

<< Assessing Earth's Inorganic Hydrocarbons

A long-standing question, important not just for petroleum resources but possibly in the origin of life, is the degree that a series of inorganic reactions that lengthen carbon chains (known as Fischer-Tropsch type reactions) might yield hydrocarbons from mantle methane. Although several examples of such hydrocarbons have been inferred, it has been difficult to demonstrate a purely mantle, abiogenic origin in the face of abundant biogenic hydrocarbons. **Proskurowski *et al.*** (p. 604) now show that the abundance of hydrocarbons in the Lost City vent field, an off-axis system in the Atlantic Ocean, decreases systematically with chain length in a manner predicted by Fischer-Tropsch type reactions. Analysis of carbon isotopes further support an inorganic origin. Because this system is likely representative of many similar systems in the oceans, an abundant source of mantle-derived hydrocarbons may be present on Earth, as well as during Earth's early history.

Water as Glass and Liquids

When molecular liquids form glassy phases, the energetic change is often of the same magnitude as when they form crystals—in both cases, large amounts of translational and rotational energy must be lost. In that regard, the glass transition for pure water that occurs at between 120 and 160 kelvin is puzzling in that it occurs with a very modest change in heat capacity. **Angell** (p. 582) reviews the many studies of water's glass transition, including those of aqueous solutions and of water confined to nanoscopic environments. He concludes that ~ 225 kelvin, a temperature often associated with water's "second critical point," an order-disorder transition occurs that accounts for most of the energetic changes. Hence, liquid water appears to exist in two forms—a "fragile" liquid (a poor glass-former) above this temperature, and a "strong" liquid (a good glass-former) below.

More Relaxed on the Surface

The glassy state of materials, in which a liquid-like structure is frozen in place below a specific temperature, may manifest differently in the bulk of the materials versus the surface region. **Fakhraei and Forrest** (p. 600; see the Perspective by **Dutcher and Ediger**) probed the glass transition in an amorphous polymer by embedding gold nanoparticles onto the surface of a polystyrene film and allowing them to sink into the film, where they make small indentations. They then removed the gold, using mercury, and were able

to watch the surface relaxation at various temperatures. They observed enhanced surface relaxation, that is, greater mobility of the polymer chains, at the surface relative to the bulk.

Cuprate Liquid Crystal

Recent experimental work has revealed exotic electronically ordered phases in correlated electron systems akin to those seen in conventional liquid crystals. These effects have manifested themselves as anisotropic transport properties, in which conductivity depends upon direction within the sample. **Hinkov *et al.*** (p. 597, published online 10 January) used neutron scattering to investigate the role of spin fluctuations in the macroscopic, nematic liquid-crystalline electronic behavior of the high-temperature superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{6.45}$. They find that an anisotropic ordering of the spins begins at 150 kelvin, well above the temperature where static magnetism occurs, and appears to develop in parallel to the previously reported transport properties. They argue that these fluctuating spins are at the core of the electronic liquid-crystalline behavior in correlated electron systems.

Food for Thought

One of the most potentially harmful effects of climate change may be its impact on agriculture

in food-insecure regions. **Lobell *et al.*** (p. 607; see the Perspective by **Brown and Funk**) analyze the climate change–related risk for agriculture in 12 regions worldwide that collectively represent a population of nearly 1 billion people in order to identify which general approaches to adaptation will be most effective in different areas. They find that South Asia and Southern Africa are two regions particularly at risk from negative impacts on several crops, and that uncertainties vary widely by crop. Also,

because the reasons underlying a region's vulnerability differ, the adaptation priorities that ultimately need to be followed will depend on how investment institutions perceive uncertainty and risk.

Getting the Balance Right

Balancing selection, the maintenance of multiple alleles within a population, is a means by which genetic diversity may be maintained within a species. **Seidel *et al.*** (p. 589, published online 10 January) have discovered a globally distributed genetic incompatibility that causes embryonic death among natural isolates of the nematode worm, *Caenorhabditis elegans*. The incompatibility persists despite its negative consequences for fitness, which contradicts the prediction that natural selection should eliminate genetic incompatibilities from interbreeding populations.

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Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field

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in stark contrast to the regular α and β relaxation processes that are observed in bulk glass-formers.

References and Notes

- G. F. Meyers, B. M. DeKoven, J. T. Seitz, *Langmuir* **8**, 2330 (1992).
- J. A. Forrest, *Eur. Phys. J. E* **8**, 261 (2002).
- J. S. Sharp, J. A. Forrest, *Phys. Rev. Lett.* **91**, 235701 (2003).
- L. Xie *et al.*, *Phys. Rev. Lett.* **74**, 4947 (1995).
- Y. C. Jean *et al.*, *Phys. Rev. B* **56**, R8459 (1997).
- C. J. Ellison, J. M. Torkelson, *Nat. Mater.* **2**, 695 (2003).
- J. Hammerschmidt, W. Gladfelter, G. Haugstad, *Macromolecules* **32**, 3360 (1999).
- S. Ge *et al.*, *Phys. Rev. Lett.* **85**, 2340 (2000).
- Y. Liu *et al.*, *Macromolecules* **30**, 7768 (1997).
- A. D. Schwab, A. Dhinojwala, *Phys. Rev. E* **67**, 021802 (2003).
- T. Kerle, Z. Lin, H. Kim, T. P. Russell, *Macromolecules* **34**, 3484 (2001).
- E. Buck, K. Petersen, M. Hund, G. Krausch, D. Johannsmann, *Macromolecules* **37**, 8647 (2004).
- P. Gasemjit, D. Johannsmann, *J. Polym. Sci. B* **44**, 3031 (2006).
- I. Karapanagiotis, W. W. Gerberich, *Macromolecules* **38**, 3420 (2005).
- S. Fakhraei, J. A. Forrest, *Phys. Rev. Lett.* **95**, 025701 (2005).
- G. Strobl, *The Physics of Polymers* (Springer-Verlag, Berlin, ed. 2, 1997).
- V. M. Rudyoy *et al.*, *Colloid J.* **64**, 746 (2002).
- J. H. Teichroeb, J. A. Forrest, *Phys. Rev. Lett.* **91**, 016104 (2003).
- J. S. Sharp *et al.*, *Eur. Phys. J. E* **22**, 287 (2007).
- S. A. Hutcheson, G. B. McKenna, *Phys. Rev. Lett.* **94**, 076103 (2005).
- R. M. Papaléo *et al.*, *Phys. Rev. B* **74**, 094203 (2006).
- J. Turkevich, G. Garton, P. C. Stevenson, *J. Colloid Sci.* **9**, 26 (1954).
- This technique was first published in 1556 by Georgius Agricola in *De Re Metallica*, but it may have been used even in Roman times.
- R. M. Christensen, *Theory of Viscoelasticity* (Academic Press, New York, 1971).
- J. D. Ferry, *Viscoelastic Properties of Polymers* (Wiley, New York, ed. 3, 1980).
- A. Dhinojwala, G. K. Wong, J. M. Torkelson, *J. Chem. Phys.* **100**, 6046 (1994).
- J. Y. Cavaille, C. Jourdan, J. Perez, *J. Polym. Sci. B* **25**, 1235 (1987).
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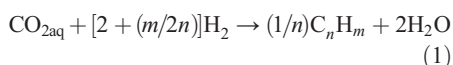
Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field

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Low-molecular-weight hydrocarbons in natural hydrothermal fluids have been attributed to abiogenic production by Fischer-Tropsch type (FTT) reactions, although clear evidence for such a process has been elusive. Here, we present concentration, and stable and radiocarbon isotope, data from hydrocarbons dissolved in hydrogen-rich fluids venting at the ultramafic-hosted Lost City Hydrothermal Field. A distinct "inverse" trend in the stable carbon and hydrogen isotopic composition of C_1 to C_4 hydrocarbons is compatible with FTT genesis. Radiocarbon evidence rules out seawater bicarbonate as the carbon source for FTT reactions, suggesting that a mantle-derived inorganic carbon source is leached from the host rocks. Our findings illustrate that the abiotic synthesis of hydrocarbons in nature may occur in the presence of ultramafic rocks, water, and moderate amounts of heat.

Fischer-Tropsch type (FTT) reactions involve the surface-catalyzed reduction of oxidized carbon to CH_4 and low-molecular-weight hydrocarbons under conditions of excess H_2 . This set of reactions has been commonly invoked to explain elevated hydrocarbon concentrations in hydrothermal fluids venting from submarine ultramafic-hosted systems (1) and in springs issuing from ophiolites (2); however, whether naturally occurring FTT reactions are an important source of hydrocarbons to the biosphere remains unclear. Although CH_4 and higher hydrocarbons have been synthesized by FTT in the gas phase from CO for more than 100 years (3), only recently were FTT reactions shown to proceed, albeit with low yields, under aqueous hydrothermal conditions, with dissolved CO_2 as the carbon source (4, 5). The reactions involved in Fischer-Tropsch reduction of aque-

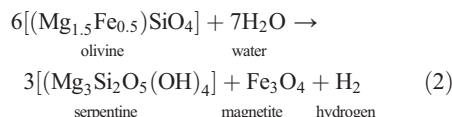
ous CO_2 can be expressed in general terms by the reaction



Here, we show that low-molecular-weight hydrocarbons in high-pH vent fluids from the ultramafic-hosted Lost City Hydrothermal Field (LCHF) at 30°N on the Mid-Atlantic Ridge (MAR) are likely produced abiotically through FTT reactions.

The LCHF is situated near the summit of the Atlantis Massif, ~15 km west of the MAR axis. Towering carbonate chimneys (up to 60 m tall) diffusely vent high-pH (9 to 11), moderate-temperature (28° to 90°C) fluids, produced by reaction of seawater with rocks originating from the mantle (6, 7). The basement directly beneath this system consists of highly serpentinized peridotites (dominated by depleted mantle harzburgites) with lesser talc schists and metagabbros exposed by long-lived detachment faulting (8, 9). Fluid circulation is driven by cooling of the underlying rocks (10), perhaps supported by minor contributions from exothermic serpentinization reactions (7, 11) or a yet undetected magmatic source.

Serpentinization is the hydration of olivine and orthopyroxene minerals, the main constituents of ultramafic rocks, and creates a reducing chemical environment characterized by high H_2 concentrations that is well suited to abiotic hydrocarbon production. The general reaction is



At Lost City, vent fluids have end-member H_2 concentrations of 0.5 to 14.4 mmol/kg (12), greater than the highest H_2 concentrations in fluids sampled within basaltic-hosted environments that are unperturbed by magmatic and eruptive events (6, 13). The highest H_2 concentrations within the LCHF approach those measured at Rainbow (16 mmol/kg) and surpass those measured at Logatchev (12 mmol/kg); both are peridotite-and-gabbro-hosted systems on the MAR (1). Rainbow and Logatchev vent fluids differ from those at the LCHF in that they have elevated concentrations of CO_2 and dissolved metals, low pH, and substantially higher temperatures (350° to 360°C): characteristics typical of high-temperature black smoker vents hosted in mid-ocean ridge basalts (MORBs) (1). In contrast, the moderate-temperature, high-pH, sulfate-bearing fluids at the LCHF are enriched in H_2 , CH_4 , and low-molecular-weight volatile hydrocarbons, but are highly depleted in CO_2 and dissolved metal contents.

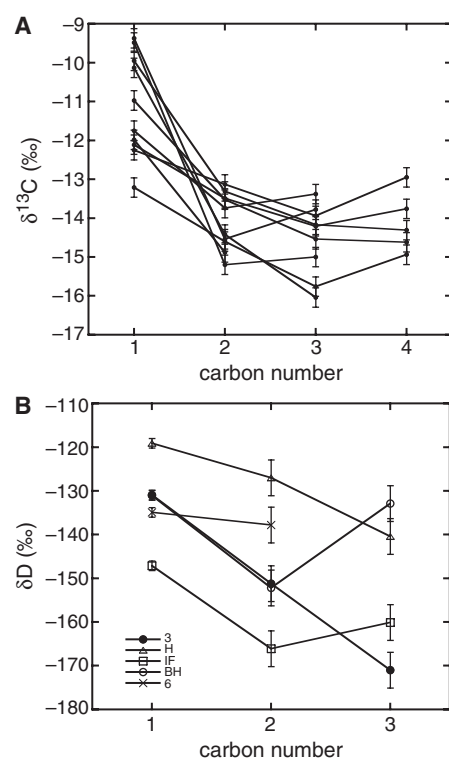
The chemistry of LCHF fluids implies that fluid temperatures beneath the seafloor may be $200^\circ \pm 50^\circ C$ (10), although oxygen isotope data from carbonate veins and low D/H ratios of H_2 argue for temperatures <150°C (8, 12). In general, H_2 concentrations in LCHF fluids are lower than values observed during laboratory experiments (14) and predicted by equilibrium models (10) and likely reflect a more limited extent of serpentinization at the lower temperatures associated with the natural system (15). The low and variable H_2 concentrations in the LCHF fluids may also reflect some removal and use of H_2 by

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Table 1. Carbon and hydrogen isotope data from Lost City vents. All isotope values are in ‰ units; $\delta^{13}\text{C}$ is reported as vPDB, and δD as vSMOW.

Sample	Marker	$\delta^{13}\text{C}\text{-CH}_4^*$	$\delta\text{D}\text{-CH}_4^\dagger$	$\delta^{13}\text{C}\text{-C}_2\text{H}_6^\ddagger$	$\delta\text{D}\text{-C}_2\text{H}_6^\S$	$\delta^{13}\text{C}\text{-C}_3\text{H}_8^\ddagger$	$\delta\text{D}\text{-C}_3\text{H}_8^\S$	$\delta^{13}\text{C}\text{-}n\text{-C}_4\text{H}_{10}^\ddagger$
3879-GT10	H	-13.6		-14.9				
3881-GT10	H	-13.2		-14.3				
H04-IGT8	H	-9.5	-119	-15.2	-127	-15.0	-140	
3865-GT7	IF	-12.3	-139	-13.1		-13.9		-13.0
H05-IGT7	IF	-11.8	-147	-13.7	-166	-13.4	-160	
3871-GT15	8	-9.9	-136	-13.3		-14.2		-14.3
3866-GT14	7	-13.2	-125	-14.6		-15.8		-14.9
3871-GT9	C	-12.1	-126	-13.5		-14.2		-13.8
3876-GT7	BH	-11.0	-127	-13.5		-14.5		-14.6
H06-IGT8	BH	-9.4	-131	-14.5	-152	-13.8	-133	
3863-GT7	3	-10.5		-13.9				
H03-IGT7	3	-11.8	-131	-14.3	-151	-14.0	-171	
3872-GT10	6	-11.8		-14.4		-16.0		
H07-IGT7	6	-12.0	-135	-14.9	-138			

* $\delta^{13}\text{C}\text{-CH}_4$ measurement uncertainty $\pm 0.2\text{‰}$. $^\dagger\delta\text{D}\text{-CH}_4$ measurement uncertainty for 2005 samples (H0x-IGTx) $\pm 1.1\text{‰}$, for 2003 samples (38xx-GTx) $\pm 6.5\text{‰}$.uncertainty $\pm 0.3\text{‰}$. $^\S\delta\text{D}\text{-C}_2\text{-C}_3$ measurement uncertainty $\pm 4.1\text{‰}$. $^\ddagger\delta^{13}\text{C}\text{-C}_2\text{-C}_4$ measurement**Fig. 1.** ^{13}C and D trends. (A) $\delta^{13}\text{C}$ versus carbon number for C_1 to C_4 LCHF alkanes. (B) δD versus carbon number for C_1 to C_3 LCHF alkanes. Trend of increasing isotopic depletion with increasing carbon number is opposite to the observed isotopic trend for thermogenically produced alkanes.

microbes. The porous carbonate structures of active vents at Lost City, created by the mixing of vent fluid with seawater, have high microbial cell counts, and phylogenetic studies indicate the presence of H_2 -utilizing microbes (7, 16, 17). Additionally, 16S ribosomal RNA genes corresponding to those of methanogens, aerobic and anaerobic methanotrophs, sulfate reducers, and sulfur oxidizers were detected in these energy-rich environments (16).

Lost City fluids have CH_4 concentrations (1 to 2 mmol/kg) greater than values from un-sedimented basalt-hosted hydrothermal systems, but similar to values in fluids from the serpentine-hosted Rainbow and Logatchev vent fields (1, 16). The concentrations are low relative to those of hydrothermal fluids from sediment-hosted environments, where CH_4 is produced by the thermal decomposition of organic matter within the sediment (16, 17). Thermogenic CH_4 in such sedimented systems is commonly characterized by $\delta^{13}\text{C}$ values of -50 to -30 per mil (‰) (18, 19). Methane $\delta^{13}\text{C}$ values at LCHF range from -14 to -9‰ [all carbon and hydrogen isotopic values are given in standard δ notation and ‰ units, referenced to the Vienna Pee Dee belemnite (vPDB) and Vienna standard mean ocean water (vSMOW) standards, respectively]. Lost City $\delta^{13}\text{C}$ values of CH_4 are similar to values of CH_4 hypothesized to be of abiogenic origin from Rainbow (-16‰), Logatchev (-14‰), and the ultramafic-hosted Zambales ophiolite seeps (-7‰) (1, 16). The high $\delta^{13}\text{C}$ values of CH_4 from Lost City fluids, as well as the lack of a sediment source rich in organic matter along the reaction path, suggest that CH_4 is not appreciably derived from a thermogenic source.

The isotopic composition of short-chain hydrocarbons at LCHF suggests that abiogenic synthesis is responsible for their formation. The carbon isotope compositions of C_1 to C_4 hydrocarbons from LCHF fluids are increasingly negative ($\delta^{13}\text{C}$ ranges from -9 to -16‰) with increasing chain length (Table 1 and Fig. 1A). This isotopic pattern is opposite to that for hydrocarbons produced thermogenically (20). Such an “inverse” isotopic trend ($\delta^{13}\text{C}_1 > \delta^{13}\text{C}_2 > \delta^{13}\text{C}_3 > \dots$) has been shown experimentally to be a possible indicator of abiogenic synthesis, and specifically of FTT reactions under conditions of incomplete (35 to 75%) conversion of CO (21). Abiotic synthesis has also been invoked to account for decreases in $\delta^{13}\text{C}$ values of C_2 to C_4 alkanes with respect to CH_4 in other natural systems (22). The hydrogen isotopic composition of Lost City C_1 to C_3 hydrocarbons

shows a similar, although less defined, trend in which molecules of longer chain length have similar or slightly lower δD values (-120 to -170‰) relative to shorter-chain alkanes (Fig. 1B). The pattern is, again, opposite to the trend expected for thermogenic gases (23), and also opposite to the trends for gases from Precambrian rocks in the Canadian Shield where an enrichment in D with increasing chain length (-425 to -250‰) was attributed to formation by polymerization of CH_4 (22). The differences between LCHF and the Canadian Shield D/H trends likely reflect different formation mechanisms and require further investigation through laboratory experiments.

In addition to their isotopic composition, the abundance and relative distribution of short-chain hydrocarbons are consistent with an abiogenic formation mechanism. At Lost City, the alkanes and ethene make up most of the volatile-gas composition, although acetylene, propene, and propyne are present in several samples (table S1). A plot of the log of the n -alkane concentration against carbon number shows a strong linear correlation with carbon number for C_2 to C_4 alkanes, with elevated CH_4 concentrations (fig. S1D). This trend is consistent with an Anderson-Schulz-Flory distribution predicted for FTT synthesis (3). However, such a trend is also consistent with thermogenic production of low-molecular-weight n -alkanes (24).

The elevated CH_4 concentrations, relative to those of C_2 to C_4 n -alkanes, suggests that FTT synthesis may not reflect the only abiogenic source of hydrocarbons to LCHF fluids. Laboratory experiments have demonstrated that reduction of CO_2 to CH_4 under hydrothermal conditions in the presence of Fe-Ni alloys is rapid and does not result in the production of C_{2+} hydrocarbons (25). Ultramafic rocks from the Atlantis Massif have Ni concentrations of 1700 to 2400 parts per million (ppm), a range that is representative of dredged ultramafic samples from numerous locations along the MAR (26). Although most of the Ni in ultramafic rocks is incorporated into silicate minerals and not catalytically available, Fe-Ni

alloys are viable catalysts and stable under highly reducing conditions associated with early stages of serpentinization and lower water/rock ratios (W/Rs) (27).

Radiocarbon measurements represent a powerful tool to constrain the origin of carbon involved in abiotic synthesis of hydrocarbons. Accelerator mass spectrometric measurements on six aqueous CH_4 samples from LCHF consistently yielded ^{14}C contents near the detectable limit (Table 1), i.e., the CH_4 at LCHF is radiocarbon dead (28). Thus, the carbon source of CH_4 cannot be seawater bicarbonate (^{14}C -seawater_{DIC} measured as modern) that has been microbially or abiogenically reduced. The absence of a modern seawater bicarbonate signal requires that bicarbonate be removed before production of the hydrocarbons in the vent fluids. This likely occurs by precipitation as CaCO_3 , either in the more permeable zones of seawater recharge, as observed in the recharge limbs of circulation cells at

black smoker systems (29) and in ridge-flank environments (30), or in the serpentinizing basement, where increasing pH leads to carbonate precipitation within the serpentinites (8, 10).

The ^{14}C content of short-chain hydrocarbons suggests that the requisite carbon for abiotic synthesis is derived by leaching of primordial radiocarbon-dead carbon from mantle host rocks. Mantle rocks and hydrothermal vent fluids typically have $\text{CO}_2/{}^3\text{He}$ ratios of $\sim 1 \times 10^9$ (31). In contrast, the ratios in the LCHF fluids are much lower, ranging from 3×10^4 to 1×10^7 . Lost City ${}^4\text{He}$ concentrations are one order of magnitude less than those of MOR samples, and CO_2 concentrations (0.1 to 26 $\mu\text{mol/kg}$) are up to six orders of magnitude less (Fig. 2 and table S2). The low $\text{CO}_2/{}^3\text{He}$ ratios at Lost City thus primarily reflect extremely low CO_2 concentrations, suggesting that mantle CO_2 has been removed from the fluids before venting. If a standard MOR value for $\text{CO}_2/{}^3\text{He}$ is assumed, an average CO_2

concentration of 2.9 ± 0.7 mmol/kg is predicted from the He content of the fluids (table S2). On an individual sample basis, total hydrocarbon concentrations can account for 35 to 56% of predicted CO_2 concentrations. These yields are high relative to the 1% yields typical of aqueous experimental studies (4, 5), but are consistent with the 35 to 75% yields of the FTT experiments that resulted in "inverse" carbon isotope trends (21). Even higher yields are predicted if, before abiotic reduction, mantle CO_2 were removed from the system by carbonate precipitation under alkaline conditions created by serpentinization reactions.

Near-quantitative reduction of mantle CO_2 to hydrocarbons is consistent with the similar ^{13}C content of CO_2 and hydrocarbons at the LCHF. The $\delta^{13}\text{C}$ value of CO_2 at LCHF is estimated to be -9‰ (32). This value is within the -10 to -5‰ range observed for $\delta^{13}\text{C}$ of CO_2 from olivine gabbro norites from the South West Indian Ridge (33). Although laboratory experiments conducted at 250°C indicate that fractionation between CO_2 and CH_4 is $\sim 35\text{‰}$ during low-yield FTT synthesis (5) and equilibrium fractionation at this temperature is of similar magnitude, quantitative conversion of CO_2 to hydrocarbons will result in the reduced carbon species inheriting the isotopic composition of the initial CO_2 . Thus, $\delta^{13}\text{C}$ values for CH_4 that range from -13.6 to -9.4‰ in LCHF fluids are consistent with the near-complete reduction of mantle-derived CO_2 with a $\delta^{13}\text{C}$ value of -9‰ . Mass balance constraints (assuming a closed system, and a fractionation factor $\epsilon = 35\text{‰}$) suggest that a -14‰ $\delta^{13}\text{C}$ value of CH_4 can be explained by an 85% conversion of a -9‰ CO_2 source. Extensive reduction of mantle-derived CO_2 is supported by a positive correlation between $\delta^{13}\text{C}$ values of CH_4 and percent conversion of mantle CO_2 calculated from ${}^3\text{He}$ content of the LCHF fluids (Fig. 3).

The possibility exists that microbial metabolic activity is partially responsible for the near-quantitative conversion of mantle-derived CO_2 to CH_4 . Indeed, the presence of methanogens is indicated in the porous carbonate structures formed by diffuse flow (7, 34, 35). Our measurements do not counterindicate methanogenesis as a source of CH_4 to Lost City fluids; however, microbial processes cannot explain the high concentrations and distinctive isotopic signature of C_{2+} hydrocarbons.

Carbon in mantle rocks occurs in a variety of forms: primarily as inorganic carbon dissolved within the mineral matrix or trapped in fluid inclusions as graphite, or amorphous carbon residing along mineral grain boundaries (36). During hydrothermal circulation at mid-ocean ridges, there is a net transfer of carbon from the host rocks to the circulating fluid during fluid-rock reactions or through magmatic degassing. If all hydrocarbons in LCHF fluids are derived from CO_2 originally stored in the underlying rocks (or CO_2 produced from carbon in them), the W/R describing the fluid reaction history can be constrained.

Fig. 2. Measured ${}^4\text{He}$ and CO_2 concentrations. LCHF ${}^4\text{He}$ and CO_2 concentrations are depleted relative to those of other hydrothermal vent sites (table S2). The plotted line represents $\text{CO}_2/{}^3\text{He} = 1 \times 10^9$ (assuming a constant ${}^3\text{He}/{}^4\text{He}$, where $R/R_a = 8.7$), a value that typifies MOR glasses and MOR hydrothermal fluids (31). LCHF data plot well to the left of the line, indicating a loss of CO_2 at LCHF.

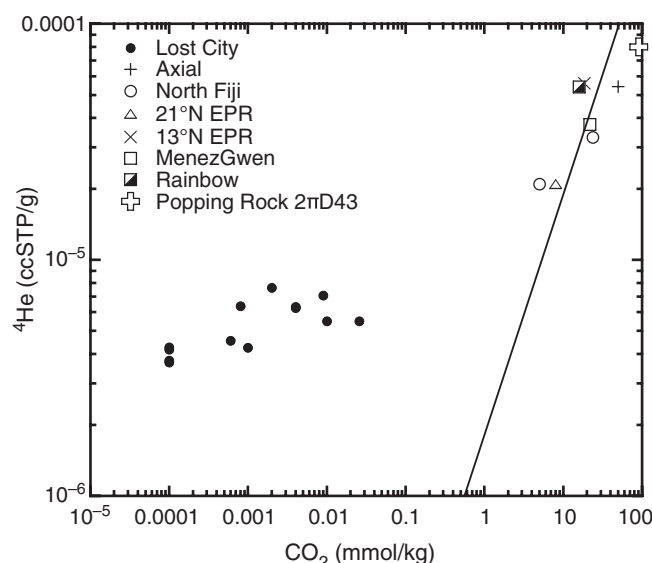
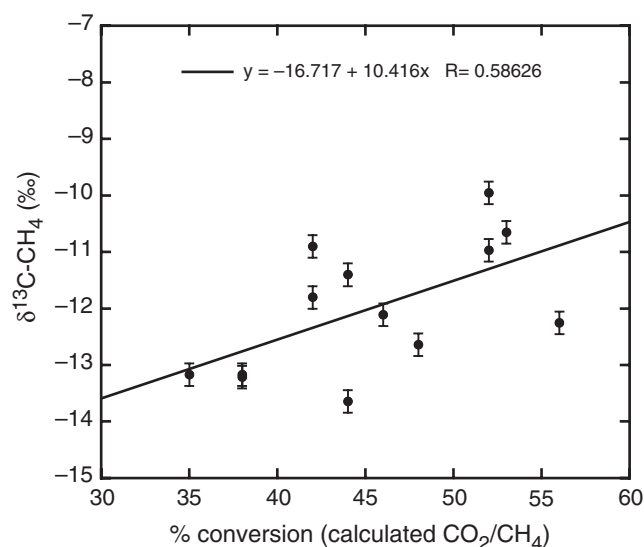


Fig. 3. ^{13}C composition of CH_4 varies with modeled conversion efficiency. Percent conversion is based on predicted CO_2 concentrations (as calculated from the LCHF ${}^3\text{He}$ value and a standard MOR value for $\text{CO}_2/{}^3\text{He}$). Higher yields correspond with $\delta^{13}\text{C}$ values of CH_4 closer to the approximately -9‰ $\delta^{13}\text{C}$ values of CO_2 at Lost City. Although calculated yields are below quantitative levels, if CO_2 is removed by non- CH_4 -forming mechanisms before FTT reactions (e.g., precipitation of CaCO_3 at high-pH conditions), these yields would increase.



For hydrocarbon (simplified in this model to just CH₄) concentrations of 1.4 mmol/kg, the maximum W/R is 64, assuming 100% conversion of CO₂ to CH₄ and an initial (but high) CO₂ concentration of ~4000 ppm in the basement rocks (37) (fig. S2). This W/R is at the low end of those predicted from the Sr and Nd isotopic compositions of LCHF serpentinites (37); however, the samples from seafloor outcrops almost certainly have a reaction history different from that of the rocks directly supplying the present-day fluids at Lost City. More typical and lower initial basement rock CO₂ concentrations would yield lower W/Rs. On the basis of a system constrained by a 400-ppm CO₂ concentration in the basement rocks (27) and a conversion of ~50% (as suggested by the He and CO₂ data), we posit that the fluids feeding the LCHF have reacted with rocks in a W/R of less than 5 (fig. S2).

Lost City may be just one of many, as yet undiscovered, off-axis hydrothermal systems. Hydrocarbon production by FTT could be a common means for producing precursors of life-essential building blocks in ocean-floor environments or wherever warm ultramafic rocks are in contact with water.

References and Notes

1. J. L. Charlou, J. P. Donval, Y. Fouquet, B. P. Jean, N. Holm, *Chem. Geol.* **191**, 345 (2002).
2. T. A. Abrajano et al., *Chem. Geol.* **71**, 211 (1988).
3. R. B. Anderson, *The Fischer-Tropsch Synthesis* (Academic Press, Orlando, FL, 1984).
4. D. I. Foustoukos, W. E. Seyfried Jr., *Science* **304**, 1002 (2004).
5. T. M. McCollom, J. S. Seewald, *Earth Planet. Sci. Lett.* **243**, 74 (2006).
6. D. S. Kelley et al., *Nature* **412**, 145 (2001).

7. D. S. Kelley et al., *Science* **307**, 1428 (2005).
8. G. L. Früh-Green et al., *Science* **301**, 495 (2003).
9. J. A. Karson et al., *Geochim. Geophys. Geosyst.* **7**, Q06016 (2006).
10. D. E. Allen, J. Seyfried, W. E. *Geochim. Cosmochim. Acta* **68**, 1347 (2004).
11. R. P. Lowell, P. A. Rona, *Geophys. Res. Lett.* **29**, 1531 (2002).
12. G. Proskurowski, M. D. Lilley, D. S. Kelley, E. J. Olson, *Chem. Geol.* **229**, 331 (2006).
13. M. D. Lilley, D. A. Butterfield, J. E. Lupton, E. J. Olson, *Nature* **422**, 878 (2003).
14. W. E. Seyfried Jr., D. I. Foustoukos, Q. Fu, *Geochim. Cosmochim. Acta* **71**, 3872 (2007).
15. B. Martin, W. S. Fyfe, *Chem. Geol.* **6**, 185 (1970).
16. M. D. Lilley et al., *Nature* **364**, 45 (1993).
17. J. A. Welhan, J. E. Lupton, *AAPG Bull.* **71**, 215 (1987).
18. M. J. Whiticar, *Chem. Geol.* **161**, 291 (1999).
19. B. Sherwood Lollar et al., *Chem. Geol.* **226**, 328 (2006).
20. J. M. Hunt, *Petroleum Geochemistry and Geology* (Freeman, New York, 1996).
21. Y. A. Taran, G. A. Kliger, V. S. Sevastianov, *Geochim. Cosmochim. Acta* **71**, 4474 (2007).
22. B. Sherwood Lollar, T. D. Westgate, J. A. Ward, G. F. Slater, C. G. Lacrampe, *Nature* **416**, 522 (2002).
23. A. Schimmelmann, A. L. Sessions, M. Mastalerz, *Annu. Rev. Earth Planet. Sci.* **34**, 501 (2006).
24. W. F. Giggenbach, *Geochim. Cosmochim. Acta* **61**, 3763 (1997).
25. J. Horita, M. E. Berndt, *Science* **285**, 1055 (1999).
26. P. A. Rona, L. Widenfalk, K. Bostroem, *J. Geophys. Res.* **92**, 1417 (1987).
27. G. L. Früh-Green, J. A. D. Connolly, A. Plas, D. S. Kelley, B. Grobety, in *The Subseafloor Biosphere at Mid-Ocean Ridges*, W. S. D. Wilcock, E. F. Delong, D. S. Kelley, J. A. Baross, C. S. Cary, Eds. (American Geophysical Union, Washington, DC, 2004), vol. 144, pp. 119–136.
28. Low concentrations of CO₂ with large contributions from modern seawater bicarbonate prevent the determination of presumably near-radiocarbon dead end-member ¹⁴C contents of Lost City fluids.
29. G. Proskurowski, M. D. Lilley, T. A. Brown, *Earth Planet. Sci. Lett.* **225**, 53 (2004).
30. J. C. Alt, D. A. H. Teagle, *Geochim. Cosmochim. Acta* **63**, 1527 (1999).
31. B. Marty, I. N. Tolstikhin, *Chem. Geol.* **145**, 233 (1998).
32. Seawater bicarbonate accounts for 55 to 98% of the measured CO₂ concentrations in LCHF fluids. The large extrapolations involved in the calculation of end-member CO₂ concentrations introduce large errors that propagate during the determination of end-member ^δ¹³C-CO₂ values by mass-isotope balance. However, measured ^δ¹³C-CO₂ values were –5 to –2‰, indicating mixing between seawater bicarbonate (–0.40‰) and an end-member more depleted in ¹³C. The best-quality sample yielded an end-member ^δ¹³C-CO₂ value of –8.7 ± 1.5‰, and samples with greater uncertainties had lower values.
33. D. S. Kelley, G. L. Früh-Green, *Geochim. Cosmochim. Acta* **65**, 3325 (2001).
34. W. J. Brazelton, M. O. Schrenk, D. S. Kelley, J. A. Baross, *Appl. Environ. Microbiol.* **72**, 6257 (2006).
35. M. O. Schrenk, D. S. Kelley, S. A. Bolton, J. A. Baross, *Environ. Microbiol.* **6**, 1086 (2004).
36. D. S. Kelley, G. L. Früh-Green, *J. Geophys. Res.* **104**, 10439 (1999).
37. A. Delacour, P. Schaeffer, S. M. Bernasconi, G. L. Früh-Green, *Eos Trans. AGU* **87**, B318 (2006).
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Prioritizing Climate Change Adaptation Needs for Food Security in 2030

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Investments aimed at improving agricultural adaptation to climate change inevitably favor some crops and regions over others. An analysis of climate risks for crops in 12 food-insecure regions was conducted to identify adaptation priorities, based on statistical crop models and climate projections for 2030 from 20 general circulation models. Results indicate South Asia and Southern Africa as two regions that, without sufficient adaptation measures, will likely suffer negative impacts on several crops that are important to large food-insecure human populations. We also find that uncertainties vary widely by crop, and therefore priorities will depend on the risk attitudes of investment institutions.

Adaptation is a key factor that will shape the future severity of climate change impacts on food production (1). Although relatively inexpensive changes, such as shifting planting dates or switching to an existing crop variety, may moderate negative impacts, the biggest benefits will likely result from more costly measures including

the development of new crop varieties and expansion of irrigation (2). These adaptations will require substantial investments by farmers, governments, scientists, and development organizations, all of whom face many other demands on their resources. Prioritization of investment needs, such as through the identification of “climate risk hot spots” (3), is there-

fore a critical issue but has received limited attention to date.

We consider three components to be essential to any prioritization approach: (i) selection of a time scale over which impacts are most relevant to investment decisions, (ii) a clear definition of criteria used for prioritization, and (iii) an ability to evaluate these criteria across a suite of crops and regions. Here, we focus on food security impacts by 2030: a time period most relevant to large agricultural investments, which typically take 15 to 30 years to realize full returns (4, 5).

We consider several different criteria for this time scale. First is the importance of the

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