

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

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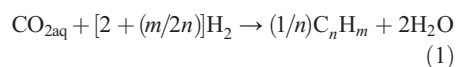
Abiogenic Hydrocarbon Production at Lost City Hydrothermal Field

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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 C₁ to C₄ 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 CH₄ and low-molecular-weight hydrocarbons under conditions of excess H₂. 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 CH₄ 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 CO₂ as the carbon source (4, 5). The reactions involved in Fischer-Tropsch reduction of aqueous

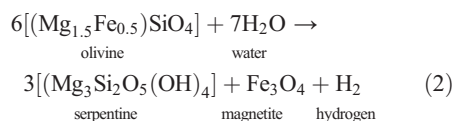
CO₂ can be expressed in general terms by the reaction



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 H₂ concentrations that is well suited to abiotic hydrocarbon production. The general reaction is



At Lost City, vent fluids have end-member H₂ concentrations of 0.5 to 14.4 mmol/kg (12), greater than the highest H₂ concentrations in fluids sampled within basaltic-hosted environments that are unperturbed by magmatic and eruptive events (6, 13). The highest H₂ 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 CO₂ 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 H₂, CH₄, and low-molecular-weight volatile hydrocarbons, but are highly depleted in CO₂ and dissolved metal contents.

The chemistry of LCHF fluids implies that fluid temperatures beneath the seafloor may be 200° ± 50°C (10), although oxygen isotope data from carbonate veins and low D/H ratios of H₂ argue for temperatures <150°C (8, 12). In general, H₂ 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 H₂ concentrations in the LCHF fluids may also reflect some removal and use of H₂ 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 ‰PDB, and δD as ‰SMOW.

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) $\pm 6.5\text{‰}$. $^\ddagger\delta^{13}\text{C}\text{-C}_{2-4}$ measurement uncertainty $\pm 0.3\text{‰}$. $^\S\delta\text{D}\text{-C}_{2-3}$ measurement uncertainty $\pm 4.1\text{‰}$.

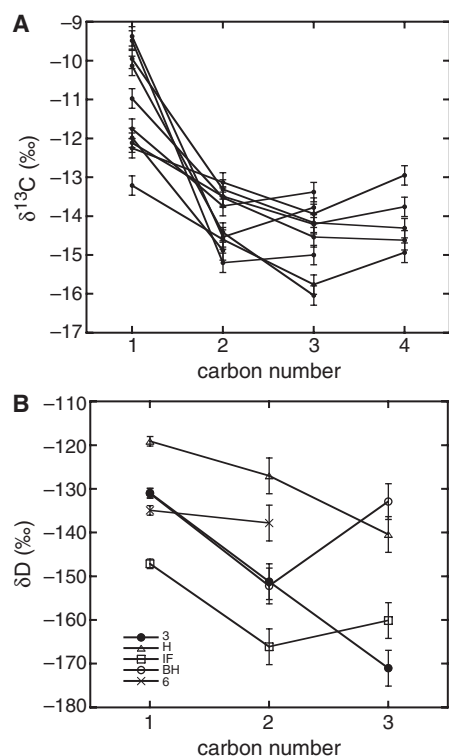


Fig. 1. ^{13}C and D trends. **(A)** $\delta^{13}\text{C}$ versus carbon number for C_1 to C_4 LCHF alkanes. **(B)** δD versus carbon number for C_1 to C_3 LCHF alkanes. Trend of increasing isotopic depletion with increasing carbon number is opposite to the observed isotopic trend for thermogenically 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 (‰PDB) and Vienna standard mean ocean water (‰SMOW) standards, respectively]. Lost City $\delta^{13}\text{C}$ 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). Abiogenic 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 CH₄ samples from LCHF consistently yielded ¹⁴C contents near the detectable limit (Table 1), i.e., the CH₄ at LCHF is radiocarbon dead (28). Thus, the carbon source of CH₄ cannot be seawater bicarbonate (¹⁴C-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 CaCO₃, 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 ¹⁴C 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 CO₂/³He ratios of ~1 × 10⁹ (31). In contrast, the ratios in the LCHF fluids are much lower, ranging from 3 × 10⁴ to 1 × 10⁷. Lost City ⁴He concentrations are one order of magnitude less than those of MOR samples, and CO₂ concentrations (0.1 to 26 μmol/kg) are up to six orders of magnitude less (Fig. 2 and table S2). The low CO₂/³He ratios at Lost City thus primarily reflect extremely low CO₂ concentrations, suggesting that mantle CO₂ has been removed from the fluids before venting. If a standard MOR value for CO₂/³He is assumed, an average CO₂

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 CO₂ 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 CO₂ were removed from the system by carbonate precipitation under alkaline conditions created by serpentinization reactions.

Near-quantitative reduction of mantle CO₂ to hydrocarbons is consistent with the similar ¹³C content of CO₂ and hydrocarbons at the LCHF. The δ¹³C value of CO₂ at LCHF is estimated to be -9‰ (32). This value is within the -10 to -5‰ range observed for δ¹³C of CO₂ from olivine gabbro norites from the South West Indian Ridge (33). Although laboratory experiments conducted at 250°C indicate that fractionation between CO₂ and CH₄ is ~35‰ during low-yield FTT synthesis (5) and equilibrium fractionation at this temperature is of similar magnitude, quantitative conversion of CO₂ to hydrocarbons will result in the reduced carbon species inheriting the isotopic composition of the initial CO₂. Thus, δ¹³C values for CH₄ that range from -13.6 to -9.4‰ in LCHF fluids are consistent with the near-complete reduction of mantle-derived CO₂ with a δ¹³C value of -9‰. Mass balance constraints (assuming a closed system, and a fractionation factor ε = 35‰) suggest that a -14‰ δ¹³C value of CH₄ can be explained by an 85% conversion of a -9‰ CO₂ source. Extensive reduction of mantle-derived CO₂ is supported by a positive correlation between δ¹³C values of CH₄ and percent conversion of mantle CO₂ calculated from ³He 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 CO₂ to CH₄. 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 CH₄ to Lost City fluids; however, microbial processes cannot explain the high concentrations and distinctive isotopic signature of C₂₊ 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 CO₂ originally stored in the underlying rocks (or CO₂ produced from carbon in them), the W/R describing the fluid reaction history can be constrained.

Fig. 2. Measured ⁴He and CO₂ concentrations. LCHF ⁴He and CO₂ concentrations are depleted relative to those of other hydrothermal vent sites (table S2). The plotted line represents CO₂/³He = 1 × 10⁹ (assuming a constant ³He/⁴He, where R/Ra = 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 CO₂ at LCHF.

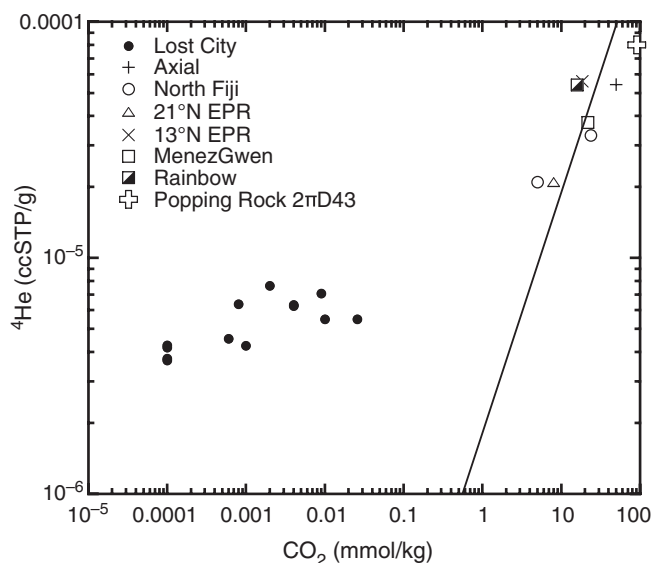
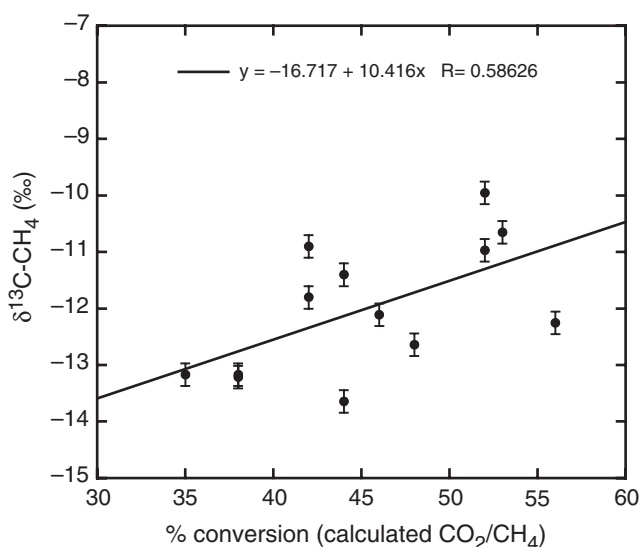


Fig. 3. ¹³C composition of CH₄ varies with modeled conversion efficiency. Percent conversion is based on predicted CO₂ concentrations (as calculated from the LCHF ³He value and a standard MOR value for CO₂/³He). Higher yields correspond with δ¹³C values of CH₄ closer to the approximately -9‰ δ¹³C values of CO₂ at Lost City. Although calculated yields are below quantitative levels, if CO₂ is removed by non-CH₄-forming mechanisms before FTT reactions (e.g., precipitation of CaCO₃ 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.

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- 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.
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Supporting Online Material

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Materials and Methods
Figs. S1 and S2
Tables S1 and S2
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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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