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GEOCHEMISTRY

Extraterrestrial electrochemistry

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Many have sought to find clues about Martians by looking for organic matter — either on Mars itself or in meteorites that have reached Earth. For the last 6 years, the Curiosity rover has explored the Gale Crater on Mars, gathering data that complement detailed studies of meteorites. Writing in *Science Advances*, Andrew Steele and colleagues not only characterize Martian organics but also propose an electrochemical mechanism for their formation from CO_2.

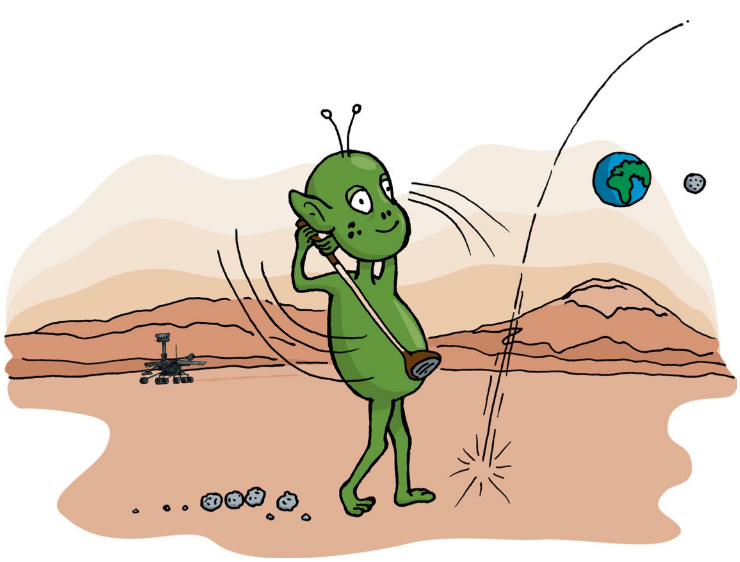
Biogenic activity on Mars had been proposed in a 1996 analysis of the meteorite Alan Hills 84001 (ALH84001), in which the globular carbonate morphology and presence of polyaromatic hydrocarbon (PAH) species were consistent with the sample once hosting microorganisms. Carbonaceous materials are not unique to ALH84001, and further confocal Raman imaging revealed reduced carbons — discrete PAHs and amorphous macromolecular carbon (MMC) — in ten Martian meteorites. On Mars itself, Curiosity has acquired mass spectra of heated sediment samples, and Steele was part of a team that showed the liberated volatiles to include organochlorines as well as organosulfur molecules such as thiophenes and thiols — species also present in sediments on Earth.

"I have been working on setting an abiotic background of organics in Mars meteorites and through Mars missions for many years," notes Steele. In search of how these compounds might have come to be, his team recast their eyes (and analytical instrumentation) on meteorites to obtain an inventory of the organic and inorganic materials present. Raman imaging enabled the team to identify sample regions of interest, after which transmission electron microscopy revealed inorganic phases such as sulfides and a mixed Ti,Fe oxide spinel that assumed a comb morphology. Between the teeth of these combs lie amorphous regions rich in Fe, Al, Si, Ti, N, Cl and O, as well as MMC, as confirmed by Raman and energy dispersive X-ray measurements. In terms of organics, scanning transmission X-ray microscopy uncovered C–O, C=O, C–N=C, C=C and C≡N groups, and time-of-flight secondary ion mass spectra featured several similar inorganic and organic fragments (the latter being unquestionably Martian on account of the extraterrestrial relative $^{2}H/^{1}H$ isotopic abundances of the carbonaceous material) also observed by the Curiosity mission.

Armed with this information, Steele's team advanced a mechanistic hypothesis for Martian abiotic organic synthesis. Aqueous solutions containing HCO_3^- and Cl^- act as electrolytes for galvanic cells featuring Ti,Fe oxide cathodes and sacrificial Fe-rich oxide anodes that decay between the intact Ti,Fe oxide structures. The reduction products likely include H_2, CO, CH_3OH and HCO_2H — compounds that could undergo Fischer–Tropsch and then Diels–Alder chemistry to assemble aromatics. The chemical diversity observed by the team points to the occurrence of other reactions, such as N_2 reduction to NH_3, and Cl^- oxidation to ClO^- and ClO_4^-.

The information gleaned from the two mutually supportive datasets — collected both on Mars and on Earth — is not enough to answer every question regarding our nearest planetary neighbour. For example, does its CH_4-rich atmosphere also result from abiotic CO_2 reduction or is it instead a result of biotic CH_4 evolution, as on Earth? The team is now testing the feasibility of abiotic synthesis and has already observed the formation of traces of CH_4 in a macrofluidic reactor loaded with Fe and TiO_2 nanoparticles and an artificial seawater/silicate solution. Steele's next trick would be to "shrink this down to microfluidic scale to mimic the actual conditions in the rock," the results of which would give us a better understanding of what could be taking place in the distant Martian sands.

David Schilter



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