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Formate and hydrogen in hydrothermal vents and their use by extremely thermophilic methanogens and heterotrophs

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Extremely thermophilic methanogens in the *Methanococci* and heterotrophs in the *Thermococci* are common in deep-sea hydrothermal vents. All *Methanococci* use H_2 as an electron donor, and a few species can also use formate. Most *Methanococci* have a coenzyme F_{420}-reducing formate dehydrogenase. All *Thermococci* reduce S^0 but have hydrogenases and produce H_2 in the absence of S^0. Some *Thermococci* have formate hydrogenlyase (Fhl) that reversibly converts H_2 and CO_2 to formate or an $NAD(P)^+$-reducing formate dehydrogenase (Nfd). Questions remain if *Methanococci* or *Thermococci* use or produce formate in nature, why only certain species can grow on or produce formate, and what the physiological role of formate is? Formate forms abiotically in hydrothermal fluids through chemical equilibrium with primarily H_2, CO_2, and CO and is strongly dependent upon H_2 concentration, pH, and temperature. Formate concentrations are highest in hydrothermal fluids where H_2 concentrations are also high, such as in ultramafic systems where serpentinization reactions occur. In nature, *Methanococci* are likely to use formate as an electron donor when H_2 is limiting. *Thermococci* with Fhl likely convert H_2 and CO_2 to formate when H_2 concentrations become inhibitory for growth. They are unlikely to grow on formate in nature unless formate is more abundant than H_2 in the environment. Nearly all *Methanococci* and *Thermococci* have a gene for at least one formate dehydrogenase catalytic subunit, which may be used to provide free formate for *de novo* purine biosynthesis. However, only species with a membrane-bound formate transporter can grow on or secrete formate. Interspecies H_2 transfer occurs between *Thermococci* and *Methanococci*. This and putative interspecies formate transfer may support *Methanococci* in low H_2 environments, which in turn may prevent growth inhibition of *Thermococci* by its own H_2. Future research directions include understanding when, where, and how formate is used and produced by these organisms in nature, and how transcription of *Thermococci* genes encoding formate-related enzymes are regulated.

KEYWORDS

formate, hydrogen, hydrothermal vent, hyperthermophiles, formate dehydrogenase, hydrogenase, *Thermococci*, *Methanococci*

1. Introduction

It was estimated that 40% of bacterial and archaeal global biomass is found in the rocky portion of the ocean crust below ocean sediments (Bar-On et al., 2018; Fleming and Wuertz, 2019). These microbes live in cracks and pores of the rocky subseafloor in the absence of sunlight and often in the absence of oxygen and rely on the gases, aqueous compounds (e.g., sulfide, sulfate, and nitrate), organic compounds, and minerals found locally for growth. In high-temperature anoxic environments, H_2 is generally considered to be the primary electron donor and CO_2 the primary carbon source for autotrophic metabolism. However, recently other electron donors and carbon sources such as formate have been considered as alternatives (Windman et al., 2007), especially in high pH environments where dissolved inorganic carbon precipitates as calcium carbonate and is largely unavailable to autotrophs (Lang et al., 2018; McGonigle et al., 2020; Brazelton et al., 2022). There are strong links between formate and H_2 in hydrothermal environments and in the physiology of microbes that consume and produce formate and H_2.

High-temperature microbes that use formate and H_2 are examined herein, namely methanogens (in the class *Methanococci* and the class *Methanopyri*) and heterotrophs (in the class *Thermococci*). These organisms are found in deep-sea hydrothermal vents on or near tectonic plate boundaries – both mid-ocean ridges and subduction zones. Thermophiles and hyperthermophiles are defined as those organisms with optimal growth temperatures above 50°C and 80°C, respectively (Stetter, 2006). In this review, the term 'extreme thermophile' will be used to describe organisms with optimal growth temperatures above 65°C. Extremely thermophilic *Methanococci* and *Thermococci* are among the more cosmopolitan and well-studied microbes found in hydrothermal vent environments. All *Methanococci* and the marine hyperthermophile *Methanopyrus kandleri* (the sole member of the *Methanopyri*) use H_2 and CO_2 as energy and carbon sources to produce CH_4, H_2O, and biomass (Thauer et al., 2008). All *Thermococci* use peptides and sugars as carbon and energy sources and reduce zero-valent sulfur (S^0) to a sulfide species or reduce 2 H^+ to H_2 in the absence of S^0 (Wu et al., 2018). However, some extremely thermophilic *Methanococci* and *Thermococci* grow using formate as an energy source only or as both energy and carbon sources (Belay et al., 1986; Kim et al., 2010; Lim et al., 2014). This raises questions about which organisms can use formate, when they use formate in nature, and for what purpose. This review describes how formate and H_2 are formed in hydrothermal vents, the concentrations of these compounds in pure hydrothermal fluids, the physiology of extremely thermophilic *Methanococci* and *Thermococci* as it relates to formate and H_2 use, transcriptional regulation of formate dehydrogenase and hydrogenase genes, and suggests likely roles for formate use by these organisms in nature.

2. Abiotic H_2 production in hydrothermal vents

Deep-sea hydrothermal vents provide one of the best access points to the hydrothermally influenced portion of the rocky subseafloor and are ideal starting points for understanding biogeochemical processes in these regions of the crust. Some hydrothermal fluids rise through the crust undiluted, so-called "end-member hydrothermal fluid," and exit the seafloor at temperatures generally above 300°C (**Table 1**). It can also mix with cold seawater on or below the seafloor creating habitats for extremely thermophilic anaerobes either within the host rock (e.g., basalt) or in metal sulfide mineral precipitates (e.g., black smoker chimneys). Most hydrothermal vent studies are focused on one of three types of sites: ultramafic sites along slow-to-ultraslow tectonic spreading centers, mafic sites along intermediate-to-fast spreading centers, and subduction-influenced sites near tectonic convergence zones (**Figure 1**).

The host rock in mafic and ultramafic sites have high concentrations of MgO and FeO, but they differ in their silica content, with ultramafic rocks having silica concentrations less than 45% (by weight), while mafic rocks have concentrations above 45%. Most abiotic formation of H_2 in hydrothermal vents occurs by hydrothermal alteration of the ultramafic rock peridotite (i.e., serpentinization) (**Table 1**). Serpentinization occurs in environments with limited magma supply where peridotite is present in the rock hosting hydrothermal circulation and is mostly associated with ultramafic sites. Olivine and orthopyroxene, the most abundant minerals in peridotite, are unstable under hydrothermal conditions, which causes dissolution-reprecipitation reactions and the formation of serpentine, magnetite, and H_2 [e.g., $6\,(Mg, Fe)_2SiO_4 + 7\,H_2O \rightarrow 3(Mg, Fe)Si_2O_5(OH)_4 + Fe_3O_4 + H_2$] (Klein et al., 2020). *Methanococci* and *Thermococci* are common in most ultramafic-influenced hydrothermal sites except at the Lost City hydrothermal vent field (**Table 1**). At Lost City, the high pH hydrothermal fluids formed by low temperature serpentinization lead to calcium carbonate precipitation and very low dissolved inorganic carbon concentrations. This likely hinders the growth of autotrophs such as *Methanococci* and *Methanopyri* unless they can grow on an aqueous carbon source such as formate.

Serpentinization is inhibited by silica and is thus less common in mafic and felsic rocks (felsic rocks are > 65% silica by weight). In mafic (basalt)-hosted hydrothermal systems, the oxidation of ferrous iron minerals, such as pyrrhotite to pyrite ($FeS + H_2S \rightarrow FeS_2 + H_2$) and magnetite to hematite ($2\,Fe_3O_4 + H_2O \rightarrow 3\,Fe_2O_3 + H_2$), and weathering of the ocean crust by oxygen-depleted water in the root zone of a hydrothermal system are also significant sources of H_2 in hydrothermal systems (Klein et al., 2020). H_2 and H_2S concentrations are controlled by chemical equilibrium between fluid and the pyrite-pyrrhotite-magnetite mineral assemblages present. Most H_2 and H_2S fluid compositions fall close to the metastable extension of pyrite-pyrrhotite equilibrium (Klein et al., 2020). H_2 concentrations in mafic hydrothermal fluids also increase significantly following a volcanic eruption as circulating fluids interact with newly injected rock (Lilley et al., 2003; Seewald et al., 2003; Von Damm and Lilley, 2004). Mafic hydrothermal vent sites generally tend to have *Thermococci* and *Methanococci* present (**Table 1**), especially following volcanic eruptions (Holden et al., 1998; Huber et al., 2002; Meyer et al., 2013), but *Methanococci* can become rare or undetectable during quiescent periods between eruptions when H_2 concentrations decrease or in low H_2 hydrothermal vents (Ver Eecke et al., 2009, 2012).

In contrast, hydrothermal vents that form along volcanic arcs at convergent plate boundaries have host rock with hydrous

TABLE 1 Physical, chemical, and microbial characteristics of hydrothermal vent sites.

Location	T_{max} (°C)	pH	H_2 (mM)[a]	Formate (μM)[a]	*Methanococci*	*Thermococci*
Ultramafic (peridotite)-influenced sites						
Kairei[b]	365	3.4–3.6	2.5–8.2	–	M	M
Logatchev[c]	350	6.2	5.9	–	F	ND
Lost City[d]	90	9.5–10.9	1.2–15.1	36–158	ND	M
Rainbow[e]	370	3.0–3.4	12.3–16.9	–	M	M
Von Damm[f]	226	5.6–6.1	9.9–18.3	82–669	F	F
Mafic (basalt-hosted) sites						
Axial Volcano[g]	351	3.5–4.4	0.06–0.43	–	F	F
Endeavor Segment[h]	352	3.7–4.5	0.03–0.17	–	M, F	M, F
9°50′N EPR[i]	386	3.1–5.2	0.33–8.9	–	M	M
Kilo Moana[j]	304	3.9–4.1	0.22–0.50	–	M	M
Lucky Strike[k]	324	3.6–3.9	0.03–0.07	–	ND	M
Piccard[l]	398	3.1–3.3	18.9–20.7	<1–4.8	F	F
Guaymas Basin[m]	315	5.9	–	–	M	M
Loki's Castle[n]	315	5.5–5.9	4.6–5.5	–	M	M
Subduction-influenced (andesite/dacite-hosted) sites						
Brothers Volcano[o]	303	2.1–4.4	0.01–0.02	–	M	M
Mariner Field[p]	359	2.4–2.7	0.03–0.18	–	ND	M
TOTO Caldera[q]	170	5.3	0.01	–	ND	M

The pH and concentrations of H_2 and formate are for end-member (zero-Mg^{2+}) hydrothermal fluid while the microbial data represent presence at the site in low-temperature fluids (F) and mineral samples (M). ND, not detected; –, not analyzed.

[a]Sometimes reported as mmol/kg or μmol/kg, respectively. [b]Takai et al. (2004b), Gallant and Von Damm (2006), Kumagai et al. (2008), and Han et al. (2018); [c]Perner et al. (2007); [d]Schrenk et al. (2004), Brazelton et al. (2006), Lang et al. (2010), and Lang et al. (2012); [e]Flores et al. (2011); [f]McDermott et al. (2015) and Reveillaud et al. (2016); [g]Ver Eecke et al. (2012), Topçuoğlu et al. (2016), and Fortunato et al. (2018); [h]Ding et al. (2005), Ver Eecke et al. (2012), Anderson et al. (2013), and Lin et al. (2016); [i]Von Damm and Lilley (2004), Ding et al. (2005), Kormas et al. (2006), McCliment et al. (2006), and Hou et al. (2020); [j]Flores et al. (2012); [k]Flores et al. (2011); [l]Reveillaud et al. (2016) and McDermott et al. (2018); [m]Von Damm et al. (1985) and Pagé et al. (2008); [n]Jaeschke et al. (2012) and Baumberger et al. (2016); [o]Takai et al. (2009) and Reysenbach et al. (2020); [p]Takai et al. (2008) and Flores et al. (2012); [q]Gamo et al. (2004) and Nakagawa et al. (2006).

FIGURE 1
Global map of the hydrothermal vents in **Table 1**. Hydrothermal vents hosted in ultramafic rock are shown in red; basalt, in black; and in subduction zones, in yellow-brown.

minerals, silica accumulation in aging oceanic crust, and more felsic character, such as dacite and andesite. The hydrothermal fluids from these rocks tend to have lower pH and lower H_2 (**Table 1**). While *Thermococci* are generally present at these sites, *Methanococci* tend to be rare or undetectable (**Table 1**) likely due to the very low H_2 concentrations (Ver Eecke et al., 2012).

Other more minor abiotic H_2 contributions in hydrothermal vents come from magmatic degassing at low hydrostatic pressures

(e.g., shallow vent sites) and radiolysis of water (Klein et al., 2020). Biotic sources of H_2 at extremely thermophilic temperatures by *Thermococci* are described in Section "4. H_2 production by *Thermococci*."

3. H_2 use by methanogens

Hydrogen is used by extremely thermophilic *Methanococci*, specifically, the genera *Methanocaldococcus* (T_{opt} 80–85°C), *Methanotorris* (T_{opt} 75–88°C), *Methanofervidicoccus* (T_{opt} 70°C), and *Methanothermococcus* (T_{opt} 65°C), and in the *Methanopyri*, which consists solely of *Methanopyrus kandleri* (T_{opt} 98°C) (**Table 2**).

3.1. Hydrogenases in *Methanococci* and *Methanopyri*

The whole genome sequences of 10 extremely thermophilic *Methanococci* plus *M. kandleri* were analyzed for known hydrogenases (see **Supplementary materials**). All 11 of the *Methanococci* and *Methanopyri* in the genome survey have at least one of the following hydrogenase genes (see Greening et al., 2016 for a review): (1) *eha* and *ehb* operons, which encode for membrane-bound multimeric hydrogenases that couple H_2 oxidation to ferredoxin reduction and are H^+/Na^+ driven for anaplerotic (Eha) and anabolic (Ehb) purposes (Porat et al., 2006; Lie et al., 2012); (2) an *frh* operon, which encodes for a soluble complex that directly couples H_2 oxidation to coenzyme F_{420} reduction (Hendrickson and Leigh, 2008); (3) an *hmd* gene, which encodes a soluble methylenetetrahydromethanopterin dehydrogenase that couples oxidation of H_2 to the reduction of methenyltetrahydromethanopterin in the archaeal Wood-Ljungdahl CO_2 fixation pathway (Hendrickson and Leigh, 2008); and (4) a *vhu* operon, which encodes for soluble heterodisulfide reductase-linked complexes that bifurcate electrons from H_2 to heterodisulfide (coenzyme M-coenzyme B) and ferredoxin (Kaster et al., 2011). These hydrogenases are described and listed in **Figure 2**, **Table 2**, and **Supplementary Table 1**. Coenzyme F_{420}, ferredoxin, coenzyme M, and coenzyme B are soluble electron carriers in methanogens (Thauer et al., 2008). Extremely thermophilic *Methanococci* and *Methanopyri* will often have two or three copies of the genes encoding these enzymes (**Table 2** and **Supplementary Table 1**).

3.2. Growth of *Methanococci* on H_2

The growth of natural assemblages of extremely thermophilic *Methanococci* in hydrothermal vent fluids from Axial Seamount is largely dependent on H_2 availability and temperature (Topçuoğlu et al., 2016). The Monod kinetic half-saturation value (K_s) for growth of extremely thermophilic methanogens was 27–66 μM with maximum methane production rates of 24–43 fmol CH_4 produced $cell^{-1}$ h^{-1} (Ver Eecke et al., 2012; Stewart et al., 2019). *Methanocaldococcus jannaschii* and *Methanothermococcus thermolithotrophicum* were shown to grow by interspecies H_2 transfer when grown in co-culture with *Thermococcus celer*, *Thermococcus stetteri*, and *Pyrococcus furiosus* (Bonch-Osmolovskaya and Stetter, 1991). When *M. jannaschii* was grown in monoculture at high (80–83 μM) and low (15–27 μM) H_2 concentrations and in co-culture with the hyperthermophilic H_2 producer *Thermococcus paralvinellae* (representing very low H_2 flux), growth and cell-specific CH_4 production rates decreased with decreasing H_2 availability (Topçuoğlu et al., 2019). However, the number of cells produced per mole of CH_4 produced (i.e., cell yield) increased six-fold with decreasing H_2 indicating increased growth efficiency when growth was limited by H_2 (Topçuoğlu et al., 2019). Relative to high H_2 concentrations, isotopic fractionation of CO_2 to CH_4 was 16‰ larger for cultures grown at low H_2 concentrations and 45–56‰ larger in co-culture suggesting reversal of the Wood-Ljungdahl pathway during methanogenesis with low H_2 flux (Valentine et al., 2004; Topçuoğlu et al., 2019). While all four types of hydrogenases were synthesized by *M. jannaschii* with high and low H_2 flux, transcript levels of *hmd* and *eha* decreased with decreasing H_2 availability (Topçuoğlu et al., 2019).

4. H_2 production by *Thermococci*

Hydrogen is produced by *Thermococci*, specifically, the genera *Thermococcus* (T_{opt} 75–90°C), *Palaeococcus* (T_{opt} 83°C), and *Pyrococcus* (T_{opt} 96–105°C) (**Table 3**).

4.1. Hydrogenases in *Thermococci*

The whole genome sequences of 30 *Thermococci* were analyzed for known hydrogenases (see **Supplementary materials**). All 30 *Thermococci* analyzed have at least one of the following hydrogenase operons: (1) An *mbh* operon, which encodes for a membrane-bound hydrogenase that couples oxidation of ferredoxin to H_2 evolution with concomitant H^+/Na^+ translocation across the membrane using antiporters (Sapra et al., 2003); (2) an *sh* operon, which encodes for a soluble sulfhydrogenase that couples oxidation of H_2 oxidation to the reduction of $NAD(P)^+$ (Van Haaster et al., 2008); (3) an *frh* operon, which encodes for cytoplasmic coenzyme F_{420} reducing-type hydrogenase that oxidizes H_2 and passes electrons to a thioredoxin reductase (Jung et al., 2020); and (4) a *codh* operon, which encodes for a membrane-bound hydrogenase that couples oxidation of CO to H_2 evolution with concomitant H^+/Na^+ translocation across the membrane using antiporters (Bae et al., 2012; Moon et al., 2012). These hydrogenases are described and listed in **Figure 3**, **Table 3**, and **Supplementary Table 2**.

All *Thermococci* have at least one *mbh* operon and all but one have at least one *sh* operon (**Table 3**). These enzymes are the core hydrogenases for *Thermococci* (Schut et al., 2012; Boyd et al., 2014). Twelve of the 30 *Thermococci* in the survey have *frh* operons. Five of the 30 *Thermococci* have *codh* operons. It was shown that the growth of *Thermococcus* sp. strain AM4 and *Thermococcus onnurineus* can be supported by CO with concomitant H_2 production (Sokolova et al., 2004; Bae et al., 2012; Moon et al., 2012), although the physiological role of this enzyme in *Thermococcus* is yet to be determined for growth in its natural environment.

TABLE 2 Growth characteristics of the classes *Methanococci* and *Methanopyri* and presence of genes for formate transport (FT), formate dehydrogenase (*fdh*), hydrogenases (*eha*, *ehb*, *frh*, *vhu*, *hmd*), and purine biosynthesis (*purT*, *purP*).

Organism	T_{opt} (°C)	Growth*	FT	*fdh*	*eha*	*ehb*	*frh*	*vhu*	*hmd*	*purT*	*purP*
Methanocaldococcus jannaschii JAL-1[a]	85	–		●	●	●	●●	●	●●●	●	●
Methanocaldococcus bathoardescens JH146[b]	82	–		●	●	●	●●	●	●●●	●	●
Methanocaldococcus fervens AG86[c]	85	ND	●	●	●	●	●	●	●●	●	●
Methanocaldococcus infernus ME[d]	85	–			●	●	●	●	●	●	●
Methanocaldococcus vulcanius M7[e]	80	–		●	●	●	●●	●●	●●●	●	●
Methanotorris igneus Kol 5[f]	88	–		●	●	●	●●●	●●	●●	●	●
Methanotorris formicicus Mc-S-70[g]	75	+	+	+	+	+	+	+	+	+	+
Methanothermococcus okinawensis IH1[h]	65	+	●	●	●	●	●●	●●	●	●	●
Methanothermococcus thermolithotrophicus SN 1[i]	65	+	+	+	+	+	+	+	+	+	+
Methanofervidicoccus abyssi HHB[j]	70	–			+	+	+	+	+	+	+
Methanopyrus kandleri AV19[k]	98	–		●	●		●●	●	●		●

The number of circles per column represents the number of times the gene(s) for that complex appears in the organism's genome.
*Growth on formate; ND, not determined.
+ In protein columns indicates genes present in draft genome sequence.
References and genome accession numbers: [a]Jones et al. (1983a), L77117; [b]Ver Eecke et al. (2013), CP009149; [c]Zhao et al. (1988), CP001696; [d]Jeanthon et al. (1998), CP002009; [e]Jeanthon et al. (1999), CP001787; [f]Burggraf et al. (1990), CP002737; [g]Takai et al. (2004a), AGJL01000032; [h]Takai et al. (2002), CP002792; [i]Huber et al. (1982), AQXV01000039; [j]Sakai et al. (2019), BFAX0000000; [k]Kurr et al. (1991), AE009439.

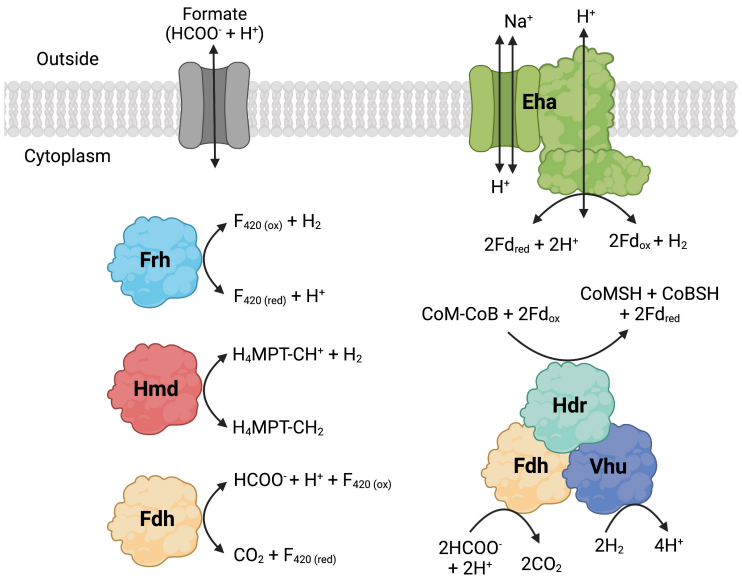

FIGURE 2
Formate dehydrogenase (Fdh), hydrogenase, and formate transporter proteins and their reactions that are found in *Methanococci* and *Methanopyri*. Fdh catalyzes the following formate oxidation reactions: cytoplasmic reduction of coenzyme F_{420} (F_{420}) and cytoplasmic reduction of coenzyme M (CoM), coenzyme B (CoB), and ferredoxin (Fd). The hydrogenases catalyze the following H_2 oxidation reactions: membrane-bound reduction of Fd (Eha), cytoplasmic reduction of F_{420} (Frh), cytoplasmic reduction of methenyl-tetrahydromethanopterin (CH-H_4MPT) (Hmd), and cytoplasmic reduction of CoM, CoB, and Fd. F_{420}, Fd, CoM, and CoB are cytoplasmic electron carriers. Methenyl-H_4MPT is an intermediate of the Wood-Ljungdahl CO_2 fixation pathway. Created with BioRender.com.

4.2. Growth of *Thermococci* with and without S^0

In *Thermococci*, the reduction of S^0 is the preferred route for electron disposal over the reduction of H^+ to H_2. In *P. furiosus*, the presence of S^0 in growth media resulted in decreases in Mbh and Sh hydrogenase specific activities, each by an order of magnitude (Adams et al., 2001). There was an immediate downregulation of *mbh* and an upregulation of *mbs* (membrane-bound sulfane reductase) (Wu et al., 2018) and *nsr* (NAD(P)H:S^0 reductase) in *P. furiosus* when S^0 was added to growth medium (Schut et al., 2001, 2007). A sulfur response regulator protein (SurR) was identified as the transcription factor regulating hydrogenase and sulfur responsive genes (Lipscomb et al., 2009, 2017). The proposed model suggests that SurR contains a redox-active cysteine disulfide that can reduce S^0 to H_2S (Yang et al., 2010). SurR is reduced

TABLE 3 Growth characteristics of the class *Thermococci* and presence of genes for formate transport (FT), formate dehydrogenase operons (*fhl, nfd*), and individuals (*fdhA*) with neighboring hydrogenase operons, individual hydrogenase operons (*mbh*, *sh*, *frh*, *codh*), and purine biosynthesis (*purT*, *purP*).

Organism	T_{opt} (°C)	$H_2 \leftrightarrow$ formate*	FT	Group 1A: *frh-fhl-mbh*	Group 1B: *frh-nfd-mbh*	Group 2: *nfd-sh*	Group 3: *fhl-sh*	Group 4: *fhl* only	Group 5: *fdhA* only	*Mbh*	*sh*	*frh*	*codh*	*purT*	*purP*
Thermococcus paralvinellae ES1[d]	82	+[b,c]	●	●				●		●●	●	●	●		
Thermococcus barophilus CH5[a]	80	+[a,c]	●	●			●			●●	●○	●	●		●
Thermococcus onnurineus NA1[e]	80	+[a,c]	●●	●		●		●		●	●●	●	●		
Thermococcus gammatolerans EJ3[f]	88	+[a,c]	●	●				○	●	●		●	○	●	●
Thermococcus piezophilus CDGS[g]	75	+[c]	●	●		●		●		●	●●	●		●	●
Thermococcus cleftensis CL1[h]	88	+[c]	●		●				●	●	●●	●		●	●
Thermococcus nautili 30-1[i]	88	+[c]	●		●				●	●	●●	●		●	●
Thermococcus kodakarensis KOD1[j]	85	+[c]	●		Δ				●	●	●			●	●
Thermococcus chitonophagus GC74[k]	85	–[a,c]						●	●	●	●●			●	●
Thermococcus eurythermalis A501[l]	85	–[c]					●	●	●	●	●	●		●	●
Thermococcus pacificus P-4[m]	88	–[c]					●			●	●	●		●	●
Thermococcus litoralis NC-S[n]	88	–[c]					●		●	●●	●●			●	●
Thermococcus barophilus MP[o]	85	–[c]							●	●●	●●		●	●	●
Thermococcus sibiricus MM 739[p]	78	–[a,c]							●	●●	●●			●	●
Thermococcus guaymasensis TYS[q]	88	–[c]						○		●	●●	●	●	●	●
Thermococcus celer Vu 13[r]	88	–[a,c]							●	●	●●			●	●
Thermococcus peptonophilus OG-1[s]	90	–[a,c]						○	●	●	●●			●	●
Thermococcus barossii SHCK-94[t]	83	–[c]							●	●●	●●		○	●	●
Thermococcus siculi RG-20[u]	85	–[c]							●	●●	●●		○	●	●
Thermococcus radiotolerans EJ2[v]	88	–[c]							●	●●	●●		○	●	●
Thermococcus profundus DT 5432[w]	80	–[a,c]							●	●	●●		○	●	●
Thermococcus indicus IOH1[x]	80	ND							●	●●	●●	○		●	●
Thermococcus camini IRI35c[y]	80	–							●	●●	●●			●	●
Thermococcus gorgonarius W-12[z]	88	–[c]						○		●	●				
Palaeococcus pacificus DY20341[aa]	83	+[c]	●			●				●●	●●			●	●

(Continued)

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TABLE 3 (Continued)

Organism	T_{opt} (°C)	H_2 ↔ formate*	FT	Group 1A: *frh-fhl-mbh*	Group 1B: *frh-nfd-mbh*	Group 2: *nfd-sh*	Group 3: *fhl-sh*	Group 4: *fhl* only	Group 5: *fdhA* only	*Mbh*	*sh*	*frh*	*codh*	*purT*	*purP*
Pyrococcus kukulkanii NCB100[ab]	105	+[c]	●	●				●	●	●	●●	●		●	●
Pyrococcus yayanosii CH1[ac]	98	+[c]	●	●						●	●●	●		●	●
Pyrococcus abyssi GE5[ad]	96	–[c]						●	●	●	●●			●	●
Pyrococcus furiosus Vc1[ae]	100	–[c]							●	●	●●			●	●
Pyrococcus horikoshii OT3[af]	98	–[c]							●	●	●			●	●

The number of circles per column represents the number of times the gene(s) for that protein or operon appears in the organism's genome. Open circles represent incomplete operons; the open triangle, and *sh-nfd-mbh* operon configuration.
*Conversion of formate to H_2 or H_2 to formate; [a]Kim et al. (2010); [b]Topçuoğlu et al. (2018); [c]Le Guellec et al. (2021); ND, not determined. References and genome accession numbers: [d]Pledger and Baross (1989), CP006965; [a]Kim et al. (2010), CP013050; [e]Bae et al. (2006), CP000855; [f]Jolivet et al. (2003), CP001398; [g]Dalmasso et al. (2016), CP015520; [h]Holden et al. (2001), CP003651; [i]Gorlas et al. (2014), CP007264; [j]Atomi et al. (2004), AP006878; [k]Huber et al. (1995), LN999010; [l]Zhao et al. (2015), CP008887; [m]Miroshnichenko et al. (1998), CP015102; [n]Belkin et al. (1985), CP006670; [o]Marteinsson et al. (1999), CP002372; [p]Miroshnichenko et al. (2001), CP001463; [q]Canganella et al. (1998), CP007140; [r]Zillig et al. (1983), CP014854; [s]González et al. (1995), CP014750; [t]Duffaud et al. (1998), CP015101; [u]Grote et al. (1999), CP015103; [v]Jolivet et al. (2004), CP015106; [w]Kobayashi et al. (1994), CP014862; [x]Lim et al. (2020), CP040846; [y]Courtine et al. (2021), LR881183; [z]Miroshnichenko et al. (1998), CP014855; [aa]Zeng et al. (2013), CP006019; [ab]Callac et al. (2016), CP010835; [ac]Birrien et al. (2011), CP002779; [ad]Erauso et al. (1993), AL096836; [ae]Fiala and Stetter (1986), AE009950; [af]González et al. (1998), BA000001.

in a redox cascade involving NAD(P)H-dependent thioredoxin reductase (TrxR) and protein disulfide oxidoreductase (Pdo) as the electron donors (Lim et al., 2017). In the absence of S^0, SurR remains reduced, binds to $GTTn_3AAC(n_5GTT)$, promotes the transcription of *mbh* and *sh* genes, and represses the expression of *mbs* and *nsr* genes (Lipscomb et al., 2009). *Thermococci* with the Frh hydrogenase also can reduce TrxR using H_2 as the electron donor (Jung et al., 2020).

5. Abiotic formate in hydrothermal vents

5.1. Formate production in hydrothermal fluids

Abiotic formation of formate, carbon monoxide, methane, and hydrocarbons in hydrothermal vents is of interest as potential growth substrates for microbes. Methane and hydrocarbons in vents were suggested to form through Fischer-Tropsch type reactions $[(2n + 1)H_2 + nCO \rightarrow C_nH_{2n+2} + nH_2O]$ or leach from fluid inclusions in plutonic rocks (Berndt et al., 1996; Horita and Berndt, 1999; McCollom and Seewald, 2001; McDermott et al., 2015). In contrast to hydrocarbons, there is a strong thermodynamic drive toward rapid C-H-O equilibrium in hydrothermal fluids within hours to days. Kinetic barriers preclude the formation of CH_4 in this equilibrium (Shock, 1990). This permits the creation of metastable formate species ($H_2 + CO_2 \leftrightarrow HCOOH$), CO ($HCOOH \leftrightarrow CO + H_2O$), formaldehyde ($HCOOH + H_2 \leftrightarrow CH_2O + H_2O$), and methanol ($CH_2O + H_2 \leftrightarrow CH_3OH$) through the sequential reduction of CO_2 using H_2 as the reductant (Seewald et al., 2006).

The abundance of formate in chemical equilibrium with dissolved inorganic carbon is strongly dependent on H_2 concentration, pH, and temperature (McCollom and Seewald, 2003; Seewald et al., 2006). In a gold-titanium reaction cell, $HCOO^-$ was formed from CO_2 at 300°C and 350 bar in less than 24 h from H_2 generated from hydrothermal alteration of olivine serving as the reductant (McCollom and Seewald, 2001). In a separate study, incubation of a 175 mmol/kg HCOOH solution at 300°C and 350 bar in the gold reaction cell led to near complete conversion to H_2 and CO_2 within 48 h, CO reached 0.83 mmol/kg, and $HCOO^-$ + HCOOH (or ΣHCOOH) decreased to 0.38 mmol/kg (Seewald et al., 2006). Reducing the temperature to 200°C and then to 150°C each led to an increase in ΣHCOOH, a decrease in CO, and C-H-O equilibrium within 115 h and 71 h, respectively. Injection of 172 mmol/kg CO led to production of H_2, ΣCO_2, and ΣHCOOH, and decreasing CO. Alkaline conditions favored the formation of HCOOH, HCO_3^-, and CO_3^{2-} (Seewald et al., 2006). Therefore, the abundance of formate, CO, and CH_3OH in seafloor hydrothermal systems will be regulated by the residence times of fluids in reactions zones, and physical and chemical conditions in the subsurface environments.

Formate is also generated across a pH gradient of more than three pH units using a mineral precipitate bridge at the interface of two fluids (Hudson et al., 2020). This may be relevant to the formation of formate on the early Earth or possibly in extraterrestrial oceans where high pH serpentinized fluids are

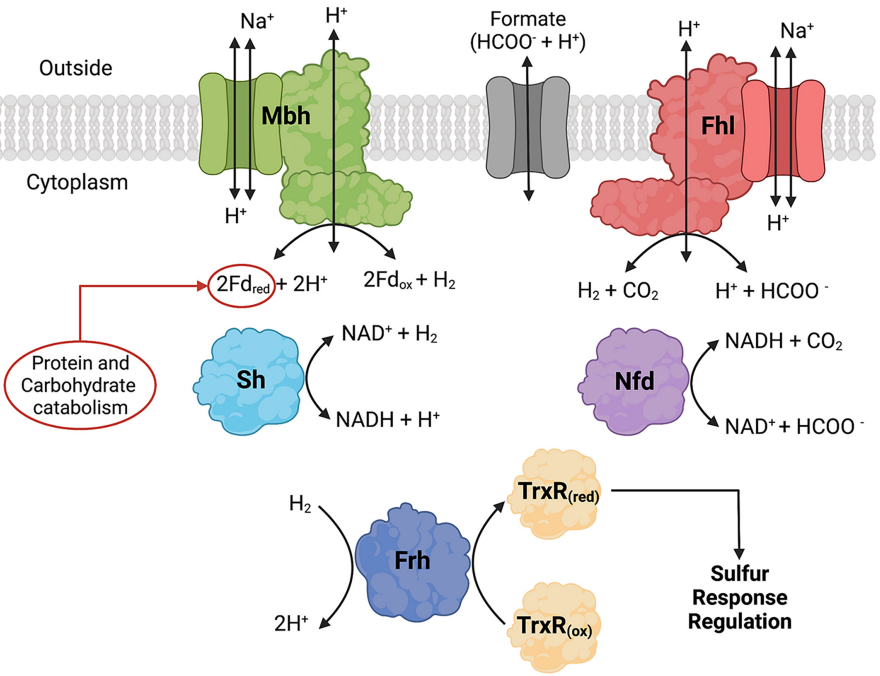

FIGURE 3
Formate dehydrogenase, hydrogenase, and formate transporter proteins and their reactions that are found in *Thermococci*. Formate hydrogenlyase (Fhl) catalyzes membrane-bound oxidation of formate to H_2 and CO_2. NAD(P)H: formate dehydrogenase (Nfd) catalyzes cytoplasmic oxidation of formate coupled with reduction of $NAD(P)^+$. The hydrogenases catalyze the following reactions: membrane-bound oxidation of ferredoxin (Fd) coupled with H_2 production (Mbh), cytoplasmic H_2 oxidation coupled with reduction of $NAD(P)^+$ (Sh), and cytoplasmic H_2 oxidation (Frd) coupled with reduction of thioredoxin reductase (TrxR). Fd and NAD(P)H are cytoplasmic electron carriers. TrxR is part of the redox cascade for sulfur response regulation using SurR. Created with BioRender.com.

emitted into an acid ocean. Under standard conditions, the generation of formate from H_2 and CO_2 is not thermodynamically favorable. However, H_2 in synthetic alkaline vent fluid (pH 12.3) passed electrons to dissolved CO_2 in a synthetic acid ocean (pH 3.9) at 25°C through a Fe(Ni)S mineral interface generating 1.5 μM $HCOO^-$ in the ocean fluid (Hudson et al., 2020). Isotopic labeling showed that protonation occurred using H_2O on the ocean side of the interface, not H_2 on the vent side. Weakening the pH gradient led to decreased concentrations of $HCOO^-$ produced. Nickel in the precipitate is a crucial part of the reduction mechanism as $HCOO^-$ yield dropped below detection without Ni in the ocean precipitation fluid.

5.2. Formate concentrations in hydrothermal fluids

There have been very few measurements of formate in natural hydrothermal fluids due in part to the analytical difficulty of measuring formate at low concentrations (Schink et al., 2017). Formate has been measured mostly at sites with high H_2 concentrations such as at the Lost City, Von Damm, and Piccard hydrothermal vent sites and were 36–669 μM (**Table 1**). Formate and H_2 were also measured at Snake Pit and TAG hydrothermal vents, which are mafic hydrothermal vents on the Mid-Atlantic Ridge, where formate concentrations were 1–2 nM and H_2 concentrations were 0.08–2.4 μM (Konn et al., 2022). At ultramafic sites, formate concentrations are generally 10–100 fold lower than that of H_2 at the same site (Lang et al., 2010; McDermott et al., 2015) while at mafic sites the formate concentration is often more than 1,000 fold lower than the H_2 concentration (McDermott et al., 2018; Konn et al., 2022).

6. Formate use by methanogens

6.1. Free formate use for *de novo* purine biosynthesis

Methanocaldococcus jannaschii was shown to incorporate ^{14}C-formate into biomass during growth (Sprott et al., 1993), which may be used in part for *de novo* purine biosynthesis. Inosine monophosphate (IMP) is a precursor for adenine and guanine synthesis for purine biosynthesis and is made from ribose-5-phosphate (**Figure 4**). In most organisms, the pathway intermediates glycinamide-ribose-5-phosphate (GAR) and aminoimidazole carboxamide-ribose-5-phosphate (AICAR) are formylated using N^{10}-formyl-tetrahydrofolate as the formyl donor. However, the genes for these enzymes are absent in *Methanococci* and *Methanopyri* and are replaced with genes that encode for enzymes that use free formate and energy from ATP to formylate their substrates (White, 1997; Brown et al., 2011). These enzymes are formylglycinamide-ribose-5-phosphate synthetase (PurT) and forminido imidazole carboxamide-ribose-5-phosphate synthetase (PurP) (**Figure 4**). *M. jannaschii* was shown

to have PurP activity and that it produced free ^{13}C-formate in the cell when incubated with H_2 and $H^{13}CO_3$ (Ownby et al., 2005). Herein, a genome survey of the eleven extremely thermophilic methanogens showed that all the organisms have homologs for *purP* and all but *M. kandleri* have homologs for *purT* (**Table 2** and **Supplementary Table 1**). This suggests that these organisms have a mechanism for formate synthesis.

6.2. Formate dehydrogenases in *Methanococci* and *Methanopyri*

Nine of the 11 *Methanococci* and *Methanopyri* genomes have genes that encode for a cytoplasmic formate dehydrogenase (**Table 2** and **Supplementary Table 1**). Formate dehydrogenases catalyze the reversible oxidation of formate to CO_2 using various electron acceptors. The catalytic α subunit (FdhA) contains tungsten, selenocysteine, and a (Fe_4-S_4) cluster as cofactors while the β subunit (FdhB) contains three (Fe_4-S_4) clusters (Niks and Hille, 2019). FdhAB in *Methanococci* and *Methanopyri* is homologous to two formate dehydrogenases in the mesophilic methanogen *Methanococcus maripaludis*, also a *Methanococci*, that use coenzyme F_{420} as their redox partner (**Figure 2**; Wood et al., 2003; Lupa et al., 2008). *M. maripaludis* grows hydrogenotrophically on H_2 and CO_2 but also grows on formate in their absence (Jones et al., 1983b). When *fdhA1* was mutated in *M. maripaludis*, the organism was unable to grow on formate and formate dehydrogenase activity in cell extracts was undetectable (Lupa et al., 2008). Observations with hydrogenase mutants in *M. maripaludis* suggest that coenzyme F_{420} is an intermediate in formate-to-H_2 conversion (Lupa et al., 2008). An *M. maripaludis*Δ*fdhA1*Δ*fdhA2* double mutant grown in purine-free defined medium grew as well as the wild-type strain suggesting that formate dehydrogenase is not essential for *de novo* purine biosynthesis (Wood et al., 2003). The absence of *fdhAB* genes in *Methanocaldococcus infernus* and *Methanofervidicoccus abyssi* (**Table 2** and **Supplementary Table 1**) also supports the idea that formate dehydrogenase is not essential for purine biosynthesis. However, it is likely that H_2 and coenzyme F_{420} are electron donors for formate production and can help meet the cellular demand for formate for purine biosynthesis.

The formate dehydrogenase (FdhA1B1) from *M. maripaludis* also forms an enzyme complex with heterodisulfide reductase, the soluble hydrogenase Vhu, and formylmethanofuran dehydrogenase (**Figure 2**; Costa et al., 2010). It was necessary for the organism's growth on formate but not on H_2 (Costa et al., 2010). Therefore, in addition to coenzyme F_{420} reduction, this formate dehydrogenase also oxidizes formate to reduce the heterodisulfide coenzyme M-coenzyme B and ferredoxin through electron bifurcation. Coenzyme M, coenzyme B, and ferredoxin are cytoplasmic electron carriers in these methanogens. Expression of the second formate dehydrogenase gene (*fdhA2*) in *M. maripaludis* increased when cells were grown under H_2 limited conditions but was unchanged under formate limited conditions (Costa et al., 2013) and was not required for growth on formate (Lupa et al., 2008) suggesting that this isoenzyme may have a separate physiological function.

6.3. Formate transporters in *Methanococci*

For extremely thermophilic methanogens, it appears that a formate transporter is required for growth on formate. Formate transporters import or export formate across the cytoplasmic membrane and require co-translocation of a H^+ (**Figure 2**). Three thermophilic methanogens in our survey (*Methanotorris formicicus*, *Methanothermococcus okinawensis*, and *Methanothermococcus thermolithotrophicus*) grew on formate in the absence of H_2 and CO_2 but not any of the other methanogens examined (**Table 2**). Each of these methanogens that grew on formate has a gene that encodes for a membrane-bound formate transporter (*fdhC*) in its genome, which is absent in all other methanogens examined, except for *Methanocaldococcus fervens* which was not tested for growth on formate (**Table 2** and **Supplementary Table 1**). *M. maripaludis* has an *fdhC* gene in an operon with *fdhA1B1* (Sattler et al., 2013). In *M. fervens* and *M. okinawensis*, the formate transporter gene *fdhC* appears to be in the same operon as *fdhAB* suggesting they are co-transcribed (**Supplementary Table 1**).

7. Formate use by *Thermococci*

7.1. Free formate use for *de novo* purine biosynthesis

Like *Methanococci*, all *Thermococci* lack the enzymes that use N^{10}-formyl-tetrahydrofolate as the formyl donor for *de novo* purine biosynthesis (Brown et al., 2011). Instead, most *Thermococci* use formate-dependent enzymes (PurT and PurP) for *de novo* purine biosynthesis (**Figure 4**, **Table 3**, and **Supplementary Table 2**). Therefore, they depend on a source of free formate in the cell for *de novo* synthesis. However, some *Thermococcus* species (*T. paralvinellae*, *T. barophilus* CH5, *T. onnurineus*, and *T. gorgonarius*) lack most or all the genes for the purine biosynthesis pathway (Brown et al., 2011) and likely rely on environmental sources of purines.

7.2. Formate dehydrogenases in *Thermococci*

All 30 *Thermococci* genomes have at least one copy of the gene that encodes for the catalytic α subunit of formate dehydrogenase (FdhA) either in the form of formate hydrogenlyase, NAD(P)$^+$-dependent formate dehydrogenase, or the catalytic subunit alone (**Table 3** and **Supplementary Table 2**). The phylogeny of FdhA in extremely thermophilic *Methanococci*, *Methanopyri*, and *Thermococci* showed one clade for *Methanococci* and *Methanopyri* and five clades among the *Thermococci* (**Figure 5**). In *Thermococci*, hydrogenase operons often flank *fdhA*-containing operons in the genome (**Figure 6** and **Supplementary Table 2**) suggesting a close association between formate and H_2 in these organisms. In Groups 1 and 2 in **Figure 5**, *fdhA* was encoded in an operon with a formate transporter gene. For Group 1, in nearly all instances,

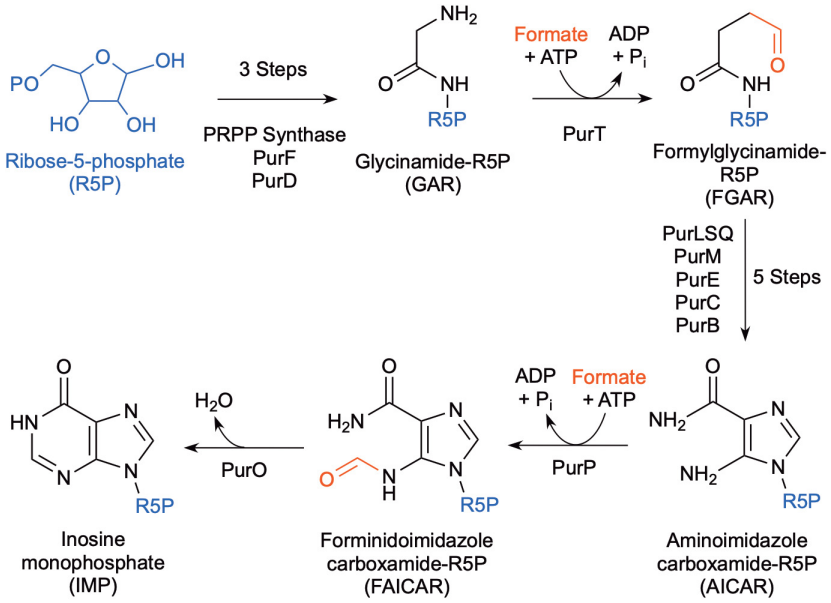

FIGURE 4
Biochemical pathway for *de novo* purine biosynthesis using free formate as the source of the formyl group (after Brown et al., 2011).

the *fdhA*-containing operon was immediately downstream from an *frh* operon and immediately upstream from one or two *mbh* operons on the same DNA strand suggesting that they may be co-transcribed (**Figure 6**). In Group 1A, *fdhA* was encoded in a formate hydrogenlyase (*fhl*) operon (Kim et al., 2010; Topçuoğlu et al., 2018; Le Guellec et al., 2021; **Table 3**; **Supplementary Table 2**). This enzyme reversibly couples formate oxidation to H_2 evolution on the cytoplasmic membrane with concomitant H^+/Na^+ translocation across the membrane *via* antiporter modules (**Figure 4**; Kim et al., 2010; Lim et al., 2014). In Group 1B, *fdhA* was encoded in a $NAD(P)^+$-dependent formate dehydrogenase (*nfd*) operon (**Figure 6**). This soluble enzyme catalyzes the reversible oxidation of formate using $NAD(P)^+$ or ferredoxin as its redox partner (Le Guellec et al., 2021; Yang et al., 2022; **Figure 4**). In Group 2, *fdhA* was encoded in an *nfd* operon but neighbored an *sh* operon in the genome instead of *frh* and *mbh* operons (**Figure 6**). These *nfd* and *sh* operons are transcribed in opposite directions from the same intergenic spacer region.

The *fdhA* from Groups 3 and 4 are in *fhl* operons that lack a formate transporter gene. In Group 3, the *fhl* operon was next to an *sh* operon (**Figure 6**). These *fhl* and *sh* operons are transcribed in opposite directions from the same intergenic spacer region. In Group 4, the *fhl* operon did not neighbor any hydrogenase operons in the genome, and in Group 5 the *fdhA* gene was the only formate dehydrogenase-related gene present in the genome (**Figure 6**). Often these solo genes in Group 5 are near the purine biosynthesis genes in genome sequences (**Supplementary Table 2**). In *T. sibiricus*, nearly all the genes for *de novo* purine biosynthesis (*purFCMTEDPSQL*) and *fdhA* are next to each other in the genome, although they are not all on the same DNA strand (**Figure 6**). In these organisms, it is unknown if *fdhA* alone encodes for a functional formate dehydrogenase or what the redox partner is for this putative enzyme. However, it is plausible that it might be used to produce formate for purine biosynthesis when other formate dehydrogenases and formate transport proteins are absent.

7.3. Formate transporters in *Thermococci*

Under defined growth conditions, 11 of the 30 *Thermococci* strains analyzed either oxidized added formate as an energy source (plus trace levels of organic compounds as a carbon source) and produced H_2 (Kim et al., 2010; Topçuoğlu et al., 2018) or secreted formate when grown on organic compounds in the presence of high background H_2 and the absence of added formate (Hensley et al., 2016; Topçuoğlu et al., 2018; Le Guellec et al., 2021). These 11 strains are the only *Thermococci* in the survey that have a formate transporter gene (**Table 3**). The other 19 *Thermococci* lack this gene and were unable to grow on formate or secrete formate (Kim et al., 2010; Le Guellec et al., 2021). Therefore, it appears that a formate transporter is required for *Thermococci* to secrete formate or, like *Methanococci*, for growth of *Thermococci* on formate. The presence of a formate transporter gene or transcript should be a criterion when determining if *Methanococci* or *Thermococci* are potentially using or producing formate in their natural habitat.

7.4. Formate production versus consumption by *Thermococci* in nature

The standard Gibbs energy for interconversion between formate and H_2 + CO_2 is small; therefore, the direction of the reaction is highly dependent upon the relative concentrations of formate and H_2 in the environment (Schink et al., 2017; Le Guellec et al., 2021). Le Guellec et al. (2021) calculated that CO_2 reduction to formate using H_2 is thermodynamically more favorable than formate oxidation to H_2 and CO_2 at

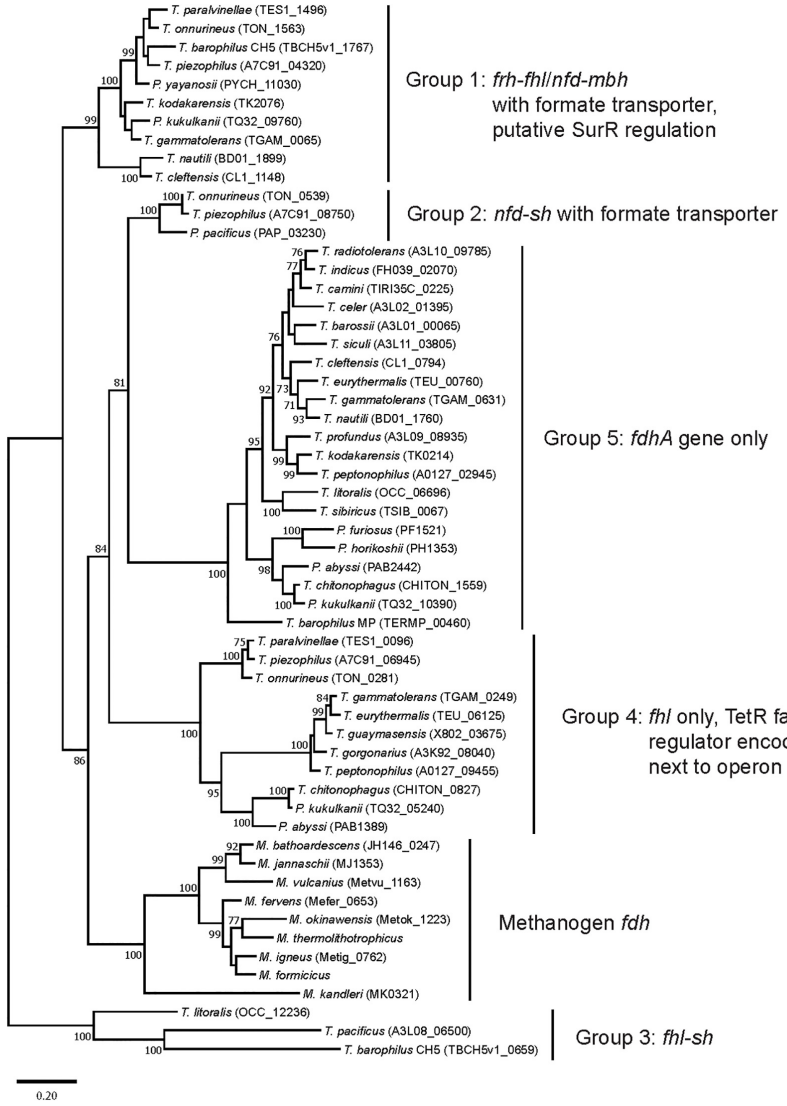

FIGURE 5
Phylogenetic tree based on catalytic subunit alpha (FdhA) for the various formate dehydrogenases found in extremely thermophilic *Methanococci*, *Methanopyri*, and *Thermococci*. The phylogeny of FdhA was inferred by using a maximum likelihood method and Jones-Taylor-Thornton (JTT) matrix-based modeling (Jones et al., 1992). After 1000 bootstrap constructions, the tree with the highest log likelihood (−31,270.37) is shown, with values next to nodes indicating the percentage of reconstructions in which the topology was preserved (values < 70% are omitted for clarity). There were a total of 736 positions in the final dataset. Branch lengths are to scale and indicate the number of substitutions per site. GenBank/EMBL/DDBJ open reading frame numbers are included in parentheses. Evolutionary analyses were conducted in MEGA11 (Tamura et al., 2021). Clade associations with operon arrangements on the genomes and the presence of a formate transporter or putative regulatory elements are shown.

Lost City, Von Damm, Rainbow, Lucky Strike, Snake Pit, and Ashadze 1 hydrothermal vent sites based on relative formate and H_2 concentrations in hydrothermal fluids. The physiological response of *Thermococcus* is in keeping with this idea. Growth of *T. paralvinellae* on a sugar or peptides when sparged with H_2 led to higher levels of *fhl1* expression and higher formate secretion relative to cultures sparged with N_2 (Topçuoğlu et al., 2018). It was concluded that *fhl* and *nfd* expression in *Thermococci* is primarily for the purpose of ameliorating H_2 inhibition rather than for growth on formate (Topçuoğlu et al., 2019; Le Guellec et al., 2021). *Thermococci* would require an environment where formate concentrations exceed H_2 concentrations to grow on formate. The formate produced by *Thermococci* may supplement the growth of *Methanococci* even when *Thermococci* produce H_2, as is observed with fermenter-methanogen relationships in mesophilic environments (Schink et al., 2017).

8. Transcriptional regulation of formate dehydrogenase genes

8.1. Transcriptional regulation in *Methanococci*

Formate consumption in *Methanococci* is closely associated with H_2 use in the cell. Therefore, a question that arises is whether

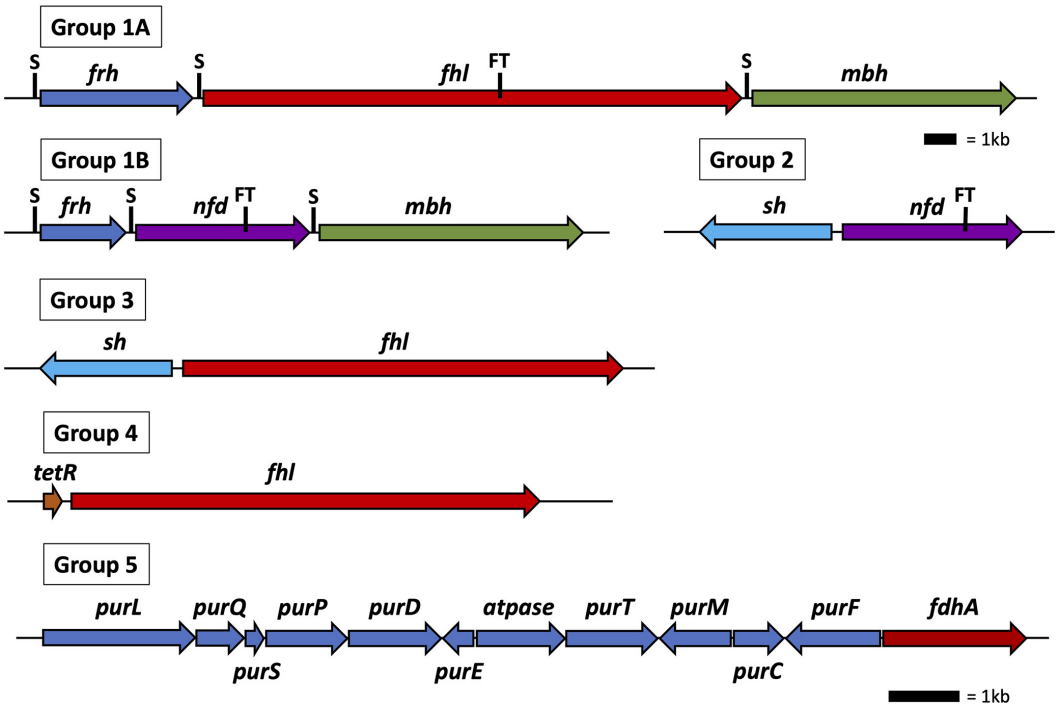

FIGURE 6
Operon and gene maps for *Thermococci* containing operons for formate hydrogenlyase (*fhl*), NAD(P)H: formate dehydrogenase (*nfd*), membrane hydrogenase (*mbh*), soluble hydrogenase (*sh*), and F_{420}-reducing-like hydrogenase (*frh*) (Groups 1–4) and genes for the catalytic subunit of formate dehydrogenase (*fdhA*), and purine biosynthesis (*pur*) (Group 5). Also shown are the locations of SurR binding sites (S), the *tetR* gene for transcriptional regulation, and the operons containing a formate transporter (FT) gene. The top scale bar is for the Group 1–4 operons; the bottom scale bar, the genes for Group 5.

formate or H_2 regulates *fdhAB* expression in these organisms. The thermophilic methanogen *Methanobacterium thermoformicicum* grows on H_2 and CO_2 as well as separately on formate. It has a formate transporter gene (*fdhC*) directly upstream of its formate dehydrogenase genes (*fdhAB*) (Nolling and Reeve, 1997). Transcripts of *fdhCAB* were present in *M. thermoformicicum* at all growth stages when grown on formate. When grown on H_2 and CO_2, *fdhCAB* transcripts were barely detectable in early exponential growth phase but increased dramatically as cells approached late exponential growth phase in a closed batch system when H_2 became more limiting. Similarly, *fdh* expression in *M. maripaludis* was controlled by the presence of H_2 and not formate (Wood et al., 2003). Using *fdhC-lacZ* gene fusions, β-galactosidase activity increased in *M. maripaludis* cells grown on H_2 and CO_2 as they approached late exponential growth phase, again when H_2 became limiting. When grown on formate, β-galactosidase activity was higher in cells with N_2 and CO_2 in the headspace relative to those with H_2 and CO_2 in the headspace. β-galactosidase activity increased in cells grown on formate plus H_2 and CO_2 after the H_2 and CO_2 was replaced mid-growth phase with N_2 and CO_2.

In *M. maripaludis*, genes for a putative response regulator and a histidine kinase are directly upstream of *fdhC*, which is three genes upstream of *fdhA1B1* and part of a putative five-gene operon (Sattler et al., 2013). Random mutagenesis showed that disruption of this putative response regulator led to slower growth of *M. maripaludis* on formate relative to the wild type. It also led to increased *fdhA1* transcriptional abundance regardless of whether H_2 and CO_2 or formate was the growth substrate. Impairment of derepression of the *fdhC-fdhA1B1* operon is a plausible explanation (Sattler et al., 2013). Therefore, H_2 present at high concentrations may interact with the histidine kinase and activate the response regulator in a two-component regulatory system that represses *fdhC-fdhA1B1* expression, which is derepressed when H_2 levels are low or absent.

8.2. Transcriptional regulation in *Thermococci*

Very little is known about transcriptional regulation of the *fhl* and *nfd* operons in *Thermococci*. Group 1 *Thermococci* genomes (**Figure 6**) encode syntenic *frh*, either *fhl* or *nfd*, and *mbh* operons with a formate transporter gene encoded in the *fhl* or *nfd* operon (**Figure 6**). These *frh*, *fhl*, *nfd*, and *mbh* operons each have $GTTn_3AAC(n_5GTT)$ in their promoter region just upstream of BRE/TATA RNA polymerase binding sites suggesting they are also regulated and promoted by the sulfur response regulator protein SurR (see Section "4.2. Growth of *Thermococci* with and without S^0"). Furthermore, Frh was shown to oxidize H_2 and reduce TrxR (Jung et al., 2020), which reduces SurR *via* Pdo, suggesting that it might serve as a regulatory hydrogenase that promotes *frh*, *fhl*, *nfd*, and *mbh* expression when H_2 concentrations increase in the cell. Therefore, like *Methanococci*, H_2 abundance appears to regulate formate use in *Thermococci*. A remaining question is whether formate also regulates gene expression in *Thermococci*. In

T. paralvinellae, expression of the Group 1A *fhl* operon containing the formate transporter gene increased when cells were grown on formate relative to growth on maltose or peptides while expression of *mbh* either remained unchanged or decreased (Topçuoğlu et al., 2018). This suggests that in addition to SurR regulation, formate either directly or indirectly regulates gene expression in *T. paralvinellae* as well. Validation and the mechanism of this putative regulation is yet to be determined.

None of the promoter regions for the *nfd*, *fhl*, or *sh* operons in Groups 2–4 had a SurR nucleotide binding sequence. All but one of the Group 4 *fhl* operons have a gene encoding for a TetR/AcrR family transcriptional regulator that is ∼350 nucleotides upstream of and transcribed in the same direction as the *fhl* operon (**Supplementary Table 2**). TetR/AcrR family transcriptional regulators are one-component systems where a single protein contains both a sensory domain and a DNA-binding domain (Cuthbertson and Nodwell, 2013). They are widely associated with antibiotic resistance and the regulation of genes encoding small molecule exporters and are usually encoded alongside target operons (Colclough et al., 2019). In *T. paralvinellae*, expression of the Group 4 *fhl* operon decreased when cells were grown on formate relative to growth on maltose or peptides (Topçuoğlu et al., 2018). The mechanism for regulation of Group 2–5 formate dehydrogenase-related genes is unknown.

9. Conclusion

Formate and H_2 are linked both in hydrothermal vent environments and in the metabolisms of extremely thermophilic *Methanococci* and *Thermococci*. *Methanococci* prefer H_2 oxidation to formate oxidation but appear to switch to the latter when H_2 is limiting. Similarly, *Thermococci* appear to prefer H_2 production to formate production but switch to the latter when H_2 is excessive and inhibitory. H_2 is typically far more abundant than formate in hydrothermal vent fluids suggesting that in high H_2 environments formate is unlikely to be used by *Methanococci* and *Methanopyri* for growth. However, in hydrothermal environments that are very low H_2 environments but rich in organic compounds, *Thermococci* may produce H_2 and formate that are then used to support the growth of extremely thermophilic methanogens. Understanding where, when, and how formate is used by extreme thermophiles in nature is largely unknown and an area of future research. Furthermore, our understanding of transcriptional regulation of *fhl* and *nfd* in *Thermococci* is nascent. A key question is if and how formate influences gene expression, especially in concert with SurR regulation of hydrogenases and sulfur responsive genes.

Author contributions

JH and HS contributed to the conceptualization, original draft preparation, review, and editing of the manuscript. JH conducted bioinformatic analyses and data compilation. Both authors read and agreed to the published version of the manuscript.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmicb.2023.1093018/full#supplementary-material

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