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 it 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 properties as they explore the hydrothermal synthesis of long-chain hydrocarbons from 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 CO by FeCO₃–OH groups. At the same time, a portion of the carbon as CO remains bonded to the Co catalyst. The bicarbonate HO₃CO⁻ 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...
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 chemi-
cal industries as well as to geochemical theory. One such exam-
ple 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, sepa-
ately 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 oce-
 Compounds that are rich in cobalt, as cobal-
nesses thought to be precipitated then at hot springs (11, 12). And serpentine
mud volcanoes at Isua also bear sulfides rich in cobalt, as cobal-
tian 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). Taken together, these
variable valence extending from Co+ through to Co4+, its vari-
ous 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 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 … that on FeOx …, which promotes the
transformation of the intermediate COOH reduced from FeCO3 to
the Co surface, leading to the formation of Fe(OH)x.” This deduc-
tion that Co acted as a promoter for an Fe–OH moiety might also
suggest the element as a nucleator of the cobaltian layered double
hydroxide analogous to fougerite (20). The potential of Co fou-
gerite 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 serpentinization, 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 combi-
nation with the peptides discussed next, of the mineral mem-
branes barriers?

Fougerite ([Fe52O66Fe48S72]2−·12H2O) 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 ammo-
nium (18, 23), and 3) an amine resulting from reaction 2 that can
amine 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 proteoenzymes (18). Indeed, Bren and
coworkers (25) have demonstrated hydrogenase activity of Co che-
lated in a minimal peptide comprising two glycines and one histi-
dine, 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 obli-
gated 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? Sit-
ting 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 Co2+ through to Co4+, its vari-
ous 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
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synthesis of long-chain hydrocarbons from
sodium bicarbonate as substrate.
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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