-1}), and $O_{2(g)}$ (205.043 J mol^{-1} K^{-1}). The standard enthalpy of formation of each chemical species of interest (ΔH^0_f) was calculated by summing the ΔH^0_f of their constituent groups as described by Domalski and Hearing [64]. Otherwise, the ΔG^0_f of *n*-alkylcyclohexanes in their crystalline forms were calculated using the dedicated linear regressions developed by Richard and Helgeson [84], the latter are also based on the work of Domalski and Hearing [64] and Cox et al. [83]. The ΔG^0_f of *n*-tridecylcyclohexane, *n*-tetradecylcyclohexane, and *n*-pentadecylcyclohexane in their liquid forms were then calculated using Eq. (13):

$$\Delta G^0_{f(l)} = \Delta G^0_{f(cr)} + \Delta^l_{cr} G^0 \quad (13)$$

where $\Delta^l_{cr} G^0$ stands for the free energy of fusion of the chemical species (Fig. 1). The latter were deduced from an extrapolation of the values of standard molal enthalpy (ΔH^0_m) and entropy (ΔS^0_m) of melting of six *n*-alkylcyclohexanes listed by Richard and Helgeson [84].

The third approach to calculate the free energies of formation of compounds not available in the literature was to calculate the missing ΔG^0_f of the tetramethylammonium ion (TMA^+, $(CH_3)_4N^+$) following the group-contribution method described by Jankowski et al. [85]. In contrast to the precedent model, this method is designed to directly calculate the ΔG^0_f of chemical species in aqueous solutions from the substructures of the molecule of interest. Therefore, ΔG^0_f of TMA^+ (46.8 kcal$_{th}$ mol^{-1}) was calculated by adding the ΔG^0_f of the $>N^+<$ group (61.4 kcal$_{th}$ mol^{-1}) to the ΔG^0_f of four methyl groups (−3.65 kcal$_{th}$ mol^{-1} each) before converting the sum to kJ mol^{-1}.

2.6. Thermodynamic considerations

The biological standard state of Gibbs energy can be used to estimate whether a chemotrophic biochemical reaction, such as a microbial catabolic reaction, is energetically favorable or more energy-yielding than another in a hypothetical reference frame called standard state. These values are useful for comparing the energy produced by various reactions in this same hypothetical frame of reference, but it must be remembered that the conditions of this hypothetical frame of reference differ from those of all natural habitats because they do not take into account the physical conditions and chemical compositions of natural environments, which are integral to the total Gibbs energy of a reaction.

In natural habitats, the actual Gibbs energy change of a given reaction is further dependent on the temperature, pressure and chemical composition of the environments considered. In fact, in natural environments, the temperature is rarely 25 °C, the concentration of bioreactive substrates are often much lower than 1 M, and the cellular pH can be far from 7 [54,86]. The activities of chemical substrates will depend also on the phase of matter of the chemical species under consideration (aq, g, l or s) and of the chemical speciation. Equations used to account for phase changes and dissolution processes are shown in Fig. 1, and equations for calculating ΔG_r as a function of actual (i.e., cellular) pH, temperature and concentrations have been compiled and discussed previously [50,76,87,88].

In addition, various biological parameters and biotic and abiotic interactions are also involved in determining occurrence and energetics of reactions in natural habitats, and reaction kinetics [51,86]. In fact, the presence of a microorganism with the necessary arsenal of transporters and enzymes, with an affinity matching the concentrations found in the natural environment, is necessary for a catabolic reaction to be biologically possible. In addition, microbial energetic reactions are also subject to biotic (e.g., competition, syntrophy …) and abiotic (e.g., presence of scavengers, toxic compounds …) interactions that can impact them positively or negatively [51,86].

If we postulate that the reactions are biologically possible and not impacted positively or negatively by biotic and abiotic interactions,

comparing the biological standard energy states of various reactions allows us to compare various microbial reactions within the same hypothetical theoretical reference frame.

3. Results and Discussion

In recent years, several articles have reviewed the state of knowledge regarding the ecological, genomic and metabolic aspects of methanogenesis, as well as the evolution of methanogenesis pathways in *Archaea* [47,89]. However, to the best of our knowledge, there is no comprehensive review reporting the substrates of methanogenesis and the associated thermodynamic data. This is the purpose of this work.

In this article, (i) we calculated the biological standard Gibbs energy change of methanogenesis reactions from a wide range of substrates in the same hypothetical reference frame, (ii) we have compiled the biological methanogenesis reactions that definitely exist in nature (i.e., demonstrated *in vitro* under given experimental conditions) and we have listed taxa that perform these reactions, and (iii) we listed the methanogenesis reactions that may occur from proposed substrates and taxa that could perform them.

3.1. Diversity of methanogenesis substrates

At the time of writing, it is established that methanogenesis can be achieved using 152 substrates, plus 41 putative substrates predicted on the basis of 'omics' and biochemical data (Fig. 2) (Table 1, Appendix B, Table B1). The biological standard Gibbs energy change of methanogenesis reactions are >0 for 6.4 % of substrates, between 0 and –30 kJ mol^{-1} CH_4 for 62.8 % of substrates, between −30 and −100 kJ mol^{-1} CH_4 for 22.7 % of substrates, between −100 and −200 kJ mol^{-1} CH_4 for 5.2 % of substrates, and <–200 kJ mol^{-1} CH_4 for 2.9 % of substrates (Table 1, Appendix B, Table B1).

3.1.1. Acetate (-like) substrates

3.1.1.1. Acetate. Acetate ($CH_3CO_2^-$) is a central metabolic intermediate that is present in virtually all known natural ecosystems. In fact, acetate is a key intermediate in the degradation of organic matter, especially in the anaerobic microbial food web, as it is the final product of acetogenesis and some fermentation pathways, and the most important volatile fatty acid produced by anaerobic microbial metabolism [54] (Fig. 3). Abiotic processes also allow the generation of acetate. In deep hot terrestrial subsurface and subseafloor sedimentary habitats with temperatures >50 °C, acetate can be generated by thermochemical conversion of buried organic matter recalcitrant to microbial consumption [107,108]. In digestive systems, acetate is also produced by microbial fermentation, especially of non-digestible foods, and this by-product can re-enter the microbial metabolic cycle, be assimilated by hosts, and/or induce hormonal secretions (e.g., in humans) [11,109].

In open-ecosystems, acetate is subject to rapid turnover and trophic competition, and is therefore rarely accumulated to high concentrations (at least in ecosystems where acetate is primarily derived from the biotic transformation of organic matter) [110,111]. From an overall quantitative point of view, however, acetate is the most available substrate for methanogenesis [92]. For thermodynamic reasons, acetoclastic methanogenesis occurs in anoxic niches where the concentrations of strong oxidants allowing anaerobic respirations are low, and where the pHs are not too alkaline, because at high pHs, acetic acid is in its anionic form and cannot diffuse directly through the membrane [112].

To date, few methanogens have been shown to convert acetate to methane and CO_2. They all belong to the orders *Methanosarcinales* (e.g., *Methanosarcina mazeii* TMA) and *Methanotrichales* (e.g., *Methanothrix soehngenii* GP6) (*Methanothrix* was formerly referred as *Methanosaeta*) [113–115]. However, although acetate accounts for about 0.5 % of all methanogenic substrates (i.e., proven + putative) (Fig. 2) and is catabolized by relatively few methanogenic taxa, its methanogenic conversion may account for about two-thirds of biological methane emissions in some anoxic wetland ecosystems such as rice fields [116]. Under biological standard conditions, the acetoclastic methanogenesis is predicted to be exergonic with a low free-energy change ($\Delta G_r^0 = -11.0$ kJ mol^{-1} CH_4) (Table 1).

3.1.1.2. Pyruvate. Pyruvate ($CH_3COCO_2^-$) is another key intermediate in

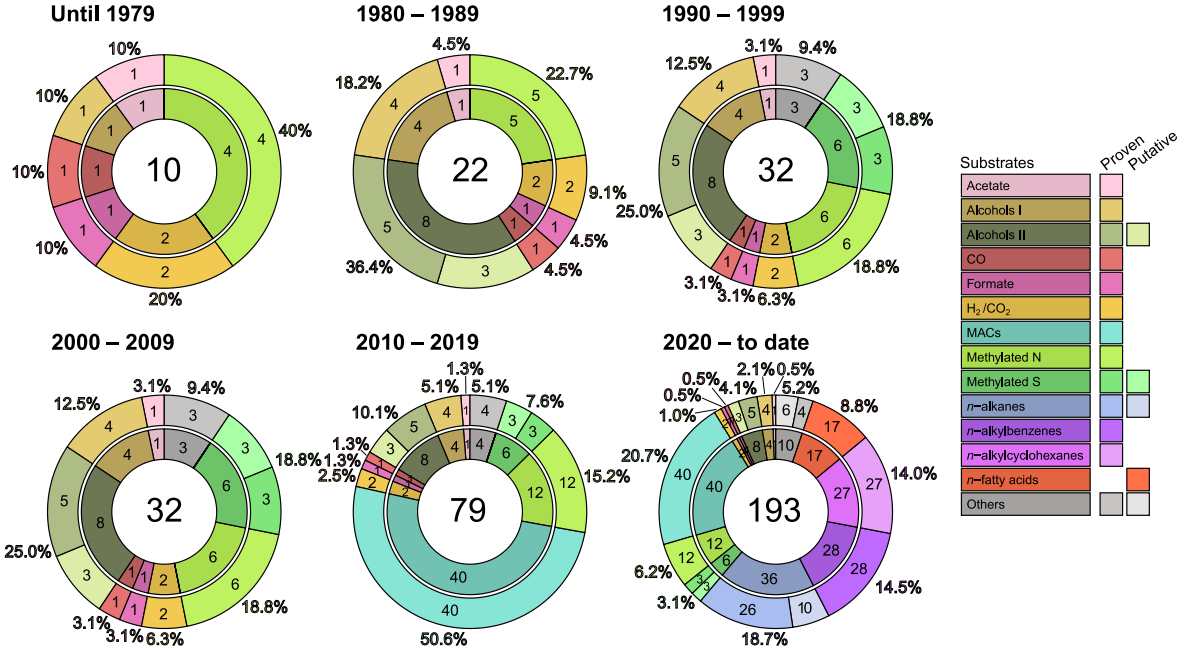

Fig. 2. Cumulated number and proportions of all proven and putative methanogenesis substrates discovered over time (expressed in decades). Inner dark circles: total number (i.e., proven + putative) of substrates in a category. Outer neutral circles: proven substrates. Outer lighter circles: putative substrates. The percentages: relative proportion of substrates in each category. The central values denote the total number of methanogenesis substrates reported at the end of a time series. Others: 2-methylfurfural, 5-methylfurfural, methyliodide, (*S*)-1-phenylethanol, 2-phenylacetate, pyruvate, toluene, *m*-xylene, *o*-xylene, *p*-xylene.

Table 1
Main substrates and potential substrates of methanogenesis, catabolic reactions and biological standard free energies changes of reactions calculated as mentioned in the materials and methods section. Reactions are listed by catabolic pathway from the most favorable to the least favorable. Standard Gibbs free energies are expressed for 298.15 K, 1 atm, pH 7 and 1 M of each chemical species (albeit proton), thus some reactions have been adapted from literature to meet these criteria. Reactions involving sulfide are expressed for $HS^-_{(aq)}$ remembering that $HS^-_{(aq)} \leftrightarrow H_2S_{(aq)}$ equilibrium is very close to neutral pH (pK_a = 6.97–7.05 [61,90]). To avoid confusion, electron donor (H^+, acetate, formate, or ethanol) involved in methyl-reducing hydrogenotrophic reactions is mentioned after the electron acceptor. Carbon dioxide, proton and methane are in their aqueous form while water is in liquid phase. All other products are in the same phase as the substrate, with the exception of 4-hydroxy-benzoic acid and phenol that are in aqueous forms. A more extensive list of methanogenesis reactions involving other substrates is available in Table B.1 (Appendix B). MMPA: 3-*S*-methylmercaptopropionate; aq., aqueous; F., formate; G., genomic potential; I: primary alcohol; II: secondary alcohol; M.: mixed approaches; P.: physiological evidence. *: equation deduced from the publication; **: hypothesized by the authors.

Catabolic pathway	Substrate (phase)	Reaction	ΔG^0_r (kJ mol^{-1})	ΔG^0_r (kJ mol^{-1} CH_4)	Evidence	Reference for evidence of methanogenesis
ACETOCLASTIC						
Acetate (–like)	Pyruvate (aq)	$4CH_3COCO_2^- + 2H_2O \rightarrow CH_4 + 4CH_3CO_2^- + 3CO_2$	−297.2	−297.2	P.	[43]
	Pyruvate (aq)	$4CH_3COCO_2^- + 4H^+ + 2H_2O \rightarrow 5CH_4 + 7CO_2$	−815.8	−163.2	P.	[91]
	Pyruvate (aq)	$CH_3COCO_2^- + H^+ + H_2O \rightarrow CH_4 + H_2 + 2CO_2$	−37.1	−37.1	P.	[91]
	Acetate (aq)	$CH_3CO_2^- + H^+ \rightarrow CH_4 + 2CO_2$	−11.0	−11.0	P.	[92]
CO_2-REDUCING HYDROGENOTROPHIC/ALCOHOLOTROPHIC/FORMATOTROPHIC						
CO_2 (–like)	Carbon monoxide (aq)	$4CO + 2H_2O \rightarrow CH_4 + 3CO_2$	−238.4	−238.4	P.	[31]
	CO_2 (aq) + H_2 (aq)	$4H_2 + CO_2 \rightarrow CH_4 + 2H_2O$	−193.0	−193.0	P.	[93]
Formate	Formate (aq)	$4HCO_2^- + 4H^+ \rightarrow CH_4 + 3CO_2 + 2H_2O$	−102.9	−102.9	P.	[94]
Alcohols I	CO_2 (aq) + Ethanol (aq)	$2CH_3CH_2OH + CO_2 \rightarrow CH_4 + 2CH_3CO_2^- + 2H^+$	−103.5	−103.5	P.	[42]
	CO_2 (aq) + Propanol (aq)	$2CH_3(CH_2)_2OH + CO_2 \rightarrow CH_4 + 2CH_3CH_2CO_2^- + 2H^+$	−98.9	−98.9	P., *	[42]
	CO_2 (aq) + Butanol (aq)	$2CH_3(CH_2)_3OH + CO_2 \rightarrow CH_4 + 2CH_3(CH_2)_2CO_2^- + 2H^+$	−89.9	−89.9	P., *	[42]
Alcohols II	CO_2 (aq) + 2-butanol (aq)	$4CH_3CHOHCH_2CH_3 + CO_2 \rightarrow CH_4 + 4CH_3COCH_2CH_3 + 2H_2O$	−34.2	−34.2	P., *	[44]
	CO_2 (aq) + 2-propanol (aq)	$4CH_3CHOHCH_3 + CO_2 \rightarrow CH_4 + 4CH_3COCH_3 + 2H_2O$	−23.8	−23.8	P.	[42]
	CO_2 (aq) + 2,3-butanediol (aq)	$4(CH_3CHOH)_2 + CO_2 \rightarrow CH_4 + 4(CH_3CO)_2 + 2H_2O$	+45.2	+45.2	P., *	[29]
	CO_2 (aq) + Cyclopentanol (aq)	$4C_5H_9OH + CO_2 \rightarrow CH_4 + 4C_5H_8O + 2H_2O$	+141.0	+141.0	P.	[29]
METHYL-REDUCING HYDROGENOTROPHIC/METHYL-REDUCING FORMATOTROPHIC						
Amines	Methylamine (aq) + H_2 (aq)	$CH_3NH_3^+ + H_2 \rightarrow CH_4 + NH_4^+$	−91.4	−91.4	P., *	[95]
	Trimethylamine (aq) + H_2 (aq)	$(CH_3)_3NH^+ + 3H_2 \rightarrow 3CH_4 + NH_4^+$	−272.5	−90.8	P.	[96]
	Dimethylamine (aq) + H_2 (aq)	$(CH_3)_2NH_2^+ + 2H_2 \rightarrow 2CH_4 + NH_4^+$	−180.0	−90.0	P., *	[95]
	Methylamine (aq) + F. (aq)	$CH_3NH_3^+ + HCO_2^- + H^+ \rightarrow CH_4 + CO_2 + NH_4^+$	−68.8	−68.8	P., *	[97]
	Trimethylamine (aq) + F. (aq)	$(CH_3)_3NH^+ + 3HCO_2^- + 3H^+ \rightarrow 3CH_4 + 3CO_2 + NH_4^+$	−204.9	−68.3	P., *	[98]
	Dimethylamine (aq) + F. (aq)	$(CH_3)_2NH_2^+ + 2HCO_2^- + 2H^+ \rightarrow 2CH_4 + 2CO_2 + NH_4^+$	−134.9	−67.5	P., *	[97]
Quaternary amines	Tetramethylammonium (aq) + H_2 (aq)	$(CH_3)_4N^+ + 4H_2 \rightarrow 4CH_4 + NH_4^+$	−483.0	−120.8	P., *	[98]
	Tetrametylammonium (aq) + F. (aq)	$(CH_3)_4N^+ + 4HCO_2^- + 4H^+ \rightarrow 4CH_4 + 4CO_2 + NH_4^+$	−276.4	−69.1	P., *	[98]
S-containing compounds	Methanethiol (aq) + H_2 (aq)	$CH_3SH + H_2 \rightarrow CH_4 + HS^- + H^+$	−72.6	−72.6	G, *	[17]
	Dimethylsulfide (aq) + H_2 (aq)	$(CH_3)_2S + 2H_2 \rightarrow 2CH_4 + HS^- + H^+$	−140.3	−70.1	G, *	[17]
	MMPA (aq) + H_2 (aq)	$CH_3S(CH_2)_2CO_2^- + H_2 \rightarrow CH_4 + HS(CH_2)_2CO_2^-$	−68.7	−68.7	P., *	[99]
	Methanethiol (aq) + F. (aq)	$CH_3SH + HCO_2^- \rightarrow CH_4 + CO_2 + HS^-$	−50.1	−50.1	P., *	[98]
	MMPA (aq) + F. (aq)	$CH_3S(CH_2)_2CO_2^- + HCO_2^- + 2H^+ \rightarrow CH_4 + CO_2 + HS(CH_2)_2CO_2^-$	−46.1	−46.1	P., *	[99]
	Dimethylsulfide (aq) + F. (aq)	$(CH_3)_2S + 2HCO_2^- + 2H^+ \rightarrow 2CH_4 + 2CO_2 + HS^-$	−55.3	−27.7	P., *	[99]
Alcohols	Methanol (aq) + H_2 (aq)	$CH_3OH + H_2 \rightarrow CH_4 + H_2O$	−113.7	−113.7	P.	[100]
	Methanol (aq) + Ethanol (aq)	$2CH_3OH + CH_3CH_2OH \rightarrow 2CH_4 + H_2O + CH_3CO_2^-$	−182.7	−91.4	P., **	[101]
	Methanol (aq) + F. (aq)	$CH_3OH + HCO_2^- + H^+ \rightarrow CH_4 + CO_2 + H_2O$	−91.2	−91.2	P., *	[97]
	Methanol (aq) + Acetate (aq)	$4CH_3OH + CH_3CO_2^- + H^+ \rightarrow 4CH_4 + 2CO_2 + 2H_2O$	−273.0	−68.2	P., **	[102]
METHYL-DISMUTATING						
Alcohol I	Methanol (aq)	$4CH_3OH \rightarrow 3CH_4 + 2H_2O + CO_2$	−262.0	−87.3	P.	[34]
S-containing compounds	Methanethiol (aq)	$4CH_3SH + 2H_2O \rightarrow 3CH_4 + CO_2 + 4HS^- + 4H^+$	−97.5	−32.5	P.	[33]
	Dimethylsufide (aq)	$2(CH_3)_2S + 2H_2O \rightarrow 3CH_4 + CO_2 + 2HS^- + 2H^+$	−87.6	−29.2	P.	[33]
	MMPA (aq)	$4CH_3S(CH_2)_2CO_2^- + 2H_2O \rightarrow 3CH_4 + CO_2 + 4HS(CH_2)_2CO_2^-$	−81.6	−27.2	P.	[38]
Amines	Methylamine (aq)	$4CH_3NH_3^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 4NH_4^+$	−172.4	−57.5	P.	[34]
	Trimethylamine (aq)	$4(CH_3)_3NH^+ + 6H_2O \rightarrow 9CH_4 + 3CO_2 + 4NH_4^+$	−510.9	−56.8	P.	[34]
	Dimethylamine (aq)	$2(CH_3)_2NH_2^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + 2NH_4^+$	−167.0	−55.7	P.	[34]

(*continued on next page*)

Table 1 (*continued*)

Catabolic pathway	Substrate (phase)	Reaction	ΔG_r^0 (kJ mol^{-1})	ΔG_r^0 (kJ mol^{-1} CH_4)	Evidence	Reference for evidence of methanogenesis
	Dimethylethanolamine (aq)	$2(CH_3)_2N(CH_2)_2OH + 2H_2O \rightarrow 3CH_4 + 2H_2N(CH_2)_2OH + CO_2$	−100.6	−33.5	P.	[41]
	Methylethanolamine (aq)	$4(CH_3)NH(CH_2)_2OH + 2H_2O \rightarrow 3CH_4 + 4H_2N(CH_2)_2OH + CO_2$	−95.6	−31.9	P.	[41]
Quaternary amines	Betaine (aq)	$4(CH_3)_3N^+(CH_2)CO_2^- + 2H_2O \rightarrow 3CH_4 + 4(CH_3)_2N^+(CH_2)CO_2^- + CO_2$	−722.0	−240.7	P.	[40]
	Choline (aq)	$4(CH_3)_3N^+(CH_2)_2OH + 6H_2O \rightarrow 9CH_4 + 4H_2N(CH_2)_2OH + 3CO_2$	−1015.2	−112.8	P.	[41]
	Tetramethylammonium (aq)	$(CH_3)_4N^+ + 2H_2O \rightarrow 3CH_4 + CO_2 + NH_4^+$	−290.1	−96.7	P.	[37]
Halogens	Methyliodide (aq)	$4CH_2I + 2H_2O \rightarrow 3CH_4 + CO_2 + 4I^- + H^+$	−461.9	−154.0	P.	[38]
METHOXYL-DISMUTATING						
Aromatics	3,5-dimethoxy-4-hydroxybenzoate (aq)	$2C_6H_5(OCH_3)_2OHCO_2^- + 2H_2O \rightarrow 3CH_4 + 2C_6H_5(OH)_3CO_2^- + CO_2$	−500	−167	P., *	[27]
	3,4-dimethoxybenzoate (aq)	$2C_6H_5(OCH_3)_2CO_2^- + 2H_2O \rightarrow 3CH_4 + 2C_6H_5(OH)_2CO_2^- + CO_2$	−332.8	−110.9	P., *	[27]
	3,4,5-trimethoxybenzoate (aq)	$4C_6H_2(OCH_3)_3CO_2^- + 6H_2O \rightarrow 9CH_4 + 4C_6H_2(OH)_3CO_2^- + 3CO_2$	−965	−107	P., *	[27]
	2-methoxyphenol (aq)	$4C_6H_4OH(OCH_3) + 2H_2O \rightarrow 3CH_4 + 4C_6H_4(OH)_2 + CO_2$	−259.7	−86.6	P., *	[27]
	4-methoxyphenol (aq)	$4C_6H_4OH(OCH_3) + 2H_2O \rightarrow 3CH_4 + 4C_6H_4(OH)_2 + CO_2$	−257.8	−85.93	P., *	[27]
	Methoxybenzene (l)	$4C_6H_5(OCH_3) + 2H_2O \rightarrow 3CH_4 + 4C_6H_5 + CO_2$	−228.2	−76.1	P., *	[27]
	4-methoxybenzoic acid (s)	$4C_6H_5(OCH_3)CO_2H + 2H_2O \rightarrow 3CH_4 + 4C_6H_5OHCO_2^- + CO_2$	−116.4	−38.8	P., *	[27]
ALKANOTROPHIC						
n-Alkanes	Butane (aq)	$4C_4H_{10} + 6H_2O \rightarrow 13CH_4 + 3CO_2$	−182.3	−14.0	G., *	[18]
	Propane (aq)	$2C_3H_8 + 2H_2O \rightarrow 5CH_4 + CO_2$	−66.4	−12.3	G., *	[18]
	Hexadecane (l)	$4C_{16}H_{34} + 30H_2O \rightarrow 49CH_4 + 15CO_2$	−555.9	−11.3	G., *	[21]
ALKYLOTROPHIC						
n-Alkyles	Hexadecylbenzene (s)	$4C_6H_5(CH_2)_{15}CH_3 + 50H_2O \rightarrow 63CH_4 + 25CO_2$	−718.5	−11.4	M., *	[28]
	Hexadecylcyclohexane (s)	$2C_6H_{11}(CH_2)_{15}CH_3 + 22H_2O \rightarrow 33CH_4 + 11CO_2$	−89.0	+2.7	M., *	[28]
FATTY ACIDS OXIDATION						
Fatty acids	Palmitic acid (s)	$2CH_3(CH_2)_{14}CO_2H + 14H_2O \rightarrow 23CH_4 + 9CO_2$	−323.0	−14.0	M., *	[28]

organic matter degradation, as it is a common by-product of the oxidation of mono-, di-, oligo-saccharides, lipids or protein/amino acids [117–119].

In addition, pyruvate is itself a precursor of various methanogenic substrates. For example, in the rumen, pyruvate is synthetized from the degradation of hexoses and pentoses (themselves derived from dietary carbohydrates such as cellulose for example), before being metabolized into volatile fatty acids (e.g., acetate), formate, alcohols (methanol, ethanol) and CO_2/ H_2 [120]. Pyruvate-based methanogenesis is probably surpassed by more competitive metabolisms that consume pyruvate in environments containing oxidants. However, in anoxic habitats depleted of NO_3^-, Mn^{4+}, Fe^{3+}, and SO_4^{2-}, free energy change of pyruvate methanogenesis could alternatively be more ($\Delta G_r^0 = -297.2$ kJ mol^{-1} CH_4) (Table 1) or less favorable ($\Delta G_r^{0'} = -37.1$ kJ mol^{-1} CH_4) than pyruvate fermentation to lactate ($\Delta G_r^{0'} = -60.1$ kJ mol^{-1} lactate) depending on the metabolic pathway involved. Nevertheless, this compound is likely to be little or not available *in situ*.

To date, only several *Methanococcus* spp. (*Methanococcales*) and *Methanosarcina* spp. (*Methanosarcinales*) have been shown to produce methane and acetate from the oxidation of pyruvate [43,121]. In addition, a mutant of *Methanosarcina barkeri* Fusaro has also been reported to convert pyruvate to methane and CO_2 [91].

3.1.2. Dihydrogen

Dihydrogen (H_2) is present in almost all known natural ecosystems, where it plays a key role as a central metabolic intermediate or by-product for a large number of living organisms. Thus, not all biological and abiotic sources and sinks of H_2 can be listed. Nevertheless, we can mention that H_2 is released at almost every stage of the anaerobic degradation of organic matter, including hydrolysis, fermentation, and the syntrophic conversion of short-chain fatty acids (including acetate) and alcohols [122,123]. It can also result from the thermochemical transformation of buried organic material (e.g., water radiolysis, low temperature serpentinization), sometimes driven by microbial activities [108,124–126]. As H_2 is subject to a rapid turnover, it does not necessarily accumulate in anoxic environments devoid of strong oxidants. It can therefore be the subject of trophic competition, especially between sulfate-reducing *Bacteria* and methanogenic *Archaea* [92].

In fact, as well as having a higher growth yield, sulfate-reducing *Bacteria* have a higher affinity for H_2 (i.e., consumption threshold <1 *P* (H_2)) than many CO_2-reducing hydrogenotrophic methanogenic *Archaea* (>2 *P* (H_2)), thus out-competing them in H_2-limited environments [92,127–130]. By contrast, the methyl-reducing hydrogenotrophs *Methanomassiliicoccus luminyensis* B10^T (*Methanomassiliicoccales*), *Methanosphaera stadtmanae* MCB-3^T (*Methanobacteriales*), and *Methanimicrococcus blatticola* PA^T (*Methanosarcinales*) have a lower H_2 consumption threshold (≤1 *P* (H_2)), suggesting that these *Archaea* have a strong affinity for H_2 that enables them to cohabit and not compete with sulfate-reducing *Bacteria* [128].

Methanogenic *Archaea* can also maintain syntrophic relationships with H_2-producing *Bacteria* and/or protists [131–134]. As a kind of example, excessive production of H_2 in the environment by a syntrophic partner can inhibit its metabolism and cell growth [48,133]. To mitigate this phenomenon, hydrogenotrophic methanogens limit this excess by consuming H_2, and thus rebalance the thermodynamic equilibrium of the sum of the two reactions (i.e., ΔG_r of H_2-production + methanogenesis <0) enabling both strains to maintain their growth [48]. In

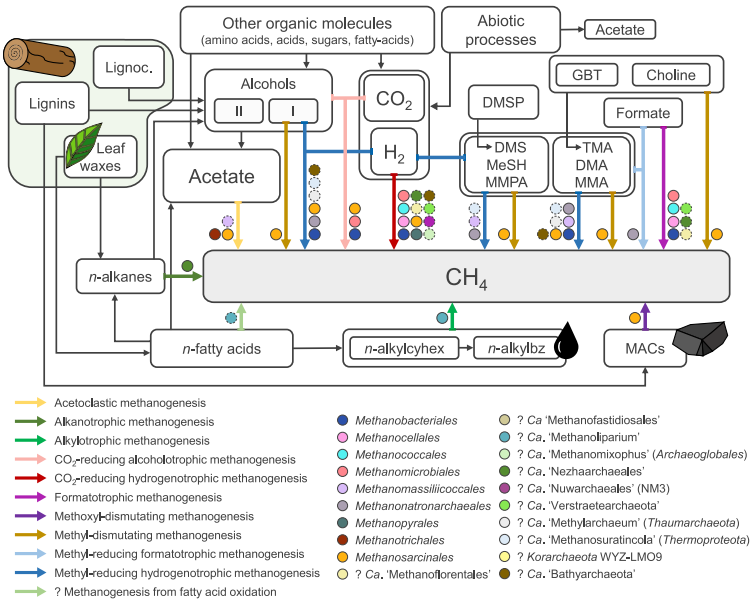

Fig. 3. Diagram illustrating the degradation of organic matter leading to the production of the main substrates of methanogenesis and the methanogenic players involved. Black arrows represent metabolic or geological processes leading to the formation of methanogenic substrates, including hydrolysis, fermentation, acetogenesis and syntrophic acetate oxidation. Homoacetogenesis is not shown. Colored arrows indicate methanogenic pathways. Solid circles indicate a metabolic property confirmed from physiological or functional approaches, while dashed circles indicate a metabolism predicted from (meta-)genomic analyses. The color of the circle indicates in which group this property has been demonstrated or suggest. Metabolism and/or lineages shown here are taken from Sowers [103] and from the references cited in the main text while those absent are cited in the following articles: Evans et al. [104], Hatzenpichler et al. [105], and Speth and Orphan [106]. Legend: *n*-alkylbz: *n*-alkylbenzenes; *n*-alkylcyhex: *n*-alkylcyclohexanes; DMA: Dimethylamine; DMS: Dimethylsulfide; DMSP: Dimethylsulfoniopropionate; GBT: Glycine betaine; I: Primary alcohols; II: Secondary alcohols; Lignoc.: Lignocellulose; MACs: methoxylated aromatic compounds; MeSH: Methanethiol; MMA: Monomethylamine; MMPA: 3-*S*-Methylmercaptopropionate; TMA: Trimethylamine. ? Putative metabolic pathway or metabolic capacity.

addition, many biotic and abiotic factors, such as temperature, pH, or substrate availability can affect these complex syntrophic interactions [6,48,92,122,133–138]. Finally, although thermodynamically favorable, syntrophic cooperation can yield little free energy change for partners in some cases, e.g., $\Delta G_r^0 = -11.0$ kJ mol^{-1} for acetate fermentation coupled to H_2/ CO_2 methanogenesis.

3.1.3. CO_2 (-like) substrates

3.1.3.1. Carbon dioxide. Like acetate and H_2, carbon dioxide (CO_2) is a key metabolite produced and consumed in virtually all known natural environments by a myriad of living organisms. For example, we can mention that CO_2 is released during almost every stage of the anaerobic degradation of organic matter, including during non-CO_2-reducing methanogenesis (e.g., acetoclastic, methyl-, and methoxyl-dismutations) [27,122]. Furthermore, geological processes like metamorphism, mantle outgassing, fluid-rock reactions, diagenesis, thermal activation of organic matter, Fischer-Tropsch reactions and so on, can also release CO_2 which can support microbial metabolism, including methanogenesis [124,139]. Until the late 2010s, CO_2-reducing hydrogenotrophic methanogenesis pathway was considered as the most ancestral way to produce methane, this form of methanogenesis being carried out by all six methanogenic orders identified at that time [140]. This paradigm has recently been challenged by the discovery of several non-CO_2-reducing hydrogenotrophic methanogen lineages and new metabolic pathways [16,47,98,141]. In the CO_2-reducing methanogenesis pathway, the formyl-methanofuran dehydrogenase (FwdABCDFG) initiates the first step of CO_2 reduction to methane *via* the carbonyl branch of the Wood-Ljungdahl (CBWL) [142]. From a thermodynamic point of view, methanogenesis based on CO_2 reduction and H_2 oxidation is exergonic, with a $\Delta G_r^{0'}$ equal to −193.0 kJ mol^{-1} CH_4.

3.1.3.2. Formate. Formate (methanoate, HCO_2^-) is a common product of fermentation deriving from a large variety of more complex molecules comprising mono-, di-, and oligosaccharides, glycine, or pyruvate, for example [92,143–145]. Formate can be found in open- (e.g., marine sediments, sewage sludge) and digestive (e.g., termite guts, red deer rumen, human colon) environments [144–148]. If formate is found in low concentration and subject to turn-over in the sulfate reduction zone of marine sediments, it could in contrast considerably accumulate in termite guts [146,147]. Similarly to H_2, formate is also an important electron carrier involved in methanogenesis, but also in the interspecies electron transfers taking place in microbial syntrophic relationships [92, 134,145,148–151]. Formate can either be dehydrogenated into CO_2 and H_2 by a formate dehydrogenase (FdhAB) (i.e., a reversible reaction) in the formatotrophic pathway, before entering the CO_2-reducing hydrogenotrophic pathway, or serve as an electron donor for the reduction of various methylated compounds (i.e., methyl-reducing formatotrophic methanogenesis) (see below) [94,98]. If the first reaction is performed by the majority of CO_2-reducing hydrogenotrophic methanogens without cytochromes, the latter has only been demonstrated for some *Methanonatronarchaeales* representatives (see below) [98,123]. Disproportionation of formate followed by its methanogenic conversion through the CBWL is an exergonic reaction, with a $\Delta G_r^{0'}$ equals to −102.9 kJ mol^{-1} CH_4.

3.1.3.3. CO. Carbon monoxide (CO) is a toxic molecule widely distributed on Earth, being produced by abiotic (e.g., biomass combustion) and biotic reactions. For example, it can be produced by yeast, *Cyanobacteria* and other (non-)phototrophic *Bacteria*, green algae, higher plants, and even siphonophores [152,153]. CO can also result from abiotic conversion of buried organic material [124,126]. From a physiological point of view, the resulting products of CO oxidation are H_2 and CO_2, the latter both entering the CBWL pathway to form

methane. Interestingly, *in vitro* concentrations of H_2 and CO seems to regulate the activity of CO-based methanogenesis [154]. If *Methanothermobacter marburgensis* Marburg (*Methanobacteriales*), *Methanothermobacter thermautotrophicus* ΔH^T, *Methanosarcina acetivorans* $C2A^T$, and *Methanosarcina barkeri* (several strains) are the most studied CO-metabolizing methanogenic *Archaea*, many other have been demonstrated or suspected to perform this reaction [31,155–161]. From a thermodynamic point of view, disproportionation of CO to methane and CO_2 is very exergonic, with a $\Delta G_r^{0'}$ of −238.4 kJ mol^{-1} CH_4.

3.1.4. Alcohol substrates

Primary and secondary alcohols have been demonstrated to serve as electron donors for CO_2-reduction by some methanogenic *Archaea*. To do so, secondary and cyclic alcohols are oxidized to their corresponding ketones by alcohol dehydrogenases, while ethanol, propanol, and butanol are oxidized to monocarboxylic acids by aldehyde dehydrogenases [162]. However, while methane can be produced from secondary alcohols, these do not necessarily support cell growth [163]. Furthermore, since information on the importance of alcohols importance in nature is limited, only generalities can be given below [164].

3.1.4.1. Methanol. A common precursor of methanol in open natural environments (e.g., anoxic marine and freshwater sediments, salt marshes, soils, rice paddies, hypersaline environments) and digestive habitats (e.g., sheep and bovine rumens, human gut) is pectin, a nearly ubiquitous macromolecule that is one of the main components of plant cell walls (notably fruits and vegetables) and *Chlorophyta* algae, and of the mucilaginous wall layers of *Cyanobacteria* [165–168]. Under anoxic conditions, methanol derives from the demethylesterification of the methoxy group (–OCH_3) of homogalacturonan [168]. Other secondary precursors of methanol are lignins and xylenes [167]. In methanogens, methanol can be metabolized *via* two distinct pathways. On one hand, methanol can enter the methyl-dismutating pathway, and on the other hand, be disproportionated into methane and CO_2. This metabolism has been observed in various *Methanosarcinales* [169]. On the other hand, methanol can also serve as an electron acceptor for the oxidation of H_2, formate, acetate or – potentially – ethanol [16,97,101,102]. These catabolic capacities have been demonstrated for *Methanomassiliicoccus luminyensis* $B10^T$, *Methanonatronarchaeum thermophilum* AME^T, *Methanosarcina* sp. TM-1 and *Methanosphaera* sp. WGK6 (*Methanobacteriales*), respectively. It is noteworthy that methanol is consider a 'non-competitive' substrate for methanogenesis, as it is not degraded by sulfate-reducing *Bacteria* [170]. Under biological standard conditions, methanogenesis from methanol is rather energetic, with a $\Delta G_r^{0'}$ of up to −87.3 kJ mol^{-1} CH_4 when methanol is disproportionated in the methyl-dismutating pathway, and −113.7, −91.2, and −68.2 kJ mol^{-1} CH_4, when methanol is reduced by H_2, formate or acetate oxidation, respectively (Table 1).

3.1.4.2. Ethanol. Ethanol (CH_3CH_2OH) is present in a large number of anoxic open-environments (sediments, soils, wetlands) and digestive tracts [164,171,172]. It usually results from the direct or indirect conversion of molecules derived from plants including lignocellulose, starch, pentose and hexose sugars (e.g., D-glucose, D-xylose), and even carbon monoxide (Fig. 3) [173–175]. Some of the best-known natural ethanol producers are yeasts, but this metabolite can also be produced by various representatives of facultative and strictly anaerobic acetoclastic bacterial genera [172,175–178]. Moreover, recent studies suggest that ethanol may also be a metabolic by-product released by diverse uncultivated archaeal taxa inhabiting the reduced layers of marine sediments ([179], and references therein). Ethanol does not accumulate much in nature, as it is either directly converted to acetate by homoacetogenic or sulfate-reducing *Bacteria*, or consumed through a syntrophic association between the latter and a CO_2-reducing hydrogenotrophic methanogen [137,180]. To date, only *Methanogenium organophilum* CV^T and *Methanofollis ethanolicus* $HASU^T$ (two *Methanomicrobiales*) have been shown to produce methane from CO_2 reduction coupled with ethanol oxidation, *via* the CO_2-reducing alcoholotrophic pathway [181,182]. This methanogenic reaction is exergonic, with a $\Delta G_r^{0'}$ equals to −103.5 kJ mol^{-1} CH_4. As mentioned above, ethanol could probably also be used to reduce methanol to produce methane.

3.1.4.3. Other primary alcohols. To date, the natural production of *n*-butanol (1-butanol, $CH_3(CH_2)_3OH$) has only been demonstrated by a number of anaerobic representatives of the genus *Clostridium*, which produce this compound by fermenting various types of sugar- and starch substrates (e.g., wheat straws, corn) [178,183,184]. On the other hand, *n*-propanol (1-propanol, $CH_3(CH_2)_2OH$) is generally produced from 1, 2-propanediol (propylene glycol, $CH_3CHOHCH_2OH$) by fermentation carried out by several acetogenic *Bacteria*, sometimes in partnership with methanogenic *Archaea* [185,186]. Propylene glycol is derived from the anaerobic degradation of fucose and rhamnose, which are generally present in bacterial polysaccharides or plant cell walls [186]. No information could be found about natural habitats that may contain isobutanol (2-methyl-1-propanol, $(CH_3)_2CHCH_2OH$).

As for ethanol, methanogenesis based on the oxidation of *n*-propanol and/or *n*-butanol is carried out only by *Methanogenium organophilum* CV^T and *Methanofollis ethanolicus* $HASU^T$, through the CO_2-reducing alcoholotrophic pathway [42,181,187]. Furthermore, these alcohols could potentially serve as metabolic intermediates in the methanogenic degradation of *n*-fatty acids (see below). Thermodynamically, under standard biological conditions, methanogenesis from the oxidation of *n*-propanol and *n*-butanol are exergonic with $\Delta G_r^{0'}$ equal to −98.9 and −89.9 kJ mol^{-1} CH_4, respectively.

3.1.4.4. Secondary alcohols. Secondary alcohols like 2-propanol (isopropanol, $CH_3CH(OH)CH_3$) and 2-butanol (butan-2-ol, $CH_3CH(OH)CH_2CH_3$) can derive from the oxidation of their corresponding *n*-alkane (see below) by the methylotrophic *Bacteria* activity [188,189]. 2-Butanol could also be indirectly produced from 2,3-butanediol ($(CH_3CHOH)_2$), a common by-product of pyruvate fermentation. Methanogenesis from 2-propanol and 2-butanol oxidation to butanone ($CH_3C(O)CH_2CH_3$) and acetone ($(CH_3)_2CO$), respectively, can be performed by a limited number of species and strains affiliated to orders *Methanomicrobiales* (e.g., *Methanolacinia paynteri* $G\text{-}2000^T$) and *Methanobacteriales* (e.g., *Methanobacterium palustre* F^T) [182,190–192]. Methanogenesis from 2-butanol and 2-propanol oxidation are exergonic with $\Delta G_r^{0'}$ values equal to −34.2 and −23.8 kJ mol^{-1} CH_4, respectively.

Cyclopentanol ($(CH_2)_4CHOH$) has been reported to play a role in the formation of clathrate hydrates, in presence of methane [193]. Its degradation has been identified among some of the methanogenic *Archaea* capable of oxidizing secondary alcohols (e.g., *Methanobacterium congolens* C^T) [29,163]. Methane production from cyclopentanol oxidation to cyclopentanone ($(CH_2)_4CO$) is very endergonic under biological standard conditions with a $\Delta G_r^{0'}$ equals to +141.0 kJ mol^{-1} CH_4.

3.1.5. Methylated amine compounds

Methylated amines (MAs) are compounds methylated in C_1 that are common and originate from the anaerobic degradation of organic amine detritus. The most abundant amino compounds used by methanogens are monomethylamine (MMA, $(CH_3)NH_3^+$), dimethylamine (DMA, $(CH_3)_2NH_2^+$) and trimethylamine (TMA, $(CH_3)_3NH^+$) [194,195]. TMA is mainly derived from the fermentative degradation of common compounds such as carnitine, choline, or glycine betaine (GBT) as well as from the bacterial reduction of trimethylamine-*N*-oxide (Fig. 3) [13, 196–198]. These precursors are globally widespread in many ecosystems, especially in coastal environments, as they are abundantly produced by marine biota as membrane components or osmolytes [199,

200]. In digestive systems, TMA is derived from the degradation of various foods such as red meat, eggs, soy, or seafood [201,202]. MAs are considered non-competitive substrates for methanogens, because sulfate-reducing *Bacteria* are unable to degrade them [130,203–205]. Methanogenesis based on these compounds could be the dominant way of methane production in relatively sulfate-rich environments, such as the near-surface sediment layers of various marine habitats (coastal saltmarshes, cold seeps, seagrass meadows or hypersaline mud volcanoes) [124,206–210]. Many species of MA-metabolizing methanogens have also been isolated from terrestrial environments and even from the hindguts of arthropod cockroaches [211–213]. From a metabolic standpoint, TMA, DMA, and MMA can either be disproportionated through the methyl-dismutating pathway, or act as terminal electron acceptors (i.e., with H_2 and/or formate as electron donors) in the methyl-dependent hydrogenotrophic and/or methyl-reducing formatotrophic pathway. The former pathway is used by almost all representatives of the *Methanosarcinales* genera, while the latter is used by representatives of the alkaliphilic and halophilic *Methanonatronarchaeales* (e.g., *Methanonatronarchaeum thermophilum* AMET1^T, and *Ca.* 'Methanohalarchaeum thermophilum' HMET1^T) [97,98,103]. It should also be noted that *N*,*N*-dimethylethylamine ($(CH_3)_2NCH_2CH_3$) can also be degraded to methane and ethylamine by various *Methanosarcina barkeri* strains, but is not considered an important substrate for this species [32,34]. In this reaction, *N*-methylethylamine (MEA, $CH_3NHCH_2CH_3$) is a metabolic intermediate that temporarily accumulates and is subsequently consumed. Thermodynamically, $\Delta G_r^{0'}$ of TMA, DMA and MMA through the methyl-dismutating methanogenesis are −56.8, −55.7 and −57.5 kJ mol^{-1} CH_4, respectively (Table 1). If these compounds are used *via* the methyl-reducing hydrogenotrophic methanogenesis, these values reach −90.8, −90.0 and −91.4 kJ mol^{-1} CH_4, respectively. Alternatively, reactions *via* this pathway are less favorable when formate is the electron donor (−68.3, −67.5, and −68.8 kJ mol^{-1} CH_4, respectively). Biological standard free energy changes required for each demethylation step in the sequence (i.e., TMA > DMA, and DMA > MMA) are listed in Table B.1 (Appendix B) for each metabolic pathway. Since no ΔG_r^0 values could be found for *N*-methylethylamine and *N*,*N*-dimethylethylamine, no thermodynamic data could be calculated for methanogenesis reactions from these substrates.

Quaternary amines (QAs) are nitrogenous compounds in which the positively charged nitrogen atom is bonded to four alkyl or aryl groups. To our knowledge, three QAs have been demonstrated to be used as substrates for methanogenesis, namely choline (*N*,*N*,*N*-trimethylethanolamine, $(CH_3)_3N^+(CH_2)_2OH$), glycine betaine (GBT, *N*,*N*,*N*-trimethylglycine, $(CH_3)_3N^+(CH_2)CO_2^-$), and tetramethylammonium ($(CH_3)_4N^+$).

Choline is widely distributed in natural environments as a degradation product of phosphatidylcholine, a structural component of cell membranes [197]. It can be degraded to methane and ethanolamine *via* the intermediates *N*,*N*-dimethylethanolamine (DMEA, $(CH_3)_2N(CH_2)_2OH$) and *N*-monomethylethanolamine (MMEA, $(CH_3)NH(CH_2)_2OH$). To date, eight strains of *Methanococcoides* (*Methanosarcinales*) have been identified as using choline as a direct substrate [41,214,215]. DMEA can also be used as a direct substrate by fourteen strains of *Methanococcoides*, whereas no methanogenesis activity could be observed in pure cultures grown on MMEA [41,214]. Under biological standard conditions, methanogenesis from choline is predicted to be exergonic with a high free-energy change ($\Delta G_r^{0'} = -112.8$ kJ mol^{-1} CH_4) (Table 1).

Glycine betaine is a very common osmolyte produced in marine or hypersaline settings. It can be converted to methane and *N*,*N*-dimethylglycine (DMG), by five *Methanococcoides* strains and one *Methanosarcinales* (*Methanolobus vulcani* B1d) [40,214–216]. However, surprisingly, none of the strains used DMG or sarcosine (*N*-monomethylglycine) as direct substrates for methanogenesis. Under biological standard conditions, methanogenesis from glycine betaine is predicted to be one of the most exergonic reactions among all identified methanogenesis substrates, with a $\Delta G_r^{0'}$ equal to −240.7 kJ mol^{-1} CH_4.

Finally, tetramethylammonium (TMA^+), the simplest quaternary amine resulting primarily from human industrial activities (e.g., wastewater treatment, electronic chips), has been shown to be a substrate for methanogenesis, and is converted to methane and ammonium (NH_4^+) [37]. Similarly to TMA, DMA, and MMA, TMA^+ can be disproportionated by an apparent phylogenetic cluster of *Methanococcoides methylutens* strains, by strains closely related to *Methanosarcina mazei*, and by strain NY-STAYD close to *Methanomethylovorans uponensis* (*Methanosarcinales*) and isolated from a bioreactor containing tetramethylammonium [37,215,217,218]. Otherwise, *Methanonatronarchaeum thermophilum* (AMET strains) can also produce methane by reducing TMA^+ [98]. From a thermodynamic point of view, TMA^+ disproportionation into methane, CO_2, and NH_4^+ is quite exergonic since the corresponding $\Delta G_r^{0'}$ is equal to −96.7 kJ mol^{-1} CH_4. Furthermore, when TMA^+ serves as an electron acceptor, the reaction should be even more exergonic, with $\Delta G_r^{0'}$ values equal to −98.2 and −120.8 kJ mol^{-1} CH_4 with formate and H_2 as electron donors, respectively. In return, this reaction is only possible at low (<5 mM) concentrations of TMA^+ due to the toxicity of this compound at high pH [98]. Note, however, that neither formate nor H_2 were explicitly listed as the electron donors for these reactions in the original publication so we chose to present both values [98].

It would not be surprising to discover in the future new strains or lineages of methanogenic *Archaea* degrading QA and other amine molecules (proline betaine, homarin, β-alanine betaine, ectoin, carnitine, *etc.*) serving as substrates for methanogenesis, as efforts to culture isolated methanogens on different substrates remain limited. Furthermore, as demonstrated with TMA^+, incubations of choline and glycine betaine with formate and/or H_2 should be tested to determine whether these compounds might be involved in a methyl-reducing hydrogenotrophic and/or methyl-reducing formatotrophic methanogenesis process or not.

3.1.6. *S*-containing compounds

Methanethiol, dimethylsulfide, and 3-*S*-methylmercaptopropionate (MMPA, $CH_3S(CH_2)_2CO_2^-$) are environmentally significant organosulfur compounds. In anoxic marine sediments, MT, DMS and MMPA are conversion products of dimethylsulfoniopropionate (DMSP), a compatible solute present in various organisms including phytoplankton and marine *Bacteria* [219,220] (Fig. 3). MT and DMS are also the major volatile organic sulfur compounds in freshwater sediments, and they are present in a wide range of habitats including peat bogs, oceans, salt marshes, oil reservoirs and marine hydrothermal vents [221–226]. MT is present in various animal tissues and feces, and is found in environments where there is decaying organic matter. In addition to being a derivative from DMSP, DMS can also be derived from the anaerobic degradation of dimethylsulfonium, *S*-methylmethionine, dimethylsulfoxide and from reduction of methoxylated aromatics coupled to sulfide oxidation [223,227,228].

One or several of these organosulfur compounds can be converted to methane by few *Methanosarcinales*. For example, *Methanohalophilus zhilinae* WeN5^T, *Methanohalophilus oregonense* WAL1^T, *Methanolobus bombayensis* B-1^T and *Methanolobus taylorii* GS-16^T are able to produce methane from DMS [219,229–231], *Methanosarcina* sp. MTP4, *Methanosarcina acetivorans* C2A^T and *Methanosarcina siciliae* T4/M^T from DMS and MMPA [33,219], and *Methanosarcina semesiae* MD1^T and *Methanomethylovorans hollandica* DMS1^T from both DMS and MT [212,232]. *Methanosarcina barkeri* strain MS^T is able to convert DMS and MMPA to methane when the strain is grown on acetate [36]. Recently, members of order *Methanonatronarchaeales* have also been shown to produce methane from MT, DMS and MMPA reduction coupled to H_2 and/or formate oxidation by using the methyl-reducing hydrogenotrophic and/or methyl-reducing formatotrophic pathway, respectively [17,99]. Under biological standard conditions, methanogenesis

from organosulfur compounds with methyl groups is exergonic, with a ΔG_r^0 ranging from −32.5 kJ mol^{-1} CH_4 for methanogenesis on MT alone, to −70.1 kJ mol^{-1} CH_4 for methanogenesis on DMS and H_2 (and −27.7 kJ mol^{-1} CH_4 with formate as the electron donor) (Table 1). In anoxic marine sediments, DMS is subject to competition between methanogens and sulfate reducers when present at low concentrations, but at high DMS concentrations, methanogens could be the major players in DMS conversion [233].

3.1.7. Methoxylated aromatic compounds

Perhaps one of the most enthusiastic discoveries about methanogenesis in the past decade is the finding that some methanogenic *Archaea* can fuel their methanogenesis by *O*-demethylation of a wide variety of methoxylated (R–OCH_3) aromatic compounds (MACs), including homocycles such as benzenes, benzoates, cinnamates and phenols, as well as heterocycles like pyridine. To date, forty MACs (mono-, di- and tri-MACs) have been identified to support methanogenesis, representing nearly one-fifth (20.7 %) of all methanogenesis substrates identified (Fig. 2) [27].

Myriads of MACs are derived from the degradation of lignins synthetized by vascular plants (Fig. 3) and even some red algae and present in their cell walls [234]. Lignins are complex macromolecules composed of three kinds of cross-coupled methoxylated monomers called monolignols (4-coumaryl, coniferyl and sinapyl alcohols, respectively), which are themselves based on phenylalanine [235–237]. Because of their structural complexity, lignins usually remain quite refractory to degradation processes such as peatification, and are therefore buried along with other organic moieties (e.g., *n*-alkanes, see below) to form coal (i.e., coalification) and eventually petroleum under particular conditions of pressure and temperature [238]. Nevertheless, immature coal (i.e., lignite), peat bogs, sediments and soils may also be rich in MACs, which could therefore be available to acetogenic and sulfate-reducing *Bacteria* or methanogenic *Archaea* [67,239–242].

The ability to demethoxylate a large number of MACs has only been demonstrated *in vitro* for two strains of *Methermicoccus shengliensis* (ZC-1^T and AmaM, respectively) (*Methanosarcinales*), and to a very less extent, for *Methanomethylovorans hollandica* DMS1^T and *Methanosarcina barkeri* MS^T [27,243]. In addition, several genes putatively involved in growth by methoxyl-dismutating methanogenesis were also found in *Methanolacinia petrolearia* SEBR 4845^T (*Methanomicrobiales*) and *Methanothermobacter tenebrarum* [243].

From a metabolic point of view, methanogenesis from MACs leads to the production of CH_4, CO_2, and a hydroxylated form of the substrate (i.e., R–OCH_3→ R–OH). The metabolic pathway involved in this reaction is quite similar to that based on methyl-disproportionation, using a set of homologous enzymes. However, one of the main differences between them is the transfer of the methyl group from the MAC to the tetrahydromethanopterin (H_4MPT) – rather than to coenzyme–M – using the methyltransferases MtoAB$_{1,2}$C and the corrinoid protein activase MtoD, which are similar enzymes to those in acetogenic *Bacteria* [47,243]. Furthermore, while the methanogenic conversion of 2-methoxybenzoate to 2-hydroxybenzoate seems obvious, the order of demethoxylation of di- and tri-MAC substrates remains unclear. In fact, *Methermicoccus shengliensis* ZC-1^T mainly converted 3,4,5-trimethoxybenzoate ($C_6H_2(OCH_3)_3CO_2^-$) to 3-hydroxy-4,5-dimethoxybenzoate ($C_6H_5(OCH_3)_2OHCO_2^-$), at the expense of 4-hydroxy-3,5-dimethoxybenzoate [243]. If similar questions regarding *O*-demethylation of methoxylated compounds have been addressed before, no clear answer could have been given, thus require further investigations [244,245]. Each di- and tri-MACs *O*-demethylation could potentially lead to one or more intermediates, thereby greatly expanding the range of substrates for methanogenesis. For example, twenty potential combinations of substrates could be derived solely from the six di- and tri-methoxybenzoates mentioned above, some of which are naturally present in environmental microbial habitats.

Unfortunately, most of ΔG_f^0 values for methoxylated substrates and/or their hydroxylated derivatives could not be calculated. Conversely, the ΔG_r^0 of methanogenic conversions of 3,4,5-trimethoxybenzoate to 3,4,5-trihydroxybenzoate (−107 kJ mol^{-1} CH_4), methoxybenzene to phenol (−76.1 kJ mol^{-1} CH_4), 4-methoxybenzoic acid to 4-hydroxybenzoate (−38.8 kJ mol^{-1} CH_4), 4-methoxyphenol to 4-hydroxyphenol (−85.9 kJ mol^{-1} CH_4), or 3,5-dimethoxy-4-hydroxybenzoate to 3,4,5-trihydroxybenzoate (−167 kJ mol^{-1} CH_4) (Table 1) could be calculated.

Finally, it should be noted that the aforementioned *Archaea* species have been isolated from a variety of ecosystems (i.e., hydrocarbon-rich reservoirs, eutrophic freshwater sediments, domestic sewage sludge digester), and can also produce methane from a variety of other substrates *via* the CO_2-reducing hydrogenotrophic, acetoclastic, and/or methyl-dismutating pathways [212,246–249]. Altogether, these observations not only expand the phylogenetic and metabolic diversity of methanogenic *Archaea* capable of methoxyl-dismutating methanogenesis, but also question the evolution and ecological importance of this metabolic pathway in open and digestive environments.

3.1.8. N-alkanes and n-alkylated hydrocarbons

In addition to methoxylated aromatic compounds, one of the major recent discoveries on methanogenesis is the ability of some methanogenic *Archaea* to consume an impressive panel of *n*-alkanes (36 molecules, including 10 suspected), *n*-alkylcyclohexanes (*n*-alkylcyhex, 28 molecules) and *n*-alkylbenzenes (*n*-alkylbz, 27 molecules) [18,21,28]. These three groups of compounds alone account for nearly half (47.2 %) (Fig. 2) of all methanogenesis substrates identified to date, encouraging a thorough re-evaluation of the metabolic diversity of methanogenic *Archaea* and their place in global carbon fluxes. To prevent confusion, the numbers (C_n) in the text correspond to the number of carbon atoms in the (side-)chain of the compounds.

Cuticular waxes of higher terrestrial plants (grasses, shrubs, trees) and aquatic macrophytes are one of the main sources of *n*-alkanes (mainly C_{21} – C_{37}) (Fig. 3) [250–254]. In sedimentary systems, *n*-alkanes from decaying plants can be deposited and accumulate on sediments, along with those produced by benthic macroalgae (mainly C_{13} – C_{24} *n*-alkanes) and some *Bacteria* (e.g., C_{15} – C_{17} in *Nostoc muscorum*) [250,251,255–259]. Once in the sediments, *n*-alkanes can either serve as a carbon and energy source for a multitude of aerobic and anaerobic living organisms (e.g., algae, *Fungi*, *Bacteria* and *Archaea*), or they can become refractory to degradation and be buried in the sediment [260–263]. In a broader geological context, preserved *n*-alkanes can be deeply buried in geological layers with other molecules (e.g., fatty acids and triglycerides, acidic and alcoholic moiety straight chain esters, algaenans, *etc.*) and undergo a series of diagenetic alterations (e.g., thermolysis) [264–266]. These phenomena ultimately lead to the production of even more *n*-alkanes, constituting various forms of petroleum (e.g., C_{18} – C_{30} in bitumen), oils (C_8 – C_{40+}), kerogens (e.g., C_6 – C_{35}) or coals (e.g., C_{16} – C_{33}) [264,265,267–269].

In addition to *n*-alkanes, *n*-alkylcyclohexanes and *n*-alkylcyclobenzenes have also been detected in a wide range of hydrocarbon-rich environments, including oils (e.g., C_{12} – C_{24} *n*-alkylcyhex, or C_7 – C_{30} *n*-alkylbz), coals (e.g., C_7 – C_{31} *n*-alkylcyhex, or C_8 – C_{32} *n*-alkylbz), and various forms of petroleum and kerogen [264,267,268,270–274]. In addition, *n*-alkycyclohexanes have also been reported in open-environments such as mangroves (C_7 – C_{17}), where they probably derive from algal and bacterial lipid alterations [257].

Many hypotheses are proposed for the formation of long-chain *n*-alkylcyclohexanes and *n*-alkylbenzenes in buried environments. With respect to *n*-alkycyclohexanes, these include direct or indirect cyclization of fatty acids, or alkylation of alcohols with cyclohexanes (Fig. 3) [271]. *n*-alkylbenzenes could be derived from their *n*-alkylcyclohexane homolog or from the cyclization of fatty acids [268,271].

Until recently, the mineralization of *n*-alkanes into CH_4 was thought to require syntrophic cooperation between bacterial metabolizers and

methanogenic *Archaea* [263,275–277]. Yet, this paradigm was recently challenged when it was shown that representatives of the genus *Ca.* 'Methanoliparum' (*Ca.* 'Methanoliparia' class) are able to combine the oxidation of medium-to long-chain *n*-alkanes (C_{13}–C_{38}) with methanogenesis [28]. In addition, it has also been suggested that various representatives of the class *Ca.* 'Methanoliparia' (i.e., *Ca.* 'Methanoliparium thermophilum' NM1a, *Ca.* 'Methanolliviera hydrocarbonicum' NM1b, *Ca.* 'Methanoliparia_GoM_oil' and *Ca.* 'Methanoliparia_GoM_asphalt') could perform methanogenesis from the oxidation of shorter *n*-alkanes, including *n*-propane, *n*-butane, and potentially mid- or long-chains [18,21]. In contrast, no methane formation based on $< C_{13}$ alkanes was observed *in vitro* from the *Ca.* 'Methanoliparia' representatives obtained in enrichment cultures from crude oil [28]. From a metabolic point of view, *n*-alkanes are first bound to an alkyl–CoM before possibly undergoing several oxidation steps to reach the β-oxidation pathway and the CBWL pathway, and then the methyl–CoM reductase [18,21,28]. While most of the gene encoding enzymes of this pathway have been clearly identified, the metabolic intermediates between alkyl–CoM and acyl–CoA have not yet been identified, and thus have only been inferred. In short, the *n*-alkanes would be sequentially split into corresponding alcohols, aldehydes, and fatty-acids before being bound to CoA. Thermodynamically, the free energy changes of disproportionation of *n*-alkanes, listed in Table 1 and Table B.1 (Appendix B), to CH_4 and CO_2, range from −14.0 (*n*-butane, C_4H_{10}) to −8.5 (*n*-pentane, C_5H_{12}) kJ mol^{-1} CH_4 under biological standard conditions.

As for *n*-alkanes, methane production from *n*-alkylcyclohexanes and *n*-alkylbenzenes was known until recently only in the context of syntrophic interactions between acetate and H_2-producing *Bacteria*, and methanogenic *Archaea* [278,279]. In addition, *n*-alkylcyclohexanes and *n*-alkylbenzenes can also be consumed directly by a number of *Fungi* and *Bacteria* [280]. To date, only representatives of the genus *Ca.* 'Methanoliparum' have been shown to perform alkylotrophic methanogenesis, disproportionating C_{13} – C_{39-40} side-chains of *n*-alkylcyclohexanes and *n*-alkylbenzenes into CH_4 and CO_2 [28]. Interestingly, their apparent inability to consume *n*-alkyl with $C_{\leq 12}$ side-chains has not yet been elucidated. From a metabolic standpoint, very similar sets of enzymes involved in the alkanotrophic pathway could be used, however with possible benzene breakdown steps between the benzoyl–CoA and the β-oxidation pathway [21,28,47]. Under biological standard conditions, methanogenesis from *n*-alkylbenzenes is predicted exergonic with a low free-energy change ranging from −11.6 (*n*-pentadecylbenzene, $C_6H_5(CH_2)_{14}CH_3$) to −11.1 (*n*-nonatriacontylbenzene, $C_6H_5(CH_2)_{38}CH_3$) kJ mol^{-1} CH_4. Methanogenesis derived from *n*-alkylcyclohexanes is predicted to be slightly more unfavorable than that of *n*-alkylbenzenes, from slightly exergonic to endergonic, with free-energy changes ranging from −4.6 (*n*-tetracontylcyclohexane, $C_6H_{11}(CH_2)_{39}CH_3$) to +4.3 (*n*-tridecylcyclohexane, $C_6H_{11}(CH_2)_{12}CH_3$) kJ mol^{-1} CH_4 produced. If these thermodynamics values seem rather puzzling at first sight, one should not forget to consider that these values can be quite different in the non-standard conditions prevailing in natural environments.

3.1.9. Other substrates

3.1.9.1. Methyliodide. Methyliodide (MeI; CH_3I) plays an important role in the natural iodine cycle and is one of the most abundant organoiodine compounds in natural settings [281]. In aquatic habitats, it can be biologically released (e.g., by *Cyanobacteria*, macro-algae, or phytoplankton) or abiotically produced by photochemical degradation of dissolved organic carbon in seawater [282–286]. Production of CH_3I from terrestrial sources has been reported for rice paddies, flood soils, salt-marsh plants and forests [287–290]. Methyliodide can also be produced abiotically in seawater by photochemical degradation of dissolved organic carbon [285]. Finally, this compound also has an anthropogenic source as it has been widely used as a fumigant in several countries since the 90s to control a wide variety of soil pests and weeds [291]. To date, methanogenic degradation of CH_3I has only been demonstrated for *Methanococcoides methylutens* TMA-10^T, *via* the methylotrophic pathway [39]. $\Delta G_r^{0'}$ required to convert methyliodide into methane, CO_2 , and iodide (I^-) is estimated to be −154.0 kJ mol^{-1} CH_4 (Table 1), and is therefore very exergonic. Nevertheless, it should be noted that this reaction was only observed under low concentrations (<160 μM) of methyliodide, and that methanogenesis was inhibited at higher concentrations [39].

3.1.9.2. 5-Methylfurfural and 2-methylfurfural. Little information is available on the precursors of 5-methylfurfural (5-methyl-2-furaldehyde, 5-MF, $C_4H_2OCHOCH_3$). This compound is naturally present in some plants (e.g., in *Pinus densiflora* needles) [292]. It is also a Maillard reaction products between an amino acid (lysine or arginine) and a reducing sugars (arabinose and/or xylose) acting as flavoring agent in food products such as balsamic vinegar [293,294].

The conversion of 5-MF to methane and furfural was only demonstrated for *Methanococcus* sp. Strain B which uses the methyl groups of methylfurfural as the sole carbon source for growth and methanogenesis through the methylotrophic pathway [30]. The latter strain is also capable to produce methane and furfural from 2-methylfurfural ($C_4H_2OCHOCH_3$) [30]. In addition, the *Methanococcus deltae* ΔLH mutant, has been shown to reduce furfuryl to furfural alcohol without methane production, presumably for furfuryl detoxification purposes [295,296]. Finally, syntrophic degradation of furfural by a mixed culture of *Desulfovibrio* sp. (strain B) and *Methanosarcina barkeri* 227 has also been reported, with acetate being the metabolic intermediate [297]. These compounds are likely to be present in only a very small number of ecological niches and therefore probably represent a marginal source of natural and anthropogenic methane production.

3.1.10. Uncertain substrates

There are also a number of hypothetical substrates for methanogenesis, for which catabolic degradation is not clearly demonstrated, including some secondary alcohols, methylated thiols and aromatic hydrocarbons.

In 1986, secondary alcohols were identified as electron donors for CO_2 reduction (see above) [42]. Among them, 1,3-butanediol ($CH_3OHCH(CH_2)_2OH$) poorly promoted growth and methanogenesis of *Methanospirillum hungatei* SK (*Methanomicrobiales*). However, the product resulting from the oxidation of 1,3-butanediol has not been identified and could therefore correspond to either 4-hydroxy-2-butanone (2-hydroxyethyl methyl ketone, $CH_3CO(CH_2)_2OH$) or to 3-hydroxybutanal (acetaldol, $CH_3OHCHCH_2CHO$).

It is also worth mentioning that *in vitro* experiments with cell-free extracts of cells have shown that cyclohexanol ($C_6H_{11}OH$), 2,3-butanediol ($(CH_3CHOH)_2$), 2-pentanol ($CH_3(CH_2)_2CHOHCH_3$), and acetoin ($CH_3COCHOHCH_3$) can be oxidized to their corresponding ketones by certain alcohol dehydrogenase of some secondary-alcohol oxidizing methanogenic *Archaea Methanocorpusculum parvum* XII^T (*Methanomicrobiales*) or *Methanobacterium palustre* F^T (*Methanobacteriales*) [29,191]. Although these reactions have not been fully deciphered to date, further investigations are needed to ascertain the metabolic role of these alcohols in methanogenesis. Nevertheless, cyclohexanol could not serve as electron donor for methanogenesis for 16 different tested strains affiliated to genera *Methanobacteriales*, *Methanococcales* and *Methanomicrobiales* [192].

Furthermore, another study showed that some methylated thiol compounds (e.g., methylmercaptopropanol, $CH_3S(CH_2)_2COH$) were converted to methane at low rates by extracts of acetate-grown *Methanosarcina barkeri* MS^T cells incubated under H_2 [36]. Unfortunately, no publication reporting strain growth or methane production from these methylated thiols could be found.

More recently, McKay et al. [25] suspected that the acetoclastic

methanogen *Ca.* 'Methanothrix paradoxa' PRB (*Methanotrichales*) could directly or indirectly decompose a number of hydrocarbons, namely, toluene, xylenes, 2-phenylacetate, and (*S*)-1-phenylethanol, to produce biomass and/or gain energy. However, it is purely hypothetical as it relies solely on the detection of putative protein sequences.

Toluene ($C_6H_5CH_3$) and xylene isomers (ortho-, meta-, and para-xylene, respectively, $C_6H_4(CH_3)_2$) are aromatic hydrocarbons notably found in petroleum, crude oil, coal tar, and/or aquifer sediments, and are often regrouped with ethylbezene and benzene under the BTEX acronym [298]. (*S*)-1-phenylethanol ($C_6H_5CH_3OH$) is a characteristic intermediate of anaerobic degradations of ethylbenzene and acetophenone carried out by various denitrifying or sulfate-reducing *Bacteria* [299]. Oxidation of these hydrocarbons can be performed by an array of anaerobic *Bacteria* using NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} or carbonates as electron acceptors. In the absence of other electron acceptors, methanogenic oxidation of BTEX hydrocarbons occurs *via* syntrophy between *Bacteria* and acetoclastic and/or hydrogenotrophic methanogens [300]. To date, no BTEX-degrading methanogen has been isolated.

Finally, 2-phenylacetate ($C_6H_5CH_2CO_2^-$) has been demonstrated as a common intermediate in the methanogenic degradation of organic matter such as phenylalanine in syntrophic methanogenic consortia [301–303]. Growth by methanogenesis from 2-phenylacetate was studied in *Methanothrix soehngenii* Opfikon^T (*Methanotrichales*), an oxygen tolerant acetoclastic methanogen, but no methane production nor cell growth was observed during incubation with this latter as sole substrate [114].

Based on metagenomic analyses, Wang et al. [304] proposed that the korarchaeotal WYZ-LMO9 MAG could be derived from taxa representing a new metabolically versatile *Korarchaeota* family. According to their genomic predictions, the consensus genome of closely related *Korarcheaota* strains corresponding to this WYZ-LMO9 MAG, encodes genes to couple alkane oxidation to sulfite reduction, but also to produce methane by reducing methanol, MMA or MeSH and DMS using either dihydrogen or sulfide as an electron source. If functional evidence supports the hypothesis that the latter reaction can take place within a single cell, this would open up new perspectives in the understanding and study of methanogenesis. Nevertheless, the authors proposed that methane might otherwise be oxidized and sulfite reduced, and suggested that this organism might alternatively be a methanotroph and not a methanogen.

Finally, *n*-fatty-acids are also potential metabolic intermediates in the methanogenic degradation of *n*-alkanes through the alkanotrophic pathway. Direct oxidation of environmental short-, medium-, and long-chain *n*-fatty-acids (SCFAs, MCFAs and LCFAs, respectively) into methane by representatives of *Ca.* 'Methanoliparia' was hypothesized based on the presence of several copies of medium- and long-chain acyl–CoA synthetases genes in their genomes [18,21,28]. *n*-fatty acids are virtually found in all open and digestive environments, in which they are directly produced by (micro-)organisms (e.g., C_{12} – C_{36} chain length in plant waxes), or derive from anaerobic degradation of mono- and oligomers (e.g., amino acids, peptides, sugars) by fermenters [253,305,306]. Methanogenesis from *n*-fatty acids has been mainly described in the context of a syntrophic consortium between a methanogenic *Archaea* and a bacterial partner. For example, a co-culture of the anaerobic bacterium *Syntrophomonas curvata* GB8-1^T and the CO_2-reducing hydrogenotrophic methanogen *Methanobacterium formicicum* MF^T was reported to degrade most *n*-fatty acids between butyrate (butanoate, $CH_3(CH_2)_2CO_2^-$) to *n*-octadecanoic acid (stearic acid, $CH_3(CH_2)_{16}CO_2H$) [307]. This syntrophic relationship allows to limit the accumulation of H_2 that inhibits bacterial growth (i.e., see the dedicate section above). Nevertheless, no direct experimental evidence of methanogenesis from *n*-fatty acids in a single organism has yet been provided. From a thermodynamic point of view, disproportionations of SCFAs, MCFAs, and LCFAs into methane, CO_2 are exergonic reactions under biological standard conditions. When excluding formate and acetate (i.e., see respective sections above), $\Delta G_r^{0'}$ of methanogenic reactions from *n*-fatty acids range from -18.1 kJ mol^{-1} CH_4 for *n*-octanoate (caprylate, $CH_3(CH_2)_6CO_2^-$) to -13.2 kJ mol^{-1} CH_4 for *n*-propionate ($CH_3CH_2CO_2^-$).

4. Conclusion

Over the past decade, methanogenesis from novel substrates has been demonstrated and a very large diversity of putative substrates has been proposed, bringing the number of proven substrates for methanogenesis to 152, plus 41 putative substrates. This result implies that methanogens may be more metabolically versatile than previously thought. Some methanogenic taxa can use a wide range of substrates, sometimes deriving energy and carbon from up to 35 different substrates (*e.g.*, *Methermicoccus shengliensis* ZC-1^T). It is now clear that methanogenesis is not strictly confined to strictly anoxic areas and that some non-competitive substrates can be degraded in areas containing oxidants such as nitrate, ferric iron or sulfate. For all these reasons, methanogens may populate more ecological niches than previously assumed. In the context of rapid climate change, it is crucial to identify methane precursors and the habitat boundaries of methanogens, and to determine the importance of these new substrates in the methane balance of natural environments.

Conflict of interest and authorship conformation form

Marc Cozannet: Conceptualization, Formal analysis, Investigation, Methodology, Writing – Original draft, Writing – Reviewing and Editing. **Sébastien Le Guellec**: Writing – Reviewing and Editing. **Karine Alain**: Writing – Reviewing and Editing, Supervision, Funding acquisition.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Abbreviations and notations

BTEX	Benzene, toluene, ethylbenzene, and xylenes
bz	Benzene
CBWL	Carbonyl branch of the Wood-Ljungdahl
cr	Crystal
cyhex	Cyclohexane
C_n	Number of carbon atoms in a compound
C^0	Standard state concentration (mol kg^{-1})
DMA	Dimethylamine
DMEA	*N*,*N*-dimethylethanolamine
DMG	*N*,*N*-dimethylglycine
DMS	Dimethylsulfide
DMSP	Dimethylsulfoniopropionate
$\Delta^{aq}_{g}G^0$	Standard Gibbs free energy of hydration (kJ mol^{-1})
$\Delta^{g}_{cr}G^0$	Standard Gibbs free energy of sublimation (kJ mol^{-1})
$\Delta^{l}_{cr}G^0$	Standard Gibbs free energy of fusion (kJ mol^{-1})
ΔG^0_r	Change in Gibbs energy under standard state (kJ mol^{-1})
$\Delta G^{0'}_r$	Change in Gibbs energy under biological standard state (kJ mol^{-1})
ΔG^0_f	Standard Gibbs energy of formation of a compound (kJ mol^{-1})
ΔH^0_f	Standard enthalpy of formation of a compound, or of a functional group (kJ mol^{-1})
ΔH^0_m	Standard molal enthalpy of melting (kJ mol^{-1})
ΔH^0_r	Change in standard enthalpy (kJ mol^{-1})
K_c	Equilibrium constant
MA	Methylamine
MACs	Methoxylated aromatic compounds
MEA	Methylethylamine
MMA	Monomethylamine
MMEA	*N*-monomethylethanolamine
MMPA	3-*S*-methylmercaptopropionate
MT	Methanethiol
n	Normal
p-	Para
P_0	Standard pressure state (in kPa, or in atm)
P_{sub}	Sublimation pressure of a compound (in kPa, or in atm)
P_{vap}	Vapor pressure of a compound (in kPa, or in atm)
pK_a	Negative logarithm of the equilibrium constant K_c of a compound (unitless)
R	Gas constant ($\sim$8.31451 J mol^{-1} K^{-1}, or $\sim$0.082057844 atm J mol^{-1} K^{-1})
ΔS^0_m	Standard molal entropy of melting (J mol^{-1} K^{-1})
ΔS^0_f	Standard entropy of formation of a compound (J mol^{-1} K^{-1})
ΔS^0_r	Change in (molar) standard enthalpy (J mol^{-1} K^{-1})
S^0	Standard entropy of a compound (J mol^{-1} K^{-1})
TMA	Trimethylamine
TMA^+	Tetramethylammonium ion

Appendix A. Supplementary data

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