

Supporting Information

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SI Text

Endmember and Mixed Vent Fluid Compositions. Based on their compositions and temperatures, we classify fluids into two categories: undiluted endmember fluids, which have undergone no mixing in the crustal subsurface before venting at the seafloor, and mixed fluids, which appear to have been diluted and cooled with a seawater-like fluid before venting. Our calculations also take into account mixing of hydrothermal fluids with seawater during sample collection. Endmember fluid compositions referred to in [Dataset S1](#) are assumed to be devoid of Mg due to near-quantitative Mg removal from seawater during high-temperature water–rock interactions at reaction zone conditions (1–3) and are calculated as such by extrapolating measured species concentrations to zero Mg concentration using a linear regression forced through seawater (4). When endmember fluids mix with cooler seawater-like fluids during upflow through crustal aquifers, however, the resulting mixed fluids vent with Mg concentrations that lie between the endmember fluids and seawater (5). These fluids are readily identifiable by near-identical Mg concentrations in replicate samples of the same fluid, which are unlikely to be the result of accidental sampling-related seawater admixing, and temperatures lower than nearby endmember fluids ([Dataset S1](#)). For nonconservative species, a zero Mg endmember calculated from a mixed fluid composition has no physical meaning (5). In the context of thermodynamic predictions, compositions of mixed fluids are therefore assumed to be that of the lowest measured Mg concentration, which best resembles the mixture venting at the seafloor. We arbitrarily define those fluids with similar Mg concentrations greater than 10 mmol/kg in duplicate isobaric gas-tight (IGT) samples as mixed. In fluids with less than 10 mmol/kg, compositions so closely resemble endmembers that zero Mg compositions are used. Although this approach potentially neglects minor mixing, extrapolation to zero Mg compositions does not significantly alter our thermodynamic calculations or conclusions.

In cases where only one successful sample was taken or where replicate samples yielded dissimilar Mg due to accidental seawater entrainment, the degree of purely subsurface mixing is unclear. Where replicate samples provide evidence for high Mg fluids due to subsurface mixing within a vent field (e.g., Piccard, Von Damm, 9°50'N), however, we reasonably assume that other low-temperature fluids with high Mg are also mixed in the subsurface. At the Rainbow site, the evidence that mixing alone formed low-temperature fluids (180–191 °C) is unclear. Therefore, although we use lowest Mg compositions and measured temperatures in thermodynamic calculations, we cannot preclude the effects of conductive cooling there. Regardless, the difference between model predictions at lowest Mg and calculated endmember compositions would not alter our conclusions regarding metastable equilibrium.

Assessment of Metastable Equilibrium Using Chemical Affinities.

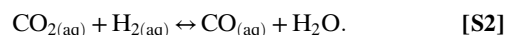
Assuming that the concentrations of species in either endmember or mixed fluids suffice to approximate activities for dissolved gases (i.e., activity coefficients equal 1), the equilibrium state of reactions (e.g., [1] and [2]) can be evaluated at the temperature and pressure conditions of venting by calculating the chemical affinity (A) from Eq. S1:

$$A = -\Delta_r G = -RT \ln(Q_r/K_{\text{eq}}), \quad [\text{S1}]$$

where R is the universal gas constant, T is the temperature of the vent fluid in Kelvin, Q_r is the reaction quotient, and K_{eq} is the

equilibrium constant at T and seafloor pressure. Calculated affinities of 0 ± 5 kJ/mol are typically assumed to be representative of equilibrium, based on estimated errors in derived $\Delta_r G^\circ$ values (6, 7).

Widespread CO₂-H₂-CO Equilibrium in Unsedimented Systems. The data presented in [Dataset S1](#) confirm the findings of Seewald et al. (8) that CO concentrations measured in hydrothermal fluids emanating from unsedimented systems are strictly regulated by equilibrium according to the water–gas shift reaction:



Calculated affinities for reaction S2 at the conditions and compositions of vent fluids from the unsedimented systems Rainbow (−0.09 to +5.7 kJ/mol) and 9°50'N (+0.9 to +4.7 kJ/mol) are all therefore close to or within reasonable error of equilibrium. In H₂-poor fluids where CO was not detectable ([Dataset S1](#)), reaction S2 predicts concentrations below the detection limit of the analytical method. Guaymas Basin fluids (172–218 °C) heavily influenced by thermal alteration of organic matter provide the only deviation (−14.3 to −19.3 kJ/mol) from near-equilibrium affinities, where high CO concentrations (26–92 μM) are in excess of equilibrium predictions according to reaction S2 (see discussion in text).

Thermodynamic Prediction of Metastable CH₃SH Abundances. The abundance of aqueous CH₃SH at metastable equilibrium according to reaction 1 was predicted for each vent fluid using the REACT module of the computer code Geochemist's Workbench (Fig. 1 and [Dataset S1](#)). For all calculations, the 50-MPa database of Amend et al. (9) was used, which includes thermodynamic data for aqueous CH₃SH at elevated temperatures (10). The effect of pressure on model predictions is negligible. Predictions cannot be reliably made for high-pH Lost City fluids due to the lack of thermodynamic data for dissociation of CH₃SH to form methanethiolate (CH₃S[−]) at vent conditions and large uncertainties in the estimation of extremely low endmember ΣCO₂ concentrations (11). Predictions are also not made for Guaymas Basin fluids because disequilibrium between CO and CO₂ (see text) invalidates the model assumptions outlined below. Respective ΣCO₂, H₂S, and H₂ concentrations and pH(25 °C) of either zero Mg endmember or mixed fluid compositions were used as initial mass balance constraints and respecified from 25 °C to vent temperatures using endmember or mixed fluid Cl concentrations (charge balanced with equivalent Na), while suppressing formation of CH₄ and any C₂₊ organic compounds or mineral phases. Activity coefficients of 1 were assumed for all neutral species in the model.

In addition to using ΣCO₂, H₂S, and H₂ to conserve mass, the speciation model also allows metastable equilibrium between single-carbon compounds [formic acid (HCOOH), formate (HCOO[−]), carbon monoxide (CO), formaldehyde (CH₂O), and methanol (CH₃OH)] and CO₂ and H₂, in addition to carbonate equilibria. It is therefore identical to that of Seewald et al. (8) except that it additionally considers CH₃SH formation and H₂S speciation. Volatile species in the model whose concentrations were determined at sea (CH₃SH, H₂, and H₂S) necessarily have units of molarity (i.e., mol/L fluid measured at room temperature). As for ΣCO₂ (mmol/kg fluid), these units can all be assumed to be comparable to corresponding units of molality (mol/kg solvent) calculated by the model. For fluids of the salinities presented in this study, explicitly correcting values would only result in a <2% difference (12), which is smaller than analytical uncertainties.

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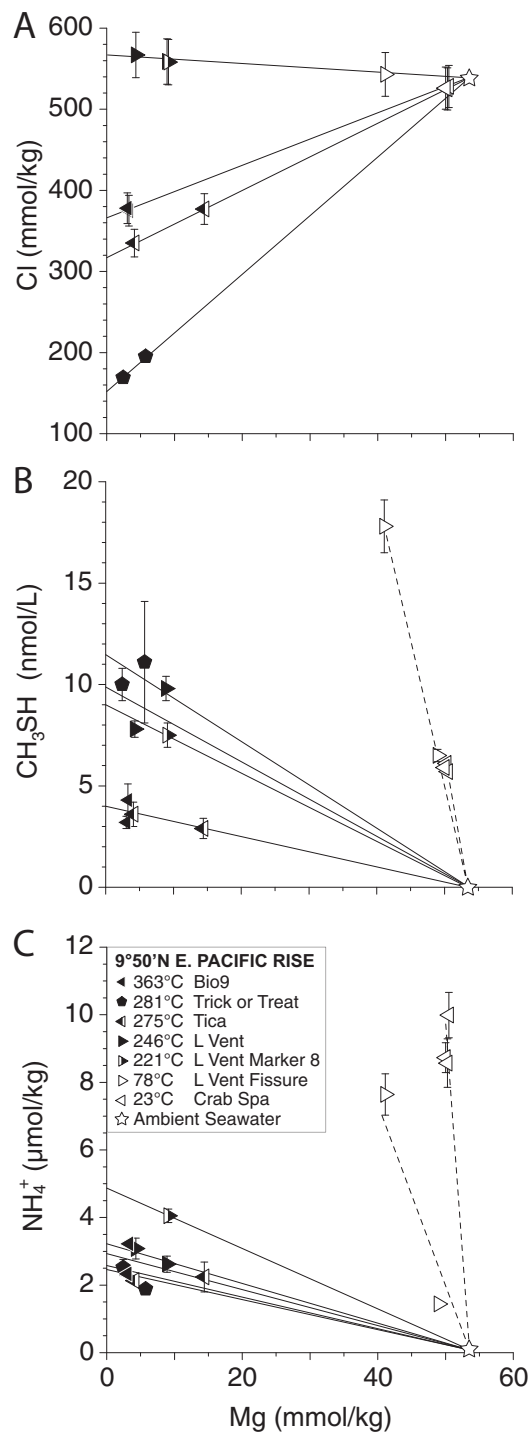


Fig. 51. Plots of measured concentrations of chloride (Cl; *A*), methanethiol (CH_3SH ; *B*), and ammonium (NH_4^+ ; *C*) versus Mg in fluid samples from 9°50'N East Pacific Rise hydrothermal fluids, showing CH_3SH and NH_4^+ production there. Various L Vent fluids shown refer to separate orifices on the L Vent structure described previously (1), with L Vent Fissure being a nearby low-temperature vent sharing the same endmember precursor. Crab Spa is a low-temperature vent located near Tica, which is its likely endmember parent. Both low-temperature mixed fluids (open symbols) have elevated CH_3SH and NH_4^+ relative to conservative dilution of their respective source fluids. Despite wide variations in Cl at this site (e.g., L Vent versus Trick or Treat vent), CH_3SH does not vary inversely with Cl as is typical for other volatile species, suggesting that it must form subsequent to phase separation. Uncertainties (2s) not shown are smaller than data symbols.

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Dataset S1. Measured and calculated concentrations of dissolved species in hydrothermal fluids

[Dataset S1](#)

Complete dataset containing measured temperatures, pH(25 °C), and concentrations of Mg, Cl, H₂, H₂S, ΣCO₂, CO, CH₄, NH₄⁺, and CH₃SH (and predicted CH₃SH) and corresponding endmember or lowest Mg values for species used in the thermodynamic model (bold entries). Data for temperature, pH(25 °C), Mg, Cl, and CH₄ for Rainbow and Lucky Strike IGT samples shown here have been published previously (1, 2). A bottom seawater NH₄⁺ concentration of 0.1 μmol/kg is assumed based on typical values (e.g., ref. 3). Only maximum temperatures measured during sampling of an individual vent are reported. Units: mm, mmol/kg fluid; mM, mmol/L fluid; μm, μmol/kg fluid; μM, μmol/L fluid; nM, nmol/L fluid; nmolal, nmol/kg H₂O. Methanethiol and NH₄⁺ errors (2s) are the greater of either error of reproducibility or 5% analytical error of standard, and *n* refers to the number of CH₃SH measurements per IGT. nd, not determined; BD, below detection.

*Model predictions not possible for Lost City and Guaymas Basin (see *Thermodynamic Prediction of Metastable CH₃SH Abundances*).

[†]Bottom seawater CH₃SH was below detection in an IGT sample of ambient bottom seawater from the East Pacific Rise and is therefore assumed absent.

[‡]Lost City and TAG chloride data are not available for 2008. Given the temporal stability of the system (4), the most recent Cl endmember (669 mmol/kg) was used for TAG endmember modeling.

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