



Cobalt: A must-have element for life and livelihood

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Cobalt is in the news—demanded by life's metabolisms and seemingly irreplaceable in our technological world, yet the element averages only 25 ppm in Earth's crust. So, impending deficiency for both life and technology is always looming. For humans and other animals, cobalt is the active center of vitamin B₁₂ involved in methyl, and other, biochemistries. Although it is toxic in excess, we need ~40 ng of Co daily, while other animals need their proportionate share, as do many microbes. In vitamin B₁₂, the variable valence metal is coordinated within a corrin ring by four nitrogen ligands. The same Co-bearing core, although attached to iron sulfide, is central also to life's acetyl coenzyme-A pathway (1). Indeed, Co had, and has, a vital part to play in the emergence and evolution of both the animate and the technological systems. Right down at the bottom of our evolutionary tree, the acetogens and the methanogens require such Co corrinoid iron sulfide enzymes for methyl biochemistry (2). This would be impossible without this Co(FeS) protein needed to mediate the attachment or detachment of a methyl group to or from carbon monoxide or another entity involved in the biosynthesis of acetyl-CoA (1, 2). In industry, cobalt is best known today as an obligatory constituent of batteries and smartphones as well as wear-resistant tools, whereas it was already playing a central role in the chemical industry as the "cobalt blue" of paints and pigments in the 19th century and as a catalyst in the 20th century.

In PNAS, He et al. (3) revisit cobalt's catalytic propensities as they explore the hydrothermal synthesis of long-chain hydrocarbons from sodium bicarbonate as substrate. Previous geochemical experiments on hydrothermal syntheses of hydrocarbons involved the hydrogenation of CO as in the Fischer–Tropsch reaction—a reaction assumed to operate during exothermic serpentinization reactions produced by waters convecting within ultramafic (Mg > Fe silicate) rocks (1, 3, 4). Past work on the geochemical reduction

of CO₂ to long-chained hydrocarbons using F–T syntheses apparently generated polymers ranging from C₂ to >C₃₅ from aqueous solutions of formic acid in stainless steel vessels at 175 °C (4). However, these previous attempts to synthesize the abiotic generation of methane and the higher hydrocarbons have been called into question due to a variety of possible contaminants, from steel autoclaves, to the use of rubber bungs, to the use of methane-sorbed rocks employed in various attempts at reducing CO₂ entrained in serpentinizing solutions (5).

Experimentation

He et al.'s (3) elegant experimental high-pressure and high-temperature operando X-ray technique sidesteps any such issues by demonstrating the absence of hydrocarbons beyond methane in blank runs without Co powder (3). Cobalt and its iron metal carrier are stabilized within a stainless steel microautoclave by reaction with sodium bicarbonate under a pressure of 30 MPa at 300 °C. While the iron oxidizes to Fe–OH, the Co remains unoxidized, transformed to a honeycomb of metallic nanosheets, a structural form particularly prized in catalysis. And it is in this guise that the authors demonstrate catalysis of the reductive synthesis of hydrocarbons from C₁₃ to C₂₁ (mode at C₁₆). So, the bicarbonate is used not only as the carbon resource standing in for CO₂ in the real world but also to promote the in situ generation of the Co nanosheets. First, the adsorbed carbonate is reduced to the intermediate HCOO[−] which then transfers from the Co surface to that of the iron, leading to the formation of Fe–OH groups. At the same time, a portion of the carbon as CO remains bonded to the Co catalyst. The bicarbonate HCO₃[−] adsorbs on the surface of Fe, as the formation of FeCO₃ is thermodynamically favorable in the presence of Co. Thus the oxidation/hydroxylation products of the iron are a crucial part of the reduction mechanism. The authors go on to argue for an equivalent behavior in Earth's crust where a

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comparable CoFe catalyst—the mineral alloy wairauite—is found in some serpentinites, and they point out that the mineral should work to the same effect within Earth’s hydrated Mg–Fe silicate mantle.

Wider Significance

He et al.’s (3) results impinge upon, and connect, a number of transdisciplinary endeavors, significant as they are to the chemical industries as well as to geochemical theory. One such example is the reaction’s independence from the noble metals such as Pt or Ru for CO₂ utilization and synthesis of long-chained hydrocarbons. Yet, as noted, Co itself is a rare element, reserves are limited, and distribution is uneven, with nearly half of it occurring in central Africa. In Earth’s crust, the metal is usually concentrated as sulfide along with Ni and Cu—“always the bride but never the bridegroom” in Smith’s (6) pithy phrase. It is also found, and mined, although less commonly, in veins of the so-called “five-element association” comprising native silver associated with Co, Bi, and Ni arsenides. Interestingly, separately derived methane has been considered the reductant in the hydrothermal genesis of this ore association at ~300 °C (7).

Cobalt’s ultimate source is as a trace (~110 ppm) element in the ultramafic rocks associated with Earth’s present ocean mantle and best represented geologically in Earth’s early history, where it may have been locally augmented by metallic meteorites (8). However, even today, Co can be found in high-temperature hydrothermal precipitates comprising the so-called Black Smoker chimneys, and from thence disperses to also precipitate in deep sea manganese–iron nodules (9). One of the mineral hosts in these nodules is the mineral green rust, or fougérite (10). Cobalt and fougérite likely precipitated, too, with the earliest banded iron formations at Isua, Greenland, although the element now mainly resides in layered sulfides thought to be precipitated then at hot springs (11, 12). And serpentinite mud volcanoes at Isua also bear sulfides rich in cobalt, as cobaltian pentlandite (~Co₁₁Ni₂FeCuS₁₃), which has been interpreted as a vestige of ancient hot spring deposits. Indeed, Pons et al. (13) even remarked that such hydrothermal mud volcanoes “may have fostered the emergence of life on our planet.” That cobalt is hard to come by certainly meets the expectation that life emerged associated with ultramafic oceanic rocks.

Emergence of Life

In a similar vein, He et al.’s (3) recognition of the two distinct pathways during the hydrothermal reduction of NaHCO₃—one to formate and the other to the long-chain hydrocarbons—feeds into two separate expectations of the submarine alkaline hydrothermal vent theory for life’s emergence (the AVT) (1, 8). Formate, reduced from CO₂, marks the initial carboxylation step in the ancient acetyl coenzyme-A metabolic pathway (1, 14). Assuming further carboxylations of the unsaturated hydrocarbons produced by He et al. to fatty acids with Fe and Ni catalysts (15), Jordan et al. (16) demonstrated how C10 to C15 single-chain amphiphiles rapidly self-assemble to form lipid vesicles in saline and strongly alkaline 70 °C hydrothermal solutions. These putative lipids—supplied in hydrothermal fluids—were taken to represent the first organic membranes (16).

However, the AVT has it that the very first membranes were inorganic—oxyhydroxides and sulfides of Fe, Mg, Ni, Co, and Zn—comprising a submarine hydrothermal precipitate mound at such an alkaline vent (1, 8, 17). Indeed, the expectation is that the ferrous–ferric oxyhydroxide fougérite, along with FeS, comprised the first barrier that kept the disequilibria between

the alkaline hydrothermal solutions and the early carbonic ocean at bay, necessary for driving life’s onset (8, 17, 18). It is worth remarking here that fougérite can absorb and host long-chain carboxylic acids in its interlayers, acids that could be released to the alkaline vent on delamination (19).

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In this lower-temperature (~70 °C) hydrothermal context, He et al. (3) offer another clue. To quote, “In the presence of Co, the formation of Fe–OH is attributed to the higher-adsorption energy of COOH on Co ... than that on FeO_x ... , which promotes the transformation of the intermediate COOH reduced from FeCO₃ to the Co surface, leading to the formation of Fe(OH)_x.” This deduction that Co acted as a promotor for an Fe–OH moiety might also suggest the element as a nucleator of the cobaltian layered double hydroxide analogous to fougérite (20). The potential of Co fougérite as a localized redox reactant or catalyst for the autonomous synthesis of lipids is a possibility completely unexplored. Such a demonstration might absolve earliest life from relying on remotely delivered organic molecules through serpentinitization, and be a lead into the autotrophic “in-house” protometabolic provision of long-chain fatty acids at the Hadean hydrothermal mound itself—an introduction of the lipid world as a partial organic takeover, in combination with the peptides discussed next, of the mineral membranes barriers?

Fougérite ([Fe²⁺_{6x}Fe³⁺_{6(x-1)}O₁₂H_{2(7-3x)}}]²⁺•[(CO₃²⁻)•3H₂O]²⁻) is a variable valence “soft” 2D electrolyte hosting cationic and anionic substitutes and is capable of conformational change in response to its “hard” solid electrolyte properties, and, as a battery, it is rechargeable (17, 21). As such, it has been shown to mimic biology-like transformations such as the production of 1) pyrophosphate from phosphate and acetyl phosphate in microfluidic inorganic membranes produced in pH gradients (22), 2) the eight-electron reduction of the high-potential electron acceptor nitrate to ammonium (18, 23), and 3) an amine resulting from reaction 2 that can aminate pyruvate to the amino acid alanine (24). We are now approaching a peptide world where short polymers can further sequester anions such as phosphates and sulfides, and cations such as cobalt, to act as organic protoenzymes (18). Indeed, Bren and coworkers (25) have demonstrated hydrogenase activity of Co chelated in a minimal peptide comprising two glycines and one histidine, to give an N4 coordination sphere analogous to the flexible corrinoid macrocycle ring discussed earlier. Taken together, these various abiotic syntheses of protobiotic entities—some of them obligated to Co—provide further experimental targets for investigating life’s emergence at alkaline submarine hydrothermal springs.

So, what is it about cobalt that makes it indispensable? Sitting between Fe and Ni in the periodic table, the element is particularly “energy dense” with paired electrons in the outer orbit. And its occurrence as a metal alloy in serpentinites with a variable valence extending from Co⁺ through to Co⁴⁺, its various spin states, and its contrasting conformations render it unique, with untold contributions to be made to electronics, catalysis, and the emergence of life. Indeed, Co–Fe cooperation has just been investigated at the opposite end of the redox spectrum—the electrocatalysis of the O₂ evolution reaction (26). Substitutions of Co are either unfeasible, as in metabolism and

in some double-atom catalysis, or they lie in the somewhat remote future.

Although learning from nature is an old mantra for engineers, the roles are now being reversed, with emergence-of-life researchers looking to electrochemistry, nanotechnology, and microfluidics for their inspiration (1, 8, 14, 17, 18, 22, 24). The

autogenic scenario for the origin of life predicts such a scheme of events, alluded to by He et al. (3) and described herein. More specifically, the AVT stipulates metabolism to have onset exclusively based on prebiotic macromolecular metal-ligated catalysts as redox centers, semiconductors, and free-energy transforming nanoengines (17).

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