Timing Earth's Abiotic Kitchen: Short Hydrothermal Fluid Residence Times in Serpentinizing Oceanic Crust

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Key Points:

- Many recent models for prebiotic organic synthesis and the emergence of early life prominently feature hot, reducing waters circulating through ultramafic rock
- Timescales of subsurface fluid flow in such settings have historically been poorly understood
- Moore *et al*. (2021) present novel observations of unusual short-lived ^{223}Ra excess in fluids venting at the Lost City serpentinite system, proposing a model for very short (<2 yr) circulation times, limiting timescales these fluids could produce or destroy potential non-biological organic molecules in Earth's crust

Abstract

Hydrothermal alteration of ultramafic rock (serpentinization) creates extremely reducing (H_2-rich) fluids in the oceanic crust, resulting in strong thermodynamic drives to reduce CO_2 to organic molecules in the absence of life. Timescales on which such hydrothermal fluids circulate (thus produce or destroy such organic molecules) have remained enigmatic. In their new publication, Moore *et al*.(2021, https://doi.org/10.1029/2021JC017886) present compelling radioisotope-based estimates of fluid residence times in a widely known site of purported abiotic synthesis – the Lost City Hydrothermal Field. Using a model that accounts for the sorptive behavior of Ra radionuclides during circulation, they find that fluids at Lost City must have inordinately short residence times, averaging 0.5 to 2 yr or less. The study represents a critical step forward in our understanding of Earth's abiotic organic 'kitchen', as it now places a constraint on the timeframe in which such organic molecule creation should occur in such fluids (if at all) prior to venting at the seafloor.

Plain Language Summary

Deep sea hot springs are widespread along Earth's ~60,000 km of mid-ocean ridge crust. These systems host some of the planets most diverse geologic fluids, as well as extreme ecosystems that depend on their chemicals for chemosynthetic energy. Hence, understanding the behavior and timing of hydrothermal fluid circulation in oceanic crust prone to seafloor venting is of paramount importance to understanding linkages between geologic processes and extreme life. Compared to other seafloor hydrothermal systems, the ghostly 'Lost City' hot springs on the Mid-Atlantic Ridge are spectacular and unusual in their chemistry, providing a window into heated fluid reactions with mantle rock. Critically, we have lacked insights into the timescales these heated fluids spend circulating in the subsurface aquifer, limiting our understanding of geochemical reactions that depend on time. In their new paper, Moore *et al*.(2021) use a short-lived radionuclide of Radium (^{223}Ra) – abundant in Lost City fluids, to constrain subsurface lifetimes of fluids there to less than 0.5 to 2 years, similar to other seafloor hot springs. This time constraint is crucial to further investigating hydrothermal carbon transformation reactions that may have led to the formation of Earth's first biomolecules, and perhaps ultimately early life itself.

1. Commentary

Convective circulation of seawater-derived fluids beneath mid-ocean ridge crust is inherently obscured from direct observation, yet both the timing and scale of such hydrothermal fluid movement have implications not just for geochemical processes during metasomatism, but also their ultimate outward expressions – seafloor hot springs. Given the challenges of probing systems of active hydrothermal convection by drilling (potentially disturbing circulation, *e.g.* Ildefonse *et al*. 2007), or tracking crustal fluid flow by other means (*e.g.* subsurface tracer injection, Neira *et al*. 2016), much of what we understand of hydrothermal fluid behavior in oceanic crust has had to be inferred from actively venting seafloor hydrothermal fluids and associated deposits accessible by submersible. Hydrologic timescales of circulation in heated crust aquifers are poorly constrained in a great many systems, with implications for many key geochemical reactions with kinetic limitations.

The majority of known seafloor hydrothermal systems circulate predominantly through mafic (*i.e.* MORB) host rock, typically generating high temperature (up to ~400°C), acidic, H_2-poor and H_2S- and metal-rich fluids (German & Seyfried, 2014). Systems where fluids circulate through ultramafic host rock (*e.g.* exposed mantle peridotites, troctolites, olivine-rich gabbroic intrusives *etc*.), have attracted increasing attention (see Rona *et al*. 2010) since the serendipitous discovery of the spectacular Lost City Hydrothermal Field (LCHF) in 2001 (Kelley *et al*. 2001). Hosted in variably altered ultramafic and metagabbroic rocks, Lost City lies on the southern flank of Atlantis Massif, a detachment fault-dominated 'oceanic core complex' on the Mid-Atlantic Ridge (Kelley *et al*. 2001, 2005; Denny *et al*. 2016), emanating milder temperature (~96–116 °C) fluids, with reducing, uniquely alkaline chemistry. Extensive interest has arisen in this style of hydrothermal fluid venting for non-biological (abiotic) organic molecule formation, its relevance to life's potential hydrothermal origin (*e.g.* Martin & Russell, 2006; Martin *et al*., 2008; Preiner *et al*. 2020), and the search for life associated with hydrothermal alteration of ultramafic rock elsewhere in the Solar System (*e.g.* Glein *et al*. 2015; Waite *et al*. 2017).

The generation of Lost City fluid compositions primarily reflects oxidation of the Fe(II) component of olivine (by H_2O; the serpentinization reaction) under moderate subsurface temperatures (~150–300°C; Foustoukos *et al*. 2008; Seyfried *et al*. 2015), forming serpentinite rock composed of various serpentine clays, brucite and magnetite. H_2 production from H_2O by serpentinization creates highly favorable thermodynamic conditions to reduce inorganic carbon (ΣCO_2) to organic molecules at such temperatures (McCollom, 2008; McCollom & Seewald, 2013). While thermodynamics provides the energetic driving force for such reactions, it is ultimately the realm of chemical kinetics (*i.e.* time-dependent mechanistic constraints), however, that dictates whether such 'abiotic' carbon reduction can actually proceed or not in serpentinizing fluids. Over a third of Earth's ~60,000 km long mid-ocean ridge system occurs under slow-ultraslow spreading (<20mm/yr full rate) tectonic conditions

favoring exposure of olivine-rich rock to hydrothermal alteration (Dick *et al*. 2003; Baker *et al*. 2004; Hannington *et al*. 2005; German *et al*. 2016), and (as yet) unclear fluxes of heated fluids circulate through these systems (Cannat *et al*. 2010), on unknown timescales. Quantifying these timescales is a major step toward building comprehensive physico-chemical models for abiotic organic geochemical reactions in these systems that are bounded in realistic temporal constraints.

Despite the increasing interest in ultramafic-hosted hydrothermal circulation and serpentinization, timescales of fluid flow associated with this key crustal alteration process have until now been a mystery. Previous efforts to constrain residence times of vent fluids in oceanic crust have focused exclusively on 'bare-rock' basalt-hosted hydrothermal systems, mainly along the Juan de Fuca Ridge, where serpentinization does not occur. Short-lived radionuclides in high temperature (>300°C) 'black smoker' fluids have played a crucial role, in particular lead (^{210}Pb) and radium (^{228}Ra, ^{226}Ra) radioisotopes, derived from the decay series of uranium (^{238}U) and thorium (^{232}Th), respectively (Turekian & Cochran, 1986; Kadko & Moore, 1988; Grasty *et al*. 1988; Kadko, 1996). Activities (and activity ratios) of radionuclides measured in fluids typically reflect a mathematical balance between their production from parent isotopes, and subsequent decay, as a function of fluid residence time in the crust. Using measured ratios of short-lived ^{210}Pb to Pb, and ^{228}Ra to ^{226}Ra activity ratios (nuclides with vastly different half-lives) in high temperature (>300°C) 'black smoker' fluids, estimates of the residence time of fluids under relatively high temperature conditions, *i.e.* beginning from the onset of Mg loss and acidic pH conditions (likely above *ca*. 200°C), to venting at the seafloor, are consistently constrained to <2–4yrs (Kadko & Moore, 1988; Kadko & Butterfield, 1998).

These 'geochemical' fluid residence times are in very good agreement with independent estimates based purely on geophysical considerations of fluid flow; very similar timescales can be calculated based on potential hydrologic reservoir size, effective crustal porosity/permeability and measured heat fluxes (*e.g.* Fisher, 2003), with much more rapid timeframes (minutes to hours) inferable for hottest 'upflow' zones of systems (Converse *et al*. 1984). In summation, high-temperature hydrothermal fluids exiting basaltic seafloor have likely only resided in the ocean crust for a few years on average (as opposed to weeks or decades), not only from the geochemical perspective of radionuclides venting at the seafloor.

Writing in *Journal of Geophysical Research: Oceans*, Moore *et al*.(2021) recently expanded the application of these short-lived Ra isotope 'timers' to constrain residence times of fluids venting at Lost City. Contrasting strongly with mafic-hosted hydrothermal systems, Moore *et al*. show the Lost City fluids display extraordinary enrichments in short-lived ^{223}Ra ($t_{1/2}$ = 11.4 d) - indeed, the highest measured to date in any oceanic setting. This ^{223}Ra must ultimately have been derived from U (the ^{235}U decay series) that was strongly sequestered into the large serpentinite body beneath Atlantis

Massif from recharging seawater percolating the subsurface (*cf.* Chen *et al*. 1986). Using lessons learned from Ra behavior in terrestrial groundwaters, and considering Ra may be less mobile in alkaline fluids, similarly short fluid residence times of maximum 0.5 to 2 y are required by the Moore *et al*. model explaining these excesses.

The strong similarity to residence times from higher temperature (~200–400°C) mafic systems is perhaps not entirely unexpected. Moore *et al.* argue that density, porosity and permeability can differ between mafic and ultramafic rock types, but in essence, hydrothermal fluid flow in mid-ocean ridge crust can invariably be best described as a hot fluid rising buoyantly through a pervasively fractured medium of highly variable permeability. Fracture network geometries and spatial scales of fluid flow *i.e*. smaller scale fractures (*e.g*. at faster spreading centers like the Juan de Fuca Ridge) *vs*. larger-scale detachment fault conduits (*e.g*. Atlantis Massif), may well differ between mid-ocean ridge enviroments, but overall the medium "setting" can be considered broadly similar. Buoyancy forces on cooler (96–116°C) Lost City fluids will differ from ~350°C 'black smokers as a function of fluid density, but the latter varies less than a factor of ~2 between such temperatures at typical seafloor depths.

Since fluid residence time will naturally scale as a function of hydrologic reservoir size, as well as fluid velocity, the similarity is instead intriguing if one considers the potential spatial scale of the Lost City subsurface aquifer relative to the mafic-hosted black smoker systems. Subsurface serpentinite extends to at least *ca*. 1.4 km depth for several km over the Atlantis Massif dome, based on IODP Leg 304/305 drilling and direct submersible observation (Karson *et al*. 2006). Fluids may not currently circulate to this depth; it likely reflects a cumulative zone of ultramafic alteration through time. Instead, they are likely focused through the fault network of the detachment shear zone, mining heat from warm country rock (Titarenko & McCaig, 2016; Lowell, 2017). We currently lack geochemical proxies (*e.g*. dissolved silica geobarometry, used in mafic systems) to constrain depths of fluid reaction in ultramafic rock, due to unclear controls on dissolved SiO_2 (Humphris & Klein, 2018), hindering geochemical estimates of potential circulation depths. Given the scale (many km) of the Atlantis Massif detachment fault, potential reservoir sizes and geometry may differ substantially from mafic systems heated by shallow magma emplacement.

The critical finding of the Moore *et al*. model for observed ^{223}Ra, is that it places a reasonable estimate on average timescales fluids circulate solely within serpentinite beneath Atlantis Massif. In their model, ^{223}Ra is only introduced to Lost City fluids by radioactive decay of U highly concentrated in the serpentinite body, *i.e*. by alpha particle recoil; it does not inherently require high temperature alteration. This differs from the 'high temperature' residence times calculated in mafic systems above, which do not include the unknown timeframe of seawater recharge and heating prior to Mg loss

(<200°C; Kadko, 1996). This subsurface zone of serpentinization effectively represents the crustal 'kitchen' for the production of H_2 – the key reactant of abiotic carbon reduction and a major shaper of the biogeochemical energy 'landscape' of the seafloor vent ecosystem (Amend *et al*. 2011).

This serpentinite 'kitchen timer' is very consistent with many major geochemical traits of the Lost City fluids, not least of which are mmolar levels of H_2 and near zero Mg concentrations. Observations of rapid Mg disappearance (Seyfried *et al*. 2007) and production of comparable H_2 concentrations (McCollom *et al*. 2016) during experimental serpentinization of ultramafic rock indicate both traits are achievable within 0.5–2yr at conditions resembling the inferred LCHF subsurface (~200–300°C, 35–50 MPa). In contrast, to produce the abundant CH_4 in these fluids at the sluggish rates of abiotic CH_4 production observed during experimental serpentinization (McCollom, 2016) would require decades, possibly millennia, at these conditions (FIGURE 1). Recent shifts in the debate on the origin of CH_4 in ultramafic-hosted hydrothermal fluids now point, using multiple lines of evidence, to CH_4 instead being extracted by circulating fluids from longer-lived gas-rich fluid inclusions occluded within subsurface olivine or other minerals (McDermott *et al*. 2015; Wang *et al*. 2018; Klein *et al*. 2019; Grozeva *et al*. 2020).

Several other inorganic carbon reduction reactions, in contrast, can and do readily proceed in heated fluids (in some cases, to chemical equilibrium) on even shorter timeframes in experimental simulations at comparable conditions to Lost City (FIGURE 1). The ability to simulate realistic single-phase, representative hydrothermal fluid pressure-temperature (P-T) conditions in the laboratory has been of immense value to studies of hydrothermal carbon transformation (Reeves & Fiebig, 2020). The initial reduction from inorganic carbon (CO_2, HCO_3^-, CO_3^{2-}) to carbon monoxide (CO), *via* the intermediate formic acid (HCOOH), proceeds rapidly to equilibrium on the order of days to a few weeks (Seewald *et al*. 2006) at 200–300°C (35 MPa), and abiotic HCOOH produced in this manner is now considered to fuel bacteria inhabiting the Lost City vent structures (Lang *et al*. 2010; 2018).

Further reduction of inorganic carbon to methanol (CH_3OH, a key origin of life species, *e.g*. Preinar *et al*. 2020) is also possible under longer timescales (weeks to months), and appears to be equilibrium controlled also (FIGURE 1; Seewald *et al*. 2006; Reeves, 2010; Reeves & Fiebig, 2020). As yet no CH_3OH concentration data have been reported for seafloor hydrothermal systems to test this prediction. It may be that, while CH_3OH formation does proceed, it might not achieve equilibrium concentrations given the similarity in required timescales to subsurface residence times. It is important to note the residence time calculated by Moore *et al*. likely does not represent the total time spent at the most favorable temperatures for any given reaction to proceed strongly, and carbon reduction reaction timescales display strong kinetic sensitivity between ~150°C to ~300°C (Seewald *et al*. 2006; Reeves, 2010). Carbon-sulfur bond formation without catalysis at least appears feasible at

191 the upper limit of these conditions (Reeves, 2010; Reeves & Fiebig, 2020), even if likely subject to
192 strong kinetic limitation.
193
194 Abiotic formation of more complex molecules of prebiotic relevance under hydrothermal conditions,
195 *e.g.* forming carbon-carbon or carbon-nitrogen bonds on such timescales, is, unfortunately, far from
196 certain at the present time. Moore *et al.*(2021) argue that key abiotic molecules such as amino acids
197 would have sufficient time to be exported to the seafloor on Lost City timescales. Experimentally
198 determined half lifes of norvaline and alanine decomposition are on the order of weeks to months at
199 ~150–190°C (35 MPa), and likely even shorter above ~200°C (McCollom, 2013). Such short half-
200 lives require an even more rapid production mechanism to outpace decomposition, similar to the
201 systematics of ^{223}Ra regeneration described. We do not presently know, however, on what timeframe
202 organic nitrogen molecules can be created - if at all - under realistic physico-chemical (and now time)
203 constraints imposed by Lost City fluid compositions. Experimental amino acid synthesis using
204 reasonable reactants proven to be present in these fluids has also yet to be convincingly demonstrated
205 experimentally (Reeves & Fiebig, 2020).
206
207 While complex amino acid structures have been found in serpentinite ~175m deep beneath Atlantis
208 Massif (Menez *et al*. 2018), any *a priori* assumption of abiotic amino acid production beneath Lost
209 City remains highly questionable, not least of which by the fact that dissolved amino acids measured
210 in the Lost City fluids appear to reflect near-surface biological sources (Lang *et al*. 2013). Recent
211 work on shallower carbonates beneath Atlantis Massif furthermore reveals extensive incorporation of
212 inorganic carbon likely derived from thermal degradation of background marine dissolved organic
213 matter (Ternieten *et al*. 2021), implying ongoing transformation of pre-existing organic carbon.
214
215 Much research therefore remains to be done to constrain abiotic organic carbon and nitrogen
216 production in these systems. Moore *et al.*(2021) have, nonetheless, placed a timely and crucial
217 'kitchen timer' constraint on the Lost City serpentinite aquifer. It will be interesting to observe if such
218 short timescales are upheld by short-lived ^{223}Ra data from other ultramafic-hosted vent fluids (*e.g.*
219 Mid-Cayman Rise, Frankle *et al*. 2020). From the perspective of organic molecule production, the
220 question must now therefore be - what's cooking?

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Figure 1.

Timescales in which selected organic reactions demonstrated have been observed occur in experimental hydrothermal fluids, compared to the 0.5 to 2 year residence time calculated for Lost City fluids (Moore *et al*. 2021). Reaction timescales are calculated at temperatures resembling the likely range of subsurface fluids at Lost City (~150–300°C), and fluid pressures of 35 MPa (*i.e*. single-phase solutions). Reactions separated by "↔" refer to observable reaction equilibrium, while "→" refers to reactions observed to progress to the right only (by the % noted, using reactant-to-product label tracers such as ^{13}C). Reactions (*i*), (*ii*) and (*iii*) have already been demonstrated to occur in some seafloor hydrothermal fluids. Timescale data are calculated from the following: (*i–ii*) mineral-free experiments of Seewald *et al*. (2006); (*iii*) redox-buffered experiments, Seewald (2001); (*iv–v*) mineral-free experiments, Reeves (2010); (*vi*) olivine serpentinization experiments, McCollom & Seewald (2001), McCollom (2016); (*vii*) redox-buffered norvaline (*n*-alkyl-α-amino acid) decomposition, McCollom (2013).

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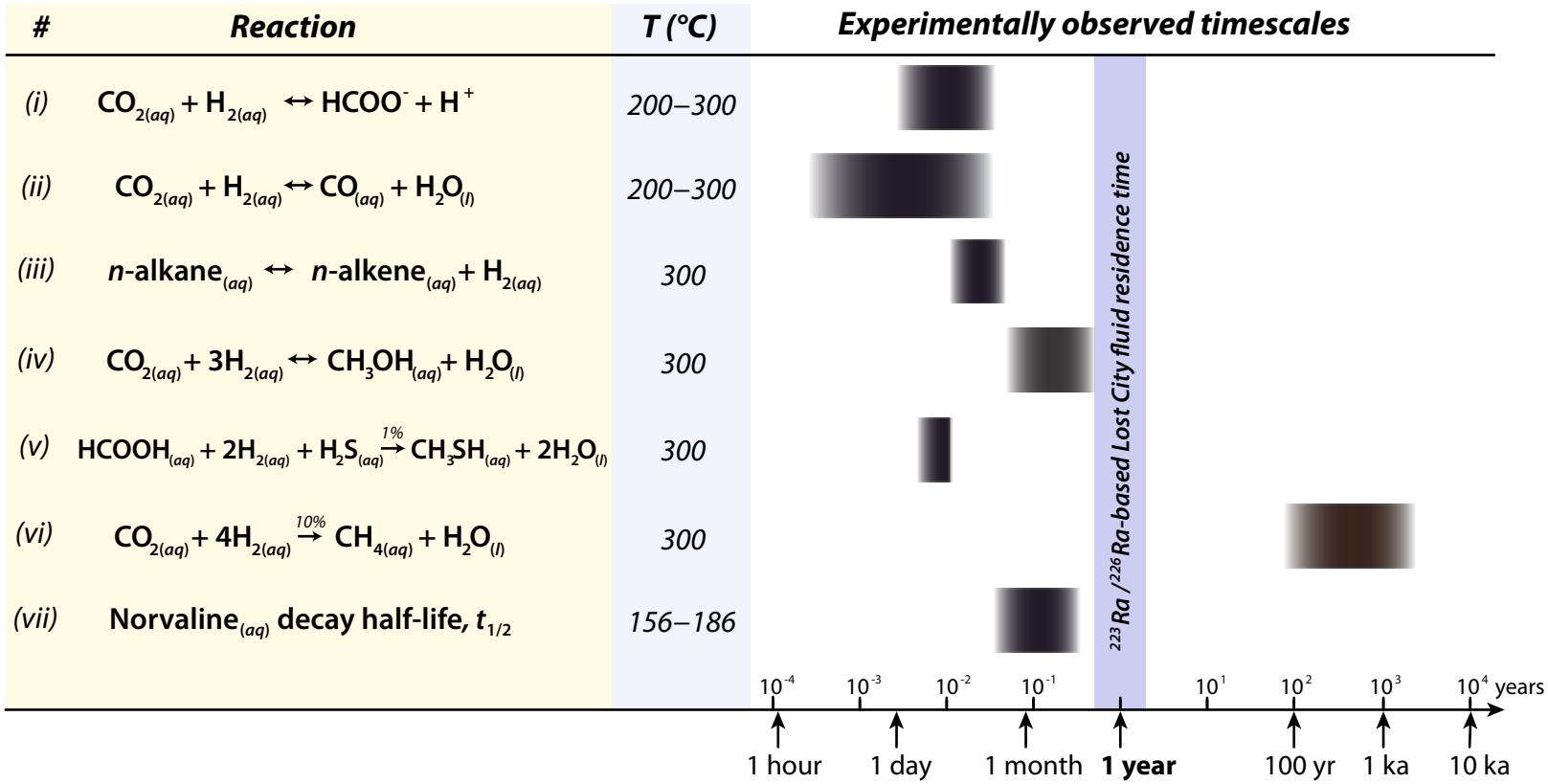
#
Reaction
T (°C)
Experimentally observed timescales
(i) $CO_{2(aq)} + H_{2(aq)} \leftrightarrow HCOO^- + H^+$ 200–300
(ii) $CO_{2(aq)} + H_{2(aq)} \leftrightarrow CO_{(aq)} + H_2O_{(l)}$ 200–300
(iii) *n*-alkane$_{(aq)}$ ↔ *n*-alkene$_{(aq)}$ + $H_{2(aq)}$ 300
(iv) $CO_{2(aq)} + 3H_{2(aq)} \leftrightarrow CH_3OH_{(aq)} + H_2O_{(l)}$ 300
(v) $HCOOH_{(aq)} + 2H_{2(aq)} + H_2S_{(aq)} \xrightarrow{1\%} CH_3SH_{(aq)} + 2H_2O_{(l)}$ 300
(vi) $CO_{2(aq)} + 4H_{2(aq)} \xrightarrow{10\%} CH_{4(aq)} + H_2O_{(l)}$ 300
(vii) Norvaline$_{(aq)}$ decay half-life, $t_{1/2}$ 156–186
^{223}Ra /^{226}Ra-based Lost City fluid residence time
10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{1} 10^{2} 10^{3} 10^{4} years
1 hour
1 day
1 month
1 year
100 yr
1 ka
10 ka

Figure 1.