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Organic chemistry on a cool and wet young Mars

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Abstract

The Curiosity rover is unveiling the persistence of habitable environments more than three-billion years ago at Gale crater, Mars. New analyses of Gale's ancient sediments show that chemical processing of organic material occurred on a liquid-water rich and freezing early Mars.

The search for organic compounds has been one of the main goals of the Mars Science Laboratory (MSL) Curiosity rover, which celebrated its fourth Martian birthday in mid-February 2020, since landing on 6 August 2012 near the paleolake sediments of the Gale crater. Writing in *Nature Astronomy*, Heather Franz and colleagues¹ describe MSL discoveries on carbon and oxygen isotopes from various rock and sediment samples analysed along the first 20 km traverse of the rover. The paper provides three specific advances to our knowledge of Mars: expansion of the range of organic compounds identified in Gale relative to previous analyses², identification of active geochemical cycling between the surface and the atmosphere, and identification of partially frozen fluids on early Mars. All three points bear important implications for past habitability and the potential for life on early Mars.

The first contribution of Franz and colleagues is to describe in situ Curiosity studies and laboratory modelling for the formation of organic materials on Mars. They use data obtained with the Sample Analysis at Mars (SAM) instrument, a suite of three complementary instruments — a mass spectrometer, a gas chromatograph and a laser spectrometer — designed to search for carbon-containing compounds and other elements associated with life on Earth, such as oxygen, hydrogen and nitrogen. They discuss fractionation processes in organic compounds that may account for the $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ values observed within and between different groupings of samples inside Gale.

The analysis of samples volatilized by the SAM instrument yield four possible sources for organic compounds on Mars. First, that some or all organic molecules identified originate in the vapour from a chemical used in the experiment (N-methyl-N-*tert*-butyldimethylsilyl-trifluoroacetamide, known as MTBSTFA) leaking into the system. Second, that all CO_2 detected by SAM comes from inorganic molecules. Third, that all Martian organics come

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from meteorite infall and mantle sources. And fourth, that organics formed in situ on Mars via processes such as abiotic photosynthesis operating over billions of years.

Franz and colleagues favour the latter two explanations, in large part because the SAM team has worked incredibly hard to definitively overturn the other two possibilities. They argue that meteoritic infall is probably happening, but the amount of carbon is too much to be explained solely by it, so the fourth source is required. In any case, they are very careful not to imply that these chemical reactions somehow amount to the emergence of life. It is true that, in analogy with terrestrial biological processes, biological fractionation³ is a potential candidate to explain some observed $\delta^{13}\text{C}$ enrichment in Gale samples. However, biological processes should be invoked as a serious possibility for the presence of organic compounds on Mars only after all potential abiogenic hypotheses have been discounted, which, as seen from the above, is not currently the case.

The second contribution of the Franz et al. work relates to the geochemical cycling of volatiles between the surface and the atmosphere, in particular between reservoirs of carbon and oxygen. This is indicated by the similar enrichment in $\delta^{18}\text{O}$ observed by SAM in atmospheric CO_2 and in oxychlorine compounds from samples obtained by scooping surface sand and after drilling some centimetres under the surface (Fig. 1). Oxychlorine compounds, particularly perchlorate, seem to be widespread on Mars at concentrations between 0.5 and 1%, and have been blamed⁴ as the agents responsible for burning organics during the thermal step of the analytical instruments sent to Mars precisely to detect them, as is the case with SAM. In the boreholes drilled by Curiosity, the highest concentration of oxychlorine measured to date appeared in the Cumberland (CB) drill hole, with one order of magnitude more inferred perchlorate than in any other borehole at Gale crater⁵. CB is also the same hole where nitrates are more abundant⁶ and, surprisingly, also one of the few boreholes in Gale where reduced carbon compounds (chlorinated hydrocarbons) have been identified by SAM⁷. This positive correlation between the abundance of perchlorates and the detection of organics in CB puts into question the assumed direct link between perchlorates and the non-detection of organics on Mars, and highlights that mechanisms protecting organic compounds (for example, the role of the different mineralogical hosts of organics) should be investigated.

Finally, the Franz et al. paper helps to place the environmental constraints on the formation of Gale sediments in a context that is extremely useful in the assessment of the climatic evolution and habitability potential of early Mars. The values of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ described by Franz et al. suggest that carbonates identified by Curiosity, though scarce, possibly precipitated from fluids isotopically fractionated with respect to the modern atmosphere. One straightforward mechanism to produce such fractionation is through partial freezing of the water in the crater, triggered by prevalent low temperatures at the time when a lake ponded into Gale. Indeed, almost all climate models for early Mars conclude that temperatures then were close to freezing or below⁸. The problem with this scenario is that Curiosity has not yet found an incontrovertible sedimentary record of an ice-covered lake in ancient Gale in the over 300 vertical metres of primarily lacustrine mudstone. For this reason, Franz and colleagues favour a formation of cryogenic carbonates in a lake (or lakes) that existed later in Gale's history or in an environment external to the crater. This apparent

contradiction could be resolved by analysing several lines of evidence that point to an icy Gale lake.

First, geomorphological surveys have identified wide glaciated terrains both on northern Gale⁹ and on the very northern rim of the crater¹⁰, indicating extensive regional glaciation. Second, mineralogy data obtained by Curiosity¹¹ indicate that sedimentary processes in Gale occurred under relatively cold conditions typical of glacial/periglacial environments. Recent analyses on the thermodynamics of clay formation also agree with this possibility¹². And third, the lack of evidence for periglacial features in the sediments studied to date by Curiosity could arise from (1) the simple fact that those sediments were deposited very early after the excavation of the crater, and before the onset of the (peri)glacial epoch; and/or (2) that the lake at Gale was ice-sealed, as periglacial structures are equally scarce in terrestrial ice-sealed lakes¹³.

All these arguments point at an enduring cool climate in early Mars at the time when lakes existed inside Gale crater, one characterized by vast extensions of ice sheets covering most of the Martian surface during the winters, and seasonal flooding and ponding of liquid water ‘on the rocks’ in springs and summers. The emerging picture of early Mars would be one with summers alike to winters in the Great Lakes, and winters similar to those in the Antarctic.

Franz et al. have made important steps in improving our understanding of the early Mars environment, including the origin of organics, geochemical cycles and the paleoclimate. Their results show that continuing in situ investigations across the planet are needed to comprehend whether the results obtained at Gale are likely to reflect local or global trends in the geological evolution of Mars. The next-generation rovers rocketing to Mars next summer (NASA’s Perseverance) and in 2022 (ESA’s Rosalind Franklin) will deepen our knowledge about the nature of the cool and wet young Mars.

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Fig. 1. Mars is grey.

The red colour of the Martian surface results from the oxidation of iron minerals present in the soil and dust. But in most cases, scratching the surface just a few millimetres, as shown in these images from the Spirit (left), Opportunity (centre) and Curiosity (right) rovers, reveals a grey, non-oxidized substrate under the thin red coating all over the planet. Franz and collaborators¹ describe a geochemical cycling between the surface and the atmosphere. Some organic compounds may have been preserved from oxidation at the surface longer than expected, by mechanisms such as trapping in minerals or reacting with sulfur in sediments, and others left fingerprints as they were attacked by oxidants or radiation. SAM has detected evidence for reduced carbon compounds in a few samples from drilling some centimetres deep, below the red coating. Credit: D. Savransky and J. Bell (Cornell)/JPL/NASA (Spirit and Opportunity images) and NASA/JPL-Caltech/MSSS (Curiosity image)