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Narrowing gaps between Earth and life

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Life is a chemical reaction. For 4 billion years (1), all microbial cells have required a source of carbon, energy, and electrons to power energy-releasing reactions forward toward growth. How did the first cells grow, where did they emerge, and from what chemical reactions did they arise? Some modern habitats might hold clues. In PNAS, Colman et al. (2) report an ancient lineage of anaerobic bacteria that live in the darkness of desert wells fed by hydrothermal vents. These bacteria obtain their carbon, energy, and electrons solely from the products of geochemical reactions. Their chemical environment might resemble the habitat where the first microbes arose, and the anaerobic lineage might reflect the lifestyle of microbes on early Earth. Their findings mesh well with the theory that life arose in hydrothermal vent environments (3), which, if true, would mean that life's origin was not powered by sunlight, but by chemical energy generated within Earth itself. The findings impact our views on early microbial evolution and the search for life beyond Earth.

The paper reports acetogens from serpentinized environments (2). For background, serpentinization is a geochemical process (4) involving the reaction of water, drawn by gravity into the crust, with rocks that are rich in Fe^{2+}. The Fe^{2+}-rich minerals react with water by giving up electrons. Fe^{2+} minerals are thereby converted to Fe^{3+} minerals, while H_2O is converted to hydrogen gas, H_2, that is carried by hydrothermal effluent to the surface. Oxygen atoms from H_2O remain in the crust as iron (III) oxides such as magnetite (Fe_3O_4). Serpentinization also generates iron and magnesium hydroxides, which makes the vent fluid alkaline. The water in the report has pH 11 and contains 3 mM H_2, orders of magnitude more than microbes need to grow (2). The process is named for its final product, serpentinite (Fig. 1), used by stonemasons for centuries.

Serpentinization has been going on in submarine crust since there was first water on Earth (1, 4). Over geological time scales, it sometimes happens, however, that pieces of submarine crust are thrust up onto the continental surface at continental margins. Such surface-exposed slabs of crust are called ophiolites. They can host serpentinization. One example is the Samail ophiolite found on the east coast of Oman. This is where Colman et al. (2) employed metagenomic tools to identify microbes that live in H_2-rich and hyperalkaline hydrothermal effluent. They found genomes of bacteria that can live from chemicals made by serpentinization: acetogens.

Acetogens are strictly anaerobic bacteria that can produce acetate as the sole end product of their energy metabolism (5). Some acetogens have an ability that puts them almost in a class by themselves and, furthermore, in the focus of theories for microbial origin: They can grow on H_2 and CO_2 as their source of carbon, energy, and electrons. The only other organisms known that share that ability are methanogens (6), strictly anaerobic archaea from the opposite side of the tree of life. This shared ability to live from H_2

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Fig. 1. Serpentinite, the rock product of serpentinization (1–4). (*Left*) A sample of serpentinite from Lost City hydrothermal field. Field of view is 6 cm. Photo provided by D. S. Kelley and M. Elend (University of Washington, Seattle, WA), and NSF Grant OCEO137206 to D. S. Kelley. (*Center*) Serpentinite from an ophiolite. This outcrop is from the Tablelands Ophiolite in Gros Morne National Park, Newfoundland, Canada. Field of view is 80 cm. Photo provided by William J. Brazelton (University of Utah, Salt Lake City, UT). (*Right*) A piece of polished serpentinite as it is commonly used in buildings. Field of view is 30 cm. White lines show paths of water flow and rock–water interactions. Photo provided by John F. Allen (University College London, London, United Kingdom).

and CO_2 forges an ancient biochemical link between lineages from both prokaryotic domains—bacteria and archaea—while also linking alkalophilic acetogens (7) to the kinds of habitats that Colman et al. (2) have probed.

At the heart of acetogen carbon and energy metabolism is the acetyl CoA pathway of CO_2 fixation (5, 8). The acetyl CoA pathway has remarkable traits. It is the only pathway of CO_2 fixation that occurs in both bacteria and archaea (methanogens use it). It is replete with transition metal catalysts—Ni, Fe, Co, and Mo or W are required by its enzymes and cofactors (9)—suggesting that transition metals preceded its enzymes as catalysts in biochemical evolution. Among known pathways of CO_2 fixation, it is the only one that is linear—all others are cyclic—and the only one that is exergonic—it releases energy, allowing cells to make ATP from the process of assimilating CO_2; all others require energy input in the form of ATP (10). These properties mark the acetyl CoA pathway as the most ancient route of CO_2 fixation (8).

Ancient biochemical reactions in acetogens—H_2 dependence, transition metal catalysis, and exergonic CO_2 fixation—are mirrored by geochemical reactions in serpentinizing hydrothermal vents, which constantly produce H_2, are rich in transition metals, and even fix CO_2 all by themselves. With the help of abiotic reactions, serpentinizing hydrothermal vents produce formate, the first intermediate in the acetyl CoA pathway, and they produce methane (11), the end product of methanogens (6). Such remarkable congruence between geochemical reactions and biochemical reactions fostered the proposal that the first microbes on Earth arose in serpentinizing systems and made a living by the chemical reactions that acetogens (bacteria) and methanogens (archaea) use today (9, 12). Yet two issues have gnawed at that theory. First, modern serpentinizing vents have plenty of H_2 but almost no CO_2, an essential substrate in the classical acetogenesis. What gives? Second, where are the acetogens in serpentinizing systems?

Microbiologists are now delivering answers. The acetogenic metabolism that Colman et al. (2) reconstruct for the genomic group called *Acetothermia* falls into two categories they call types I and II. The type II category predominates specifically in the hyperalkaline vents, where CO_2 is extremely scarce, and suggests a solution to the low CO_2 problem: There is abundant formate in the hyperalkaline Samail effluent. The hyperalkaline well NSHQ14 that harbors the type II *Acetothermia* genome has roughly 10 times more formate (1.7 μM) than dissolved forms of CO_2 (0.19 μM) (13). The type II *Acetothermia* metabolism could begin from formate rather than CO_2 because it starts with a recently characterized form of the enzyme formate dehydrogenase (14) called FdhF-HylABC, that converts formate into CO_2, reduced ferredoxin, and NADPH, without producing H_2 against the environmental H_2 supply. FdhF-HylABC delivers CO_2 required by the enzyme carbon monoxide dehydrogenase, which is essential to the acetyl CoA pathway (8). CO_2 is also required at several other key metabolic steps, for example, in the synthesis of pyruvate or C4 and C5 intermediates for biosynthesis (10). FdhF-HylABC could supply CO_2 for acetogenesis in a CO_2-poor environment if sufficient formate is available, which the Samail ophiolite provides from geochemical reactions.

And where are the acetogens in serpentinizing vents? Hiding in plain sight. The evidence for acetogens in the Samail ophiolite (2) is neither a fluke nor an outlier. Several recent reports point in the same direction. In 2010, Lang et al. (15) found large amounts of abiogenic formate (∼100 μM) plus biogenic acetate (∼10 μM) in the actively serpentinizing Lost City vent at the bottom of the Atlantic Ocean. New metagenomic data from Lost City effluent uncover evidence for acetogens and methanogens (16), in line with the theory (9). Suzuki et al. (17) studied The Cedars, an ophiolite-hosted serpentinizing vent in California. Effluent at The Cedars has pH 11, high H_2, 7 μM formate, and low CO_2 and is rich in acetogen genomes. Nobu et al. (18) report acetogen genomes from the ophiolite-hosted serpentinizing vent Hakuba Happo in Japan. The Hakuba Happo effluent has pH 11, abundant H_2, almost no CO_2, and 8 μM formate. Hakuba Happo also contains glycine (18) that is of abiotic origin, because it is the only amino acid present, indicating that serpentinization synthesizes amino acids (3).

We usually think of CO_2 fixation as a biological process requiring enzymes. Why can serpentinizing systems reduce CO_2? It is because H_2 gas in alkaline solutions generates very negative midpoint potentials (E_o), meaning that electrons in that environment are ready and able to be transferred to CO_2 as an electron acceptor, if suitable catalysts are present. To reduce CO_2 enzymatically, acetogens (and methanogens) generate reduced ferredoxin with a midpoint potential of roughly –450 mV so that electrons can flow energetically downhill to CO_2 in the formate-producing reaction (E_o of –430 mV). In cells, this entails an elegant biochemical mechanism called electron bifurcation (5, 6, 14). Because of their abundant H_2 and alkaline pH, serpentinizing vents can generate much stronger electron donating conditions than cells do, extreme values of up to –800 mV or more (17, 19), so negative that CO_2 reduction can proceed without enzymes, provided that suitable inorganic catalysts are present.

Preiner et al. (20) showed that, in the laboratory, the hydrothermal minerals awaruite (Ni_3Fe) or magnetite (Fe_3O_4) catalyze the conversion of H_2 and CO_2 to 200 mM formate, 100 μM acetate, and 10 μM pyruvate overnight in alkaline water at 100 °C—an abiotic version of the acetyl CoA pathway in which one inorganic catalyst replaces 10 enzymes and 10 cofactors (8). Their abiotic CO_2 reduction worked because the catalysts are efficient and the experiments are performed at 100 °C, pH 8, and 5.6 mM H_2 (Lost City has 10 mM H_2; the Samail ophiolite has 3 mM H_2). These conditions generate an E_o of –629 mV (20), similar to the midpoint potential of serpentinizing systems (17, 19). But neither in those experiments (20) nor in the Samail ophiolite (2) is external voltage applied. The voltage results from the natural tendency of H_2 to donate electrons in alkaline conditions: $H_2 + 2OH^- \rightarrow 2e^- + 2H_2O$.

The findings of Colman (2) and others (15–20) reveal striking congruence between geochemical reactions and the physiology of ancient microbes, acetogens, that inhabit serpentinizing systems. This opens a window to the ancient past and narrows the gap between a 4.2-billion-year-old geochemical process and the origin of microbial metabolism.

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