Abiotic redox reactions in hydrothermal mixing zones: Decreased energy availability for the subsurface biosphere

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Subseafloor mixing of high-temperature hot-spring fluids with cold seawater creates intermediate-temperature diffuse fluids that are replete with potential chemical energy. This energy can be harnessed by a chemosynthetic biosphere that permeates hydrothermal regions on Earth. Shifts in the abundance of redox-reactive species in diffuse fluids are often interpreted to reflect the direct influence of subseafloor microbial activity on fluid geochemical budgets. Here, we examine hydrothermal fluids venting at 44 to 149 °C at the Piccard hydrothermal field that span the canonical 122 °C limit to life, and thus provide a rare opportunity to study the transition between habitable and uninhabitable environments. In contrast with previous studies, we show that hydrocarbons are contributed by biomass pyrolysis, while abiotic sulfate (SO_4^{2-}) reduction produces large depletions in H_2. The latter process consumes energy that could otherwise support key metabolic strategies employed by the subseafloor biosphere. Available Gibbs free energy is reduced by 71 to 86% across the habitable temperature range for both hydrogenotrophic SO_4^{2-} reduction to hydrogen sulfide (H_2S) and carbon dioxide (CO_2) reduction to methane (CH_4). The abiotic H_2 sink we identify has implications for the productivity of subseafloor microbial ecosystems and is an important process to consider within models of H_2 production and consumption in young oceanic crust.

hydrothermal vent | subsurface biosphere | bioenergetics | biogeochemistry

At deep-sea hydrothermal vents, fluid–mineral reactions taking place at high temperatures and pressures substantially influence the chemical composition of the world's oceans (1, 2) and sustain thriving microbiological communities below and at the seafloor (3–6). Mixing between hot, chemically reduced hydrothermal fluids and cold, oxidized seawater in the subsurface creates moderate-temperature diffuse vent fluids and large amounts of potential chemical energy. Chemosynthetic microbes harness this chemical energy by catalyzing thermodynamically favorable redox reactions that support the primary fixation of inorganic CO_2 into biomass (5, 7, 8).

Numerous field investigations have demonstrated that vent fluid temperature and composition can control variability in modern-day microbial community structure and function (3–6) and provide insight into the environmental driving forces of evolution (9, 10). The close linkage between vent microbiology and fluid chemistry is further supported by thermodynamic models that estimate available energy for specific metabolic reactions (7, 11–13). Beyond serving as the primary producers at the base of the food web in hydrothermal environments, microbial activity has important biogeochemical implications, as metabolic processes can modulate the composition of diffuse fluids via the consumption and production of redox-reactive species within mixtures of endmember hydrothermal source fluids and seawater (14–23).

In addition to modification by active microbial processes, abiotic reactions and thermogenic reactions that involve thermal decomposition of living or once-living biomass can also exert important controls on diffuse fluid chemistry and microbial ecosystems. In particular, abiotic redox reactions that proceed rapidly and consume reactants utilized by microorganisms will reduce available metabolic energy, while thermogenic production of hydrocarbons represents a source of carbon and energy that can support a heterotrophic lifestyle.

Here, we report on the composition of low-temperature vent fluids (44 to 149 °C) sampled in 2012 and 2013 at the Piccard hydrothermal field, Mid-Cayman Rise (Tables 1 and 2, and *SI Appendix*, Tables S1 and S2). Hosted in unsedimented pillow basalts and sheet flows at a water depth of 4,970 m along the eastern flank of an ultraslow spreading (15 to 17 mm/y full rate), 12-km-long axial volcanic ridge, Piccard is Earth's deepest known vent field (24). Low-temperature fluid compositions indicate that they are formed by subseafloor mixing of cold (5 °C) seawater and 398 °C vent fluids represented by the nearby Beebe Vents black smokers. These high-temperature vents share a common major ion and dissolved volatile chemistry that reflects a single vapor phase, low-Cl source fluid that originates at temperatures

Table 1. Measured aqueous species abundances in mixing zones at the Piccard vent field

Vent (year)/sample*	T_{max}, °C	Mg, mm	pH, 25 °C	Ca, mm	SO_4, mm	Fe, mm	$\Sigma HCOOH$, μm
Beebe endmember[†]		0	—[‡]	6.18	0.21	6.58	–
Hot Chimlet 1 (2012)							
J2-619-IGT6	149	35.4	5.1	7.15	15.2	0.85	54
J2-619-IGT3	147	33.4	5.0	6.93	13.8	—[§]	58
Hot Chimlet 1 (2013)							
N59-IGT6	81	41.5	5.8	10.4	20.7	0.50	13
N59-IGT4	85	50.4	6.3	10.3	26.4	0.17	<1.0
Hot Chimlet 3 (2013)							
N62-IGT8	101	47.1	6.0	10.3	24.7	—[§]	55
N62-IGT7	97	35.1	5.4	10.2	16.6	0.35	167
Hot Chimlet 2 (2012)							
J2-620-IGT4	95	45.4	5.7	9.35	24.2	0.15	16
J2-620-IGT8	87	47.8	5.9	9.75	23.1	0.16	12
Shrimp Gulley 1 (2012)							
J2-620-IGT1	111	42.4	5.5	9.67	22.6	1.89	24
J2-620-IGT2	104	44.8	5.6	10.1	22.8	1.58	18
Shrimp Gulley 3 (2013)							
N63-IGT6	80	47.9	5.8	10.1	24.6	2.56	<1.0
Shrimp Gulley 2 (2012)							
J2-618-IGT1	45	47.4	6.0	10.2	25.4	0.091	9.4
J2-618-IGT3	44	48.9	5.9	10.1	25.2	0.11	8.8
Bottom seawater	~5	52.5	8.0	10.3	28.0	0.0	<1.0

*Jason (J2) or Nereus (N##) dive number and isobaric gas-tight sampler number (-IGT).
[†]Average high-temperature vent endmember [for Beebe 1, 3, 5, and Beebe Woods; McDermott et al. (25)]. See McDermott et al. (25) for IGT data from high-temperature fluid samples.
[‡]Lowest measured pH for high-temperature source fluids: 3.1 (Beebe Vent 1, 2012); 3.2 (Beebe Vent 3, 2012); 3.0 (Beebe Vent 5, 2012); 3.2 (Beebe Vent 5, 2013); 3.2 (Beebe Woods, 2012); from McDermott et al. (25).
[§]A dregs aliquot was not collected for sample J2-619-IGT3 or N62-IGT8. The dregs aliquot is composed of particles remaining in the IGT sampler following extraction of the aqueous sample; see *Methods and Materials*.
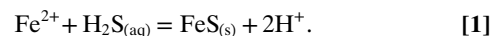
that potentially exceed 500 °C due to the great depth of the system (25). Many of the low-temperature Piccard fluids were turbid at the time of venting, suggesting that they contain fine-grained particulate material. The high-temperature Beebe Vents are characterized by dissolved H_2 concentrations as high as 20.7 mmol/L due to high temperatures in subsurface reaction zones (25), making the lower temperature diffuse fluids at Piccard ideally suited to assess processes that may consume H_2 and the abundance of other redox-reactive species in near seafloor mixing zones. The fate of H_2 generated in young oceanic crust is of high interest, as a recent synthesis study cannot account for at least 30% of all H_2 produced (26). Although uptake by subsurface microbial metabolic activity is inferred to be the primary driver for these H_2 losses, it is critically important to consider the possibility of abiotic sinks for H_2. An abiotic H_2 sink could vastly affect global H_2 budgets and estimates of subseafloor biosphere productivity.

Abiotic Processes in Subseafloor Mixing Environments

Because dissolved Mg^{2+} behaves conservatively during mixing of near-zero–Mg endmember high-temperature vent fluids and Mg-rich seawater, the effects of subseafloor mixing on a given aqueous species in a mixed vent fluid can be examined by plotting its concentration against Mg^{2+} (Fig. 1). Many species such as Cl^- show conservative behavior during mixing in the Piccard fluids (Fig. 1*A*), demonstrating their origin from simple two-component subsurface mixing between seawater and Beebe Vents fluids. However, several redox-reactive species behave nonconservatively and show significant depletions or enrichments (Fig. 1 and *SI Appendix*, Table S3). For example, concentrations of dissolved H_2, ΣH_2S ($\Sigma H_2S = H_2S + HS^- + S^{2-}$), and SO_4^{2-} show substantial depletions (Fig. 1 *B–D*), while dissolved $\Sigma HCOOH$ ($\Sigma HCOOH = HCOO^- + HCOOH$) and hydrocarbons show varying levels of enrichment (Fig. 1 *E–I*).

Dissolved Ca^{2+} and Fe^{2+} concentrations show both enrichments and depletions relative to conservative mixing (Fig. 1 *J* and *K*). In the case of Fe^{2+}, enriched concentrations may reflect entrainment of Fe-rich particles during sample collection (27). Some of the most pronounced depletions and enrichments are observed in the Hot Chimlet 1 fluids sampled in 2012. This fluid is characterized by a maximum measured temperature of 149 °C that exceeds the known temperature limit for life at 122 °C (28). Accordingly, we infer that consumption of H_2, the production of CH_4, and the nonconservative behavior of many other species at Hot Chimlet 1 (2012) must proceed via one or more abiotic processes.

Removal of dissolved ΣH_2S and Fe^{2+} from mixed fluids can be attributed to the precipitation of iron sulfide minerals due to decreases in their solubility with decreasing temperature and increasing pH. Near equimolar depletions of ΣH_2S and Fe^{2+} that range from 0.88 to 1.85 mmol/kg in the Hot Chimlet 1 fluids in both 2012 and 2013 and the Hot Chimlet 3 fluids (*SI Appendix*, Table S3) suggest pyrrhotite (FeS) formation during mixing according to the following reaction:

$$Fe^{2+} + H_2S_{(aq)} = FeS_{(s)} + 2H^+. \qquad [1]$$

Phase relations in the chemical system Fe–S–O–H indicate that pyrrhotite is the stable iron phase for the measured concentrations of ΣH_2S and H_2 in the endmember fluids to temperatures down to 150 °C (Fig. 2), consistent with pyrrhotite formation during the early stages of vent fluid mixing with cold seawater. Continued seawater mixing produces temperatures below 150 °C and reduces dissolved H_2 concentrations, shifting fluid compositions into the pyrite (FeS_2) stability field (Fig. 2). Accordingly, pyrite formation may be responsible for additional depletion in ΣH_2S and Fe^{2+} during the later stages of mixing under temperature conditions compatible with life.

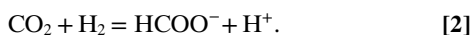# Table 2. Measured volatile species abundances and isotope values in mixing zones at the Piccard vent field

Vent (year)/ sample*	ΣH_2S, mm	$\delta^{34}S_{H2S}$, ‰	H_2, mm	ΣCO_2, mm	CH_4, μm	C_2H_6, nm	C_3H_8, nm	$n\text{-}C_4H_{10}$, nm	$i\text{-}C_4H_{10}$, nm	$\delta^{13}C_{CH4}$, ‰	$\delta^{13}C_{C2H6}$, ‰	$\delta^{13}C_{C3H8}$, ‰
Beebe endmember[†]	11.7	6.1	19.4	25.7	121	13	7.6	1.9	1.3	−23.9	−24.9	−
Hot Chimlet 1 (2012)												
J2-619-IGT6	2.47	6.6	1.94	9.09	51.2	43	28	9.0	9.7	−28.4	−33.3	−29.7
J2-619-IGT3	2.60	—	2.06	10.1	56.5	92	66	27	11	−29.9	−33.5	−28.2
Hot Chimlet 1 (2013)												
N59-IGT6	1.47	—	0.027	—	39.6	27	22	5.4	5.2	—	—	—
N59-IGT4	0.086	—	0.010	—	9.78	—	—	—	—	—	—	—
Hot Chimlet 3 (2013)												
N62-IGT8	0.45	—	0.13	—	23.0	—	—	—	—	—	—	—
N62-IGT7	2.03	—	0.45	—	64.3	36	28	7.3	7.7	—	−36.9	−29.5
Hot Chimlet 2 (2012)												
J2-620-IGT4	1.04	—	0.68	4.89	21.8	17	11	4.3	3.4	−29.2	—	—
J2-620-IGT8	0.96	—	0.52	4.08	15.6	11	8.3	3.1	<1.0	—	—	—
Shrimp Gulley 1 (2012)												
J2-620-IGT1	1.95	—	0.40	5.95	24.0	14	9.7	3.8	1.6	—	—	—
J2-620-IGT2	1.12	—	0.28	5.56	20.5	12	7.3	2.7	<1.0	—	—	—
Shrimp Gulley 3 (2013)												
N63-IGT6	0.49	—	<0.002	—	19.4	—	—	—	—	—	—	—
Shrimp Gulley 2 (2012)												
J2-618-IGT1	0.83	—	0.11	3.39	10.8	5.1	—	1.6	<1.0	—	—	—
J2-618-IGT3	0.84	—	0.13	3.64	10.9	5.1	4.0	1.8	<1.0	—	—	—
Bottom seawater	0	—	0	2.21	0	0	0	0.0	0	—	—	—

*Jason (J2) or Nereus (N##) dive number and isobaric gas-tight sampler number (-IGT).
[†]Average high-temperature vent endmember [for Beebe 1, 3, 5, and Beebe Woods; McDermott et al. (25)]. See McDermott et al. (25) for IGT data from high-temperature fluid samples.

The formation of iron sulfides such as pyrrhotite according to reaction **1** results in the generation of 2 equivalents of acidity for each mole of ΣH_2S and Fe^{2+} that precipitates. Thus, the Hot Chimlet 3 fluids that display the largest ΣH_2S and Fe^{2+} depletion of 1.85 mmol/kg will generate acidity at a level sufficient to titrate all of the alkalinity contributed by admixed seawater and create fluids characterized by pH (25 °C) <3 in the absence of other reactions that consume H^+. Measured pH (25 °C) values for all of the mixed fluids are >5, providing evidence for titration of acidity by additional geochemical processes.

Enrichment of the mixed Piccard fluids in $\Sigma HCOOH$ suggests that CO_2 reduction during mixing may account for a portion of the observed H_2 depletions. Reducing conditions, coupled with the lower temperatures and higher pH conditions of a mixed fluid, provide a thermodynamic drive for the abiotic reduction of CO_2 by H_2 to $\Sigma HCOOH$ according to the following reaction:
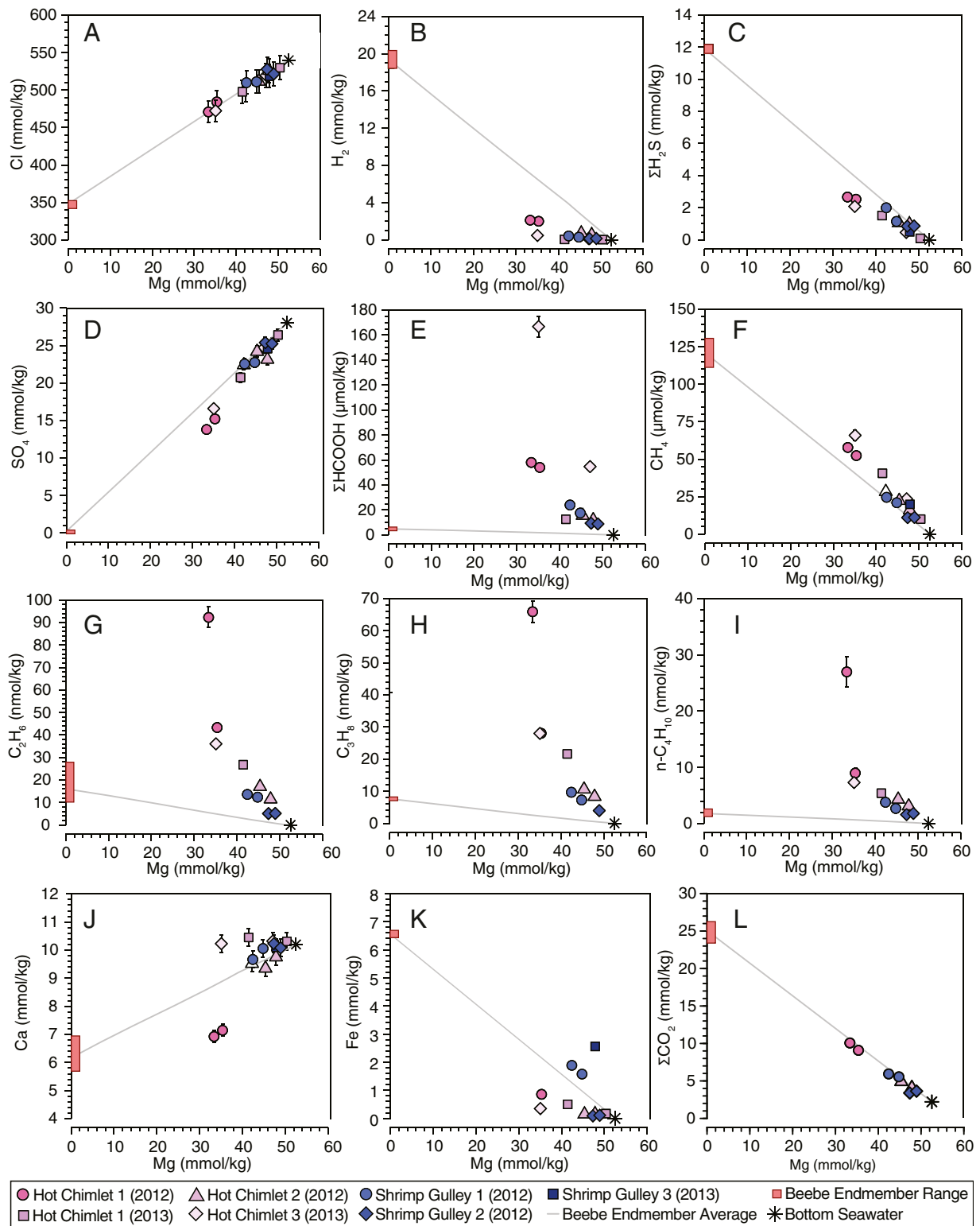
$$CO_2 + H_2 = HCOO^- + H^+. \qquad [2]$$

Calculated chemical affinities for reaction **2** in >100 °C mixed fluids are less than ±5 kJ/mol, suggesting that they have attained metastable thermodynamic equilibrium between CO_2, H_2, and $\Sigma HCOOH$. Calculated affinities in the <100 °C fluids are slightly higher than those at >100 °C with positive values of +8.6 kJ/mol, suggesting a thermodynamic drive for additional $\Sigma HCOOH$ production that may reflect slower reaction kinetics at lower temperatures of these fluids. A similar approach to equilibrium involving CO_2, H_2, and $\Sigma HCOOH$ has been documented at the nearby Von Damm vent field (29) and at the Lost City vent field, Mid-Atlantic Ridge (30). Attainment of metastable equilibrium according to reaction **2** in subseafloor mixing zones represents an abiotic pathway for the production of $\Sigma HCOOH$ that may fuel microbial metabolism (6).

Although formation of $\Sigma HCOOH$ in subseafloor mixing zones consumes H_2 according to reaction **2**, the relatively low concentrations observed indicate that it can account for only a small fraction of the H_2 depletions in the mixed fluids. For example, close examination of the 149 °C Hot Chimlet 1 fluid in 2012 (J2-619-IGT6, Tables 1 and 2) reveals a H_2 depletion of 4.3 mmol/kg (Fig. 1B) that was accompanied by production of only 0.052 mmol/kg $\Sigma HCOOH$ (Fig. 1E). Relatively minor depletions in ΣCO_2 (Fig. 1L; $\Sigma CO_2 = H_2CO_3^* + HCO_3^- + CO_3^{2-}$) indicate that reduction of ΣCO_2 to other reduced carbon species is not responsible for the large H_2 depletions in the mixed fluids. Rather, the linear relationship between ΣCO_2 and Mg abundances (Fig. 1L) largely reflects mixing of a high ΣCO_2 endmember with lower ΣCO_2 seawater. Minor amounts of H_2 may also be consumed by reaction with dissolved O_2 and NO_3^- present in admixed seawater at concentrations of ∼0.2 and ∼0.02 mmol/kg, respectively (31). Collectively, $\Sigma HCOOH$ production and O_2 and NO_3^- reduction can consume ∼0.4 mmol/kg of H_2 in the 2012 Hot Chimlet 1 fluid, requiring an additional sink for the remaining 3.9 mmol/kg of H_2 depletion.
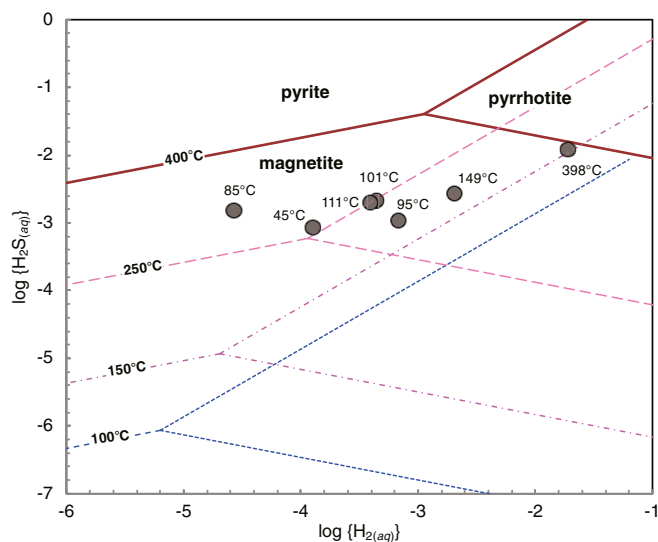
High concentrations of dissolved SO_4^{2-} in conjunction with depletions relative to conservative values in mixed fluids suggest that reactions involving the reduction of SO_4^{2-} are responsible

Fig. 1. Measured concentrations of aqueous Mg versus aqueous Cl (*A*), H$_2$ (*B*), ΣH$_2$S (*C*), SO$_4$ (*D*), ΣHCOOH (*E*), CH$_4$ (*F*), C$_2$H$_6$ (*G*), C$_3$H$_8$ (*H*), *n*-C$_4$H$_{10}$ (*I*), Ca (*J*), Fe (*K*), and ΣCO$_2$ (*L*) for mixed fluids sampled at the Piccard vent field in 2012 and 2013. For each species, the range in extrapolated zero-Mg high-temperature endmember composition is shown with the red bar along the *y* axis, and the average is shown with a gray line projected from seawater composition. Species that exhibit conservative behavior during mixing plot on the line, while species that behave nonconservatively plot above or below the line. The 2s errors are shown (or are smaller than the symbols).

for the observed H$_2$ depletions. Complete SO$_4^{2-}$ reduction results in the production of ΣH$_2$S, while partial reduction may form sulfur species in intermediate states such as sulfur (S), thiosulfate
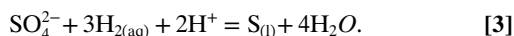
(S$_2$O$_3^{2-}$), or polysulfide (S$_x^{2-}$). Equilibrium fractionation factors for isotopic exchange between SO$_4^{2-}$ and ΣH$_2$S (32) indicate that reduction of SO$_4^{2-}$ at temperatures below 400 °C should produce

Fig. 2. Activity diagram showing phase relations in the chemical system Fe–S–O–H at 400, 250, 150, and 100 °C and 500 bar. The symbols indicate measured $H_2S(aq)$ and $H_2S(aq)$ concentrations in Piccard vent fluids. Requisite thermodynamic data for the construction of the diagram were calculated using SUPCRT92 computer code (56) and corrected for the nonstoichiometric composition of pyrrhotite in equilibrium with pyrite (57).

ΣH_2S that is highly depleted in ^{34}S relative to initial seawater SO_4^{2-} ($\delta^{34}S_{seawater\ SO4} = 21.0‰$). For example, ΣH_2S produced from seawater SO_4^{2-} at 350 °C would have a $\delta^{34}S$ value of 4.1‰ at 350 °C and −2.5‰ at 250 °C (32), resulting in decreasing $\delta^{34}S$ values for dissolved ΣH_2S in low-temperature mixed fluids. Comparison of the ^{34}S content of ΣH_2S in the high-temperature endmember fluid with the ^{34}S content of ΣH_2S in the 2012 Hot Chimlet 1 fluid reveals near-identical values of 6.1 and 6.6‰, respectively, indicating that significant amounts of ΣH_2S produced by SO_4^{2-} reduction during mixing have not been added to the low-temperature fluids. The absence of evidence for reduction of SO_4^{2-} to ΣH_2S suggests that the observed H_2 depletions relect formation of intermediate oxidation state sulfur species.

The formation of intermediate oxidation state sulfur species has been reported for several low-temperature vent environments (18, 33, 34) but was not determined in this study. We postulate that the H_2 depletions observed in the low-temperature Piccard fluids result from the formation of elemental S, $S_2O_3^{2-}$, and S_x^{2-} (Fig. 3). Indeed, the distinct turbidity that characterized many of the low-temperature Piccard fluids may reflect condensation of liquid or particulate sulfur. Reduction of seawater SO_4^{2-} to an intermediate oxidation state such as elemental S can be represented by the following reaction:

$$SO_4^{2-} + 3H_{2(aq)} + 2H^+ = S_{(l)} + 4H_2O. \qquad [3]$$

Reaction **3** predicts that each mole of SO_4^{2-} reduced will consume 3 mol of H_2 and 2 mol of H^+, indicating that formation of elemental S may represent a sink for acidity produced by precipitation of iron sulfides according to reaction **1** in addition to dissolved H_2. The 3.9 mmol/kg H_2 depletion in the 2012 Hot Chimlet 1 fluid that cannot be attributed to reduction of ΣCO_2, O_2, and NO_3^- would be consistent with the reduction of 1.3 mmol/kg SO_4^{2-}. The observed SO_4^{2-} depletion of 3.7 mmol/kg in this fluid (Fig. 1D and *SI Appendix*, Table S3) is substantially greater than this value, but includes removal of SO_4^{2-} due to anhydrite ($CaSO_4$) precipitation. Due to significant variability in the endmember fluid Ca concentration (Fig. 1K), estimates for the amount of anhydrite precipitation based on Ca
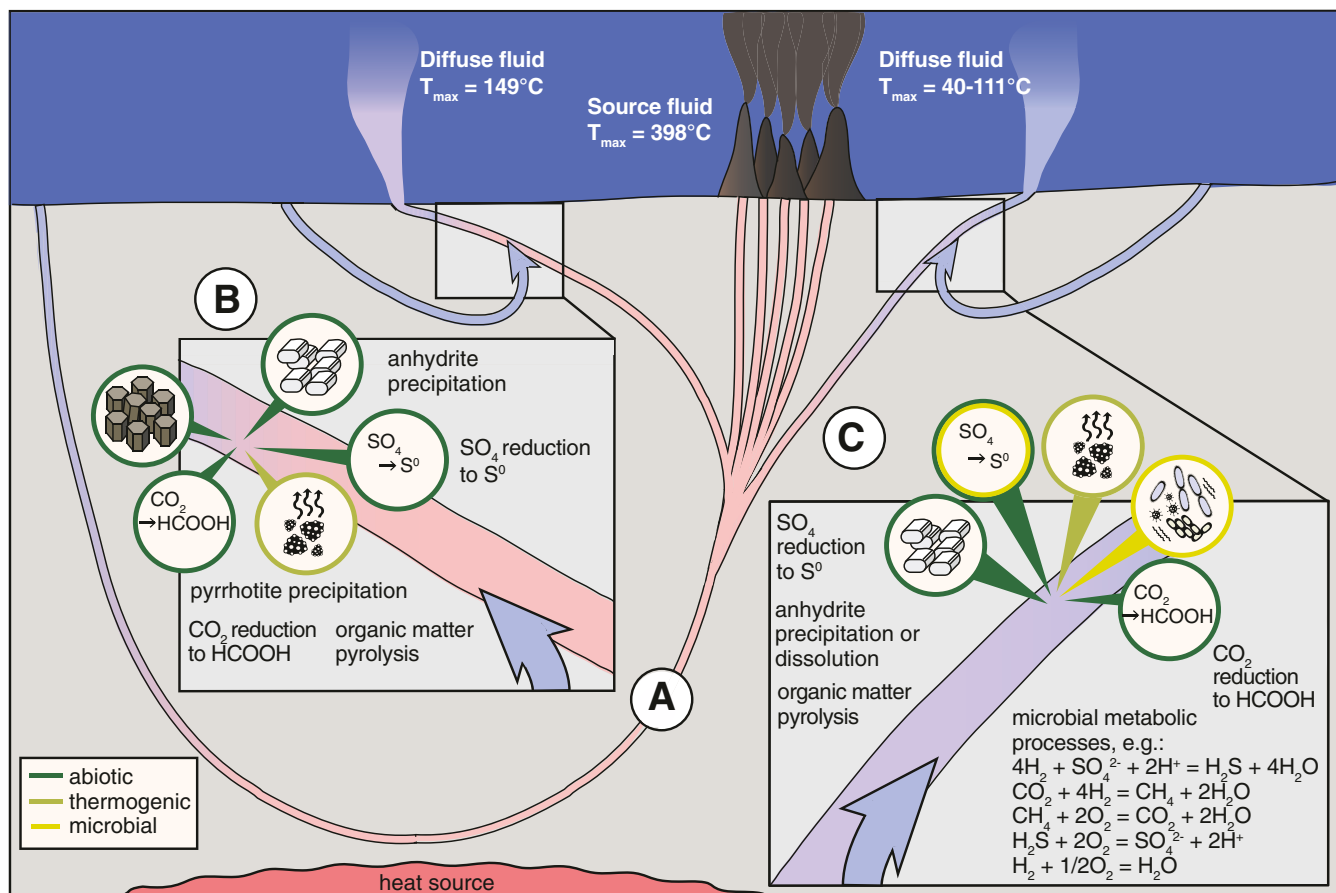
depletions vary from 1.6 to 2.3 mmol/kg, suggesting that 1.4 to 2.1 mmol/kg of the SO_4^{2-} depletion can be attributed to formation of intermediate oxidation state sulfur species. Although the low end of this range is consistent with the observed H_2 depletion via elemental S formation (reaction **3**), the higher values may suggest production of more oxidized intermediate oxidation state sulfur species, such as $S_2O_3^{2-}$, that would consume less H_2 for a given amount of SO_4^{2-} reduced.

In contrast to the Hot Chimlet 1 (2012) fluid, measured temperatures of all other mixing zone fluids collected in 2012 and 2013 are below the canonical 122 °C limit for life. Thus, the chemistry of these fluids could be impacted by active microbial processes in addition to abiotic processes (Fig. 3). It is important to note, however, that this 122 °C record is held by a methanogen grown in the laboratory under optimal conditions (28). In the natural environment, the limit for life may be closer to 80 °C, as has been shown in petroleum basin systems (35). Eleven of 13 fluids in this study match or exceed 80 °C, and thus the chemistry of the majority of our samples may reflect only abiotic or thermogenic inputs. All fluids have lost significant quantities of H_2 relative to conservative mixing calculations (0.77 to 5.98 mmol/kg H_2 lost; Fig. 1B and *SI Appendix*, Table S3). Common metabolic reactions that directly impact H_2, such as aerobic H_2 oxidation, can be eliminated as significant, due to insufficient O_2 availability to account for the magnitude of H_2 lost.

Mixed fluids sampled in 2013 at Hot Chimlet 1, Hot Chimlet 3, and Shrimp Gulley 3 have temperatures of 80, 101, and 85 °C, respectively, and are characterized by significant SO_4^{2-} depletions from 0.5 to 2.2 mmol/kg (Fig. 1D and *SI Appendix*, Table S3). These SO_4^{2-} depletions are accompanied by Ca^{2+} enrichments relative to conservative mixing (Fig. 1J and *SI Appendix*, Table S3) indicating net dissolution of anhydrite, which would have contributed additional SO_4^{2-} to the fluid in 1:1 proportion to Ca^{2+}. The observation that SO_4^{2-} has been consumed in these fluids despite an additional source from dissolving anhydrite, highlights the importance of abiotic or microbially mediated SO_4^{2-} reduction pathways as a sink for H_2.

Thermogenic Processes

In contrast to the depletions observed for inorganic redox reactive species, measured concentrations of CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, and i-C_4H_{10} in the low-temperature mixed fluids at the Piccard vent field are significantly greater than abundances expected for conservative mixing of endmember fluids and seawater, especially within the 149 °C Hot Chimlet fluid in 2012 (Table 2 and Fig. 1 F–I). Several lines of evidence suggest that these hydrocarbon enrichments are the product of thermal degradation of immature organic material. Relative to biogenic and abiotic mantle-derived hydrocarbons that are dominated by CH_4, thermogenic hydrocarbons generally contain substantially greater proportions of C_{2+} alkanes (36). Thus, substantially lower CH_4/C_{2+} values (mol/mol) of 290 to 1,000 in the low-temperature mixed fluids relative to the high-temperature endmember fluids characterized by CH_4/C_{2+} values of 2,300 to 4,500, likely reflect a large increase in the relative abundance of thermogenic C_{2+} hydrocarbons. Similar processes have been noted in the high-temperature fluids at Piccard. For example, a higher C_2H_6 concentration at Beebe Woods (354 °C, 28 nmol/kg) relative to the higher temperature Beebe Vents (398 °C, 11 to 15 nmol/kg) has been attributed to pyrolysis of dissolved organic carbon (DOC) in admixed seawater (25). Thermogenic hydrocarbon inputs are far more apparent in the mixed fluids presented here and represent a substantially greater fraction of the total hydrocarbon budgets. The linear inverse correlation of individual hydrocarbons with Mg in the diffuse fluids (Fig. 1) suggests that thermal alteration of organic matter occurs above the maximum temperature of 149 °C for the mixed fluids at

Fig. 3. Schematic representation of key processes that occur when ascending high-temperature source fluids mix with seawater (A) under relatively higher temperature (~149 °C) (B) and lower temperature (<122 °C) conditions (C). At temperatures of ~149 °C and higher, mixed fluid chemistry is impacted by abiotic reactions involving the aqueous reduction of dissolved species and mineral precipitation, along with thermogenic reactions involving the pyrolysis of living or previously living organic matter. At temperatures at and below 122 °C, microbial metabolic processes may occur in addition to abiotic and thermogenic processes. The metabolic processes could include hydrogenotrophic SO_4^{2-} reduction, anaerobic methanogenesis from CO_2 and H_2, methanotrophy by O_2, sulfide oxidation by O_2, and hydrogen oxidation by O_2.

Piccard, with subsequent seawater mixing producing decreasing hydrocarbon concentrations due to dilution.

The carbon isotopic composition of Hot Chimlet 1 hydrocarbons also supports a thermogenic origin for the hydrocarbon enrichment in the mixed fluids. The isotopic compositions of Hot Chimlet 1 hydrocarbons vary from −28.4 to −29.9‰ for CH_4 and −33.3 to −36.9‰ for C_2H_6 (Table 2). These values are significantly depleted in ^{13}C relative to the ^{13}C content of hydrocarbons in the endmember fluids that are characterized by uniform $\delta^{13}C$ values of −23.9‰ and −24.9‰ for CH_4 and C_2H_6, respectively. An isotope mass balance assuming two-component conservative mixing of hydrocarbons in endmember fluid (Table 2) with a thermogenic component added during mixing yields calculated $\delta^{13}C$ values of −39.7, −33.8, and −28.9‰ for thermogenic CH_4, C_2H_6, and C_3H_8, respectively. The calculated values fall within the range of −25‰ to −50‰ and show progressive ^{13}C enrichment with increasing carbon chain length, consistent with trends typically observed for thermogenic hydrocarbons (37–39). The presence of hydrocarbons with similar isotopic compositions in mixed fluids with temperatures above and below 122 °C suggests that they are derived from a common process occurring above and below the temperature limit for life (Fig. 3). The Piccard mixed fluids are also characterized by substantial enrichments in dissolved ΣNH_4 ($\Sigma NH_4 = NH_3 + NH_4^+$) and methanethiol ($CH_3SH$) relative to the high-temperature endmembers (40) (*SI Appendix*, Table S1). Both species are

products of thermal degradation of fresh organic matter and provide additional evidence that thermogenic processes are contributing to the chemical inventory of mixed fluids at Piccard.

Implications for Subsurface Life and Chemical Fluxes to the Ocean

Sulfate reduction rates and mechanisms have largely been studied within the context of petroleum reservoirs and sedimented basins, where SO_4^{2-} is reduced by organic matter via microbially or abiotically mediated processes (41). Sulfur cycling is also important within ancient hydrothermal systems, deep terrestrial aquifers, and in applied fields such as nuclear waste disposal. The reaction kinetics of SO_4^{2-} reduction by H_2 have been investigated in a two-phase (water plus gas) experiment conducted under hydrothermal conditions (42). Several conditions that enhance reduction kinetics were identified, including temperature, the pH-dependent speciation of SO_4^{2-}, and the initial presence of H_2S to contribute to the formation of $S_2O_3^{2-}$ and S_x^{2-} intermediates. Our results suggest that conditions in the Piccard mixing zone, where fluid residence times are estimated to be on the order of hours to days, support the reduction of SO_4^{2-} to intermediate oxidation state sulfur species such as elemental S, $S_2O_3^{2-}$, and S_x^{2-}.

The existence of a chemosynthetic subsurface biosphere inhabiting fractures in the shallow oceanic crust has been widely discussed (43). Evidence for subsurface life at oceanic spreading centers ranges from direct observations of microbial blooms

following eruptive events (44), to microbial communities inhabiting the surface and interior of young basaltic crust (45), to indirect measurements of chemical signatures in venting fluids that are presumed to be generated by thermal degradation of subseafloor microbial biomass (46). For example, elevations in long-chained and cyclic hydrocarbons and microbial lipid residues have been identified in high- and low-temperature vents, relative to their abundances in seawater (46). Some endmember fluids, including those at Piccard and Von Damm vent fields along the Mid-Cayman Rise, contain lower bulk DOC concentrations than ambient seawater, implying that thermal degradation at high temperatures is an important DOC removal mechanism in deep-sea vents (47, 48). In contrast, lower temperature vent fluids contain elevated DOC and microbial cell counts that are higher than ambient seawater (6, 47, 49).

Past studies have documented substantial depletions in H_2 and enrichments in CH_4 in low-temperature mixed hydrothermal vent fluids relative to values expected for conservative mixing (14, 15, 21, 22). Due to the presence of active microbial ecosystems in contact with the fluids (16, 17) and measured temperatures below 122 °C, the H_2 depletions and CH_4 enrichments in those studies were attributed to active microbial methanogenesis. Here, we demonstrate that H_2 depletions and CH_4 enrichments may, instead, reflect abiotic and thermogenic reaction pathways such as those occurring within hydrothermal mixing zones at the Piccard vent field at temperatures in excess of the known limits to life.
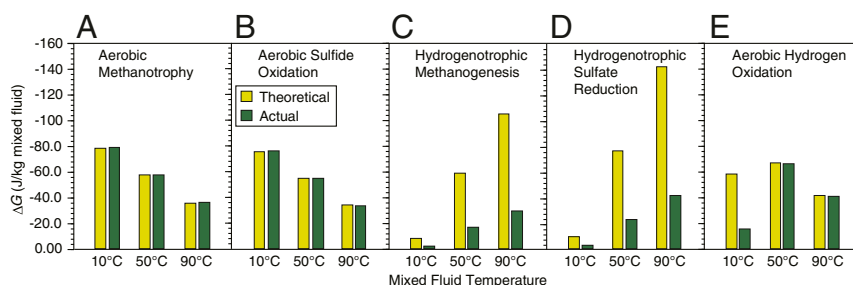
In general, previous studies that estimate Gibbs free energy available to support the subseafloor biosphere in hydrothermal settings do not consider abiotic and thermogenic reactions that consume H_2 and generate CH_4 and $C_{2–4}$ alkanes. To further quantify the implications of abiotic reactions on the energy landscape for the subsurface biosphere at Piccard, two geochemical mixing models were constructed that allow calculation of the maximum amount of potential chemical energy available to support five chemolithoautotrophic metabolic pathways using an approach that is similar to previous investigations (7, 50) (see Fig. 3 for metabolic reactions; see *SI Appendix* for calculation details). Both models involved incremental mixing of a hydrothermal fluid with 2 °C seawater over a temperature range of 160 to 5 °C at 500-bar pressure. For the first model, the starting composition of the hydrothermal fluid represents a conservative mixture of the endmember Beebe Vent fluid with anaerobic seawater to achieve a Mg concentration identical to the Hot Chimlet 1 fluid (*SI Appendix*, Table S7). For the second model, the composition of the fluid in 2012 (J2-619-IGT6, Table 1) was used for the starting composition of the hydrothermal fluid. At each step in the models, the potential Gibbs free energy available to support sulfate reduction, methanogenesis, methanotrophy, sulfide oxidation, and hydrogen oxidation was calculated using the calculated equilibrium distribution of aqueous species at temperatures less than or equal to 122 °C. Results demonstrate that the amount of Gibbs

free energy available for aerobic methanotrophy by O_2 and sulfide oxidation by O_2 increase only marginally, up to 0.1% and 0.2% per kg of mixed fluid, respectively, at a given temperature (Fig. 4 *A* and *B*). On a percent basis, a negligible amount of additional energy is made available to chemo-heterotrophic organisms that oxidize CH_4. In contrast, the potential chemical energy available for both methanogenesis involving reduction of CO_2 by H_2 and for hydrogenotrophic SO_4^{2-} reduction is reduced by 71 to 86% across the habitable temperature range (Fig. 4 *C* and *D*). In addition, the potential energy available for H_2 oxidation by O_2 is reduced by 1 to 84%, with the greatest impact at 10 °C (Fig. 4*E*). Within 50 to 90 °C mixing regimes where H_2-utilizing metabolic reactions may otherwise be expected to dominate, the energy landscape shifts to favor O_2-utilizing reactions. While thermogenic degradation of biomass can release energy to support chemo-heterotrophic organisms in submarine hydrothermal systems, our study demonstrates that abiotic processes may substantially reduce the amounts of H_2-based energy available to the subsurface biosphere on Earth. This abiotic H_2 sink could vastly affect global H_2 budgets and should be considered in tandem with biologically mediated sinks in global H_2 mass balance models.

Materials and Methods

Hydrothermal Vent Fluid Sampling. Hydrothermal fluid samples were collected by ROV *Jason II* during cruise AT18-16 aboard the R/V *Atlantis* in January 2012 and by HROV *Nereus* during cruise FK008 aboard the R/V *Falkor* in June 2013, following the approach reported in McDermott et al. (25). All fluids were collected using titanium isobaric gas-tight (IGT) samplers (51). Replicate samples were collected at each orifice when feasible. Fluid temperatures were monitored continuously with thermocouples mounted flush to the inlet of each IGT during the ~2 min required to fill each sampler. A National Institute of Standards and Technology temperature calibrator was used to confirm that all thermocouples were accurate to ±2 °C. Reported temperatures for each sample (Table 1) reflect the maximum measured temperature recorded during its collection. The elapsed time interval between sampling on the seafloor and sample recovery and processing ranged from 5 to 20 h due to differences in dive duration. Onboard extraction and processing of vent fluid samples took place within 24 h of sampler recovery.

Analytical Methods. Shipboard sampling handling and analysis, as well as shore-based analysis, were performed for pH, volatile species, nonvolatile species, and C, S, and Sr isotopes as in McDermott et al. (25). Measured metal concentrations in the dissolved, filter, and dregs fractions are reported in *SI Appendix*, Tables S4–S6. Concentration units for species measured at sea, including H_2, CH_4, and ΣH_2S, were converted from moles per liter solution to moles per kilogram solution using a uniform fluid density of 1.025 kg/L. The analytical uncertainty (2s) was ±0.05 units for pH (25 °C, 1 atm), ±5% for dissolved ΣCO_2, CH_4, C_2H_6, C_3H_8, ΣNH_4, and H_2 and ±10% for dissolved n-C_4H_{10}, i-C_4H_{10}, and ΣH_2S. Analytical uncertainties (2s) were ±3% for dissolved Na, Cl, Ca, K, SO_4, Mg, SiO_2, and Sr; ±5% for dissolved Li, Rb, Fe, Mn, Zn, Cu, Al, Pb, Co, and Cd; and ±10% for dissolved Br and Ag. The pooled SD (2s) for replicate samples was ±0.3‰ for $\delta^{13}C_{CO2}$ and ±0.8‰ for $\delta^{13}C_{CH4}$, and the instrumental analytical uncertainty (2s) was ±0.4‰ for $\delta^{13}C_{C2H6}$, ±0.7‰ for $\delta^{13}C_{C3H8}$, and ±0.3‰ for $\delta^{34}S_{\Sigma H2S}$.

Fig. 4. Catabolic energy available (joules per kilogram mixed fluid) to support five microbial metabolic pathways (*A*–*E*) in 10, 50, and 90 °C Piccard mixing zone fluids. Greater energy availability is indicated by more negative ΔG values. Energy was determined for a theoretical mixed fluid reflecting conservative endmember–seawater mixing (yellow bars) and for the actual measured mixed fluid composition that is affected by abiotic and thermogenic processes (green bars).

Mixed and Endmember Fluid Compositions. At high temperatures (>300 °C) and low water/rock ratio, hydrothermal fluids undergo near quantitative removal of Mg^{2+} and SO_4^{2-} during fluid–rock reaction with basalt and gabbro (52–55). The measurable dissolved Mg^{2+} in high-temperature ridge-crest hydrothermal fluids can be attributed to the dead volume of the IGT samplers (∼4 mL), which are prefilled with bottom seawater prior to deployment, and to inadvertent entrainment of ambient seawater during sample collection. The composition of the zero-Mg^{2+} endmembers prior to mixing were calculated via least-squares regression of an individual conservative chemical species as a function of Mg^{2+} for all samples from one vent orifice, weighted to pass through the background seawater composition and extrapolated to 0 mmol/kg Mg^{2+}.

Diffuse hydrothermal fluids (45 to 149 °C) are produced when a zero-Mg^{2+} "endmember" fluid mixes with ambient seawater below the seafloor and/or within chimney structures prior to sampling. Diffuse fluid compositions therefore reflect two-component mixing of these two compositionally distinct fluids. Nonconservative behavior occurs during subsurface mixing for some species reported here (e.g., Ca^{2+}, Sr^{2+}, SO_4^{2-}, ΣNH_4, $\Sigma HCOOH$, H_2, ΣH_2S, CH_4, C_{2+} alkanes, and transition metals). Only measured abundances are reported for these nonconservative species in lower temperature mixed fluids (Tables 1 and 2 and *SI Appendix*, Tables S1 and S2), because extrapolation to an end-member composition has no physical meaning in these instances.

Thermodynamic Affinity Calculations. The affinity for the reduction of CO_2 with H_2 to produce $HCOO^-$ and H^+ via reaction **1** was calculated as in McDermott et al. (29).

Numerical Geochemical Mixing Model. See *SI Appendix*.

Data Availability. All study data are included in the article and *SI Appendix*.

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