

Planetary Science 2023

Curiosity rover hints at the carbon cycle on Mars

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The Mars Science Laboratory carried by the *Curiosity* rover is still functioning 10 years after a jetpack lowered *Curiosity* onto the surface of Gale crater. It includes a system aimed at scooping and drilling samples of soil and rock from the sedimentary strata deposited in the lake that once filled the crater about 3.5 to 3.8 billion years ago. The system on the rover is also capable of analysing the samples in various ways. A central objective of the mission was to obtain data on oxygen and carbon isotopes in carbon dioxide and methane released by heating samples, which uses a miniature mass spectrometer. In early 2022 a paper on Martian carbon isotopes was published in the Proceedings of the National Academy of Sciences (PNAS) that I have only just found (House, C.H. *et al.* 2022. [Depleted carbon isotope compositions observed at Gale crater, Mars](#). *Proceedings of the National Academy of Sciences*, v. 119, article e2115651119; DOI: 10.1073/pnas.2115651119). PNAS deemed it to be one of the 12 most important of its articles during 2022.



Oblique view of Curiosity's landing site in Gale crater on Mars, from which the rover has traversed the lower slopes of Mount Sharp. Credit: NASA-Jet Propulsion Laboratory

Carbon isotopic analyses chart the type and degree of fractionation between carbon's two stable isotopes ^{12}C and ^{13}C . This is expressed by their relative abundances to one another in a sample and in a reference standard, signified by $\delta^{13}\text{C}$. The measure is a natural tracer of both inorganic and biological chemical processes: hence the potential importance of the paper by Christopher House and colleagues from the University of California, San Diego. The thin atmosphere of Mars contains both CO_2 and traces of CH_4 , so a carbon cycle is part and parcel of the planet's geochemical functioning. The 'big question' is: Did that involve living processes at any stage in the distant past and even now? Carbon held in various forms within Mars's ancient rocks and soils may provide at

least a hint, one way or the other. At the very least it should say something about the Martian carbon cycle.

House *et al.* focus on methane released by heating 22 samples drilled from sandstones and mudstones traversed by *Curiosity* up a slope leading from the floor of Gale crater towards its central peak, Mount Sharp. The sampled sedimentary rocks span a 0.5 km thick sequence. Carbon in the expelled methane has $\delta^{13}\text{C}$ values that range from -137 to +22 ‰ (per mil). Samples from six possibly ancient exposed surfaces were below -70 ‰. This depletion in ^{13}C is similar to the highly negative $\delta^{13}\text{C}$ that characterises carbon-rich sediments on Earth that were deposited at the Palaeocene-Eocene boundary. That anomaly is suspected to have resulted from releases of methane from destabilised gas hydrate on the sea floor during the [Palaeocene–Eocene Thermal Maximum](#). Organic photosynthesis takes up 'light' ^{12}C in preference to ^{13}C , thereby imparting low $\delta^{13}\text{C}$ to organic matter. In the case of the Mars data that might seem to point to the lake that filled Gale crater 3.5 to 3.8 billion years ago has contained living organisms of some kind. Perhaps on exposed surfaces of wet sediment primitive organisms consumed methane and inherited its $\delta^{13}\text{C}$. Some Archaean sediments of about the same age on Earth show similar ^{13}C depletion associated with evidence for microbial mats that are attributed to the activities of such methanotrophs.

Before exobiologists become too excited, no images of possible microbial mats in Gale crater sediments have been captured by *Curiosity*. Moreover, there are equally plausible scenarios with no recourse to once-living organisms that may account for the carbon-isotope data. Extreme depletion in ^{13}C is commonly found in the carbon within meteorites, almost certainly inherited from the interstellar dust from which they accreted. It is estimated that the solar system passes through giant molecular clouds every 100 Ma or so: the low $\delta^{13}\text{C}$ may be inherited from interstellar dust. Alternatively, because Mars has an atmosphere almost entirely composed of CO_2 – albeit thin at present – various non-biological chemical reactions driven by sunlight or electrically charged particles may have reduced that gas to form methane and other compounds based on C-H bonds. Carbon dioxide still in Mars's atmosphere is highly enriched in ^{13}C , suggesting that earlier abiotic reduction may have formed ^{13}C -depleted methane that became locked in sediments. Yet such an abundant supply of inorganic methane may have encouraged the evolution of methanotrophs, had life emerged on early Mars. No one knows ...

It's becoming a cliché that, 'We may have to await the return of samples from the currently active *Perseverance* rover, or a crewed mission at some unspecified time in the future.

The *Curiosity* carbon-isotope data keep the lamp lit for those whose livelihoods have grown around humans going to the Red Planet.

The Moon may have water resources in its soil

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Apart from signs of water ice in permanently shadowed areas of some polar craters, the Moon's surface has generally been considered to be very dry. Rocks returned by the various Apollo missions contain minute traces of water by comparison with similar rocks on Earth. They consist only of anhydrous minerals such as feldspars, pyroxenes and olivines. But much of the lunar surface is

coated by [regolith](#): a jumble of rock fragments and dust ejected from a vast number of impact craters over billions of years. It is estimated to be between 3 and 12 m deep. Much of the finer grained regolith is made up of silicate-glass spherules created by the most powerful impacts.



The lunar regolith at Tranquillity Base bearing an astronaut's bootprint (Credit: Buzz Aldrin, NASA Apollo 11, Photo ID AS11-40-5877)

The scientific and economic (i.e. mining) impetus for the establishment of long term human habitation on the lunar surface hangs on the possibility of extracting water from the Moon itself. It is needed for human consumption and as a source through electrolysis of both oxygen and hydrogen for breathing and also for rocket fuel. The stupendous cost, in both monetary and energy terms, of shifting mass from Earth to the Moon clearly demands self-sufficiency in water for a lunar base occupied for more than a few weeks.

Remote sensing that focussed on the ability of water molecules and hydroxyl (OH^-) ions to absorb solar radiation with a wavelength of 2.8 to 3.0 micrometres was deployed by the Indian lunar orbiter [Chandrayaan-1](#) that collected data for several months in 2008-9. The results suggested that OH^- and H_2O were detectable over a large proportion of the lunar surface at concentrations estimated at between 10 parts per million (ppm) up to about 0.1%. Where did these hydroxyl ions and water molecules come from and what had locked them up? There are several possibilities for their origin: volcanic activity that tapped the Moon's mantle (magma could not have formed had some water not been present at great depths); impacts of icy bodies such as comets; even the solar wind that carries protons, i.e. hydrogen atoms stripped of their electrons. Conceivably, protons could react with oxygen in silicate material at the surface to produce both OH^- and H_2O to be locked within solid particles. To assess the possibilities a group of researchers at Chinese and British institutions have examined in detail the 1.7 kg of lunar-surface materials collected and returned to Earth by the 2020 Chinese [Chang'e 5](#) lunar sample return mission (He, H. and 27 others 2023. [A solar wind-derived water reservoir on the Moon hosted by impact glass beads](#). *Nature Geoscience*, online article; DOI: 10.1038/s41561-023-01159-6)

He *et al.* focussed on glass spherules formed by impact melting of lunar basalts, whose bulk composition they retain. The glass 'beads' contain up to 0.2 % water, mainly concentrated in their outermost parts. This alone suggests that the water and hydroxyl ions were formed by spherules

being bathed in the solar wind rather than being of volcanic or cometary origin and trapped in the glass. An abnormally low proportion of deuterium (^2H) relative to the more abundant ^1H isotope of hydrogen in the spherules is consistent with that hypothesis. Indeed, the high temperatures involved in impact melting would be expected to have driven out any 'indigenous' water in the source rocks. The water and OH^- ions seem to have built up over time, diffusing into the glass from their surfaces rather than gradually escaping from within.

An awful lot of regolith coats the lunar surface, as many of the images taken by the Apollo astronauts amply show. So how much water might be available from the lunar regolith? The Chinese-British team reckon between 3.0×10^8 to 3.0×10^{11} metric tons. But how much can feasibly be extracted at a lunar base camp? The data suggest that a cubic metre (~ 2 t) of regolith could yield enough to fill 4 shot glasses (~ 0.13 litres). Using a solar furnace and a condenser – the one in full sunlight the other in the shade – is not, as they say, 'rocket science'. But for a minimum 3 litres per day intake of fluids per person, a team of 4 astronauts would need to shift and process roughly 100 m^3 of regolith every day. Over a year, this would produce a substantial pit. But that assumes all the regolith contains some water, yet the data are derived from the surface alone ...

See also: [Glass beads on moon's surface may hold billions of tonnes of water, scientists say](#). *The Guardian*, 27 March 2023.

Hydrogen and how the Earth formed

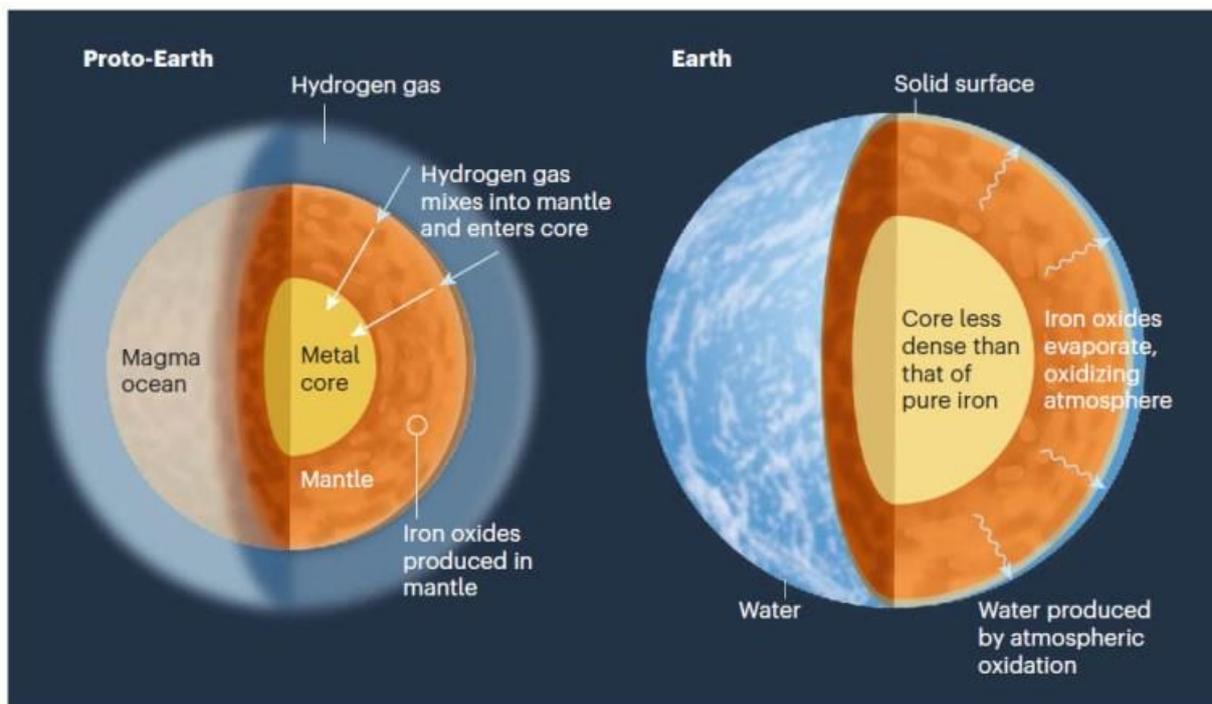
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A third piece with hydrogen as its focus in a couple of months? Well, from a galactic perspective there's a lot of it about. Modern cosmology suggests that only 4.6% of the energy in the universe consists of elemental atoms made of protons, neutrons and electrons, dwarfed by [dark energy](#) and [dark matter](#) that are something of mystery. But of the more familiar energy equivalent, tangible matter (as in $E=mc^2$), 74% of the universe is hydrogen, 24% is helium and [the other 92 elements](#) amount to just 2%. That tiny proportion of heavier elements was created by [nucleosynthesis](#) within stars from the two products of the Big Bang (H and He). Nuclear fusion reactions formed those with atomic numbers (protons in their nuclei) up to that of iron (26), whereas the heavier elements were created through neutron- and proton capture when the largest stars destroyed themselves cataclysmically as supernovae. Yet the planet whose surface we inhabit contains only minute amounts of helium and elemental hydrogen. Of course water at and beneath the surface, in the form of atmospheric vapour and locked within minerals retains some of the cosmically available hydrogen. But current estimates suggest that hydrogen accounts for a mere 0.03% of Earth's mass. Despite the fact that some forms of radioactive decay generate alpha particles that become helium it forms a vanishingly small proportion of terrestrial mass.

The solar system formed around 4.6 billion years ago by a complex gravitational accretion of the gas and dust of an interstellar cloud: mainly H and He. Its dynamic collapse resulted in gravitational potential energy being transformed into heat: in the case of the Sun, sufficient to set off self-sustaining nuclear fusion. As a body grows in this way so does its gravity and thus the speed needed for matter to escape from its pull ([escape velocity](#)). As temperature increases so does the speed at which atoms of each element vibrate; the lower the atomic mass the faster the vibration and the greater the chance of escape. So the 'blend' of elements that an astronomical body retains during its

early evolution depends on its gravity and its surface temperature. The Sun is so massive that very little has escaped its pull, despite a surface temperature of about 5 to 6 thousand degrees Celsius. Its composition is thus close to the cosmic average. Those of the giant planets Jupiter, Saturn, Uranus and Neptune are not far short because of their large gravities and low surface temperatures. Even today, the smaller Inner Planets are unable to cling on to elemental hydrogen and helium and nearly all that is left of the matter from which they formed is the 2% of heavier cosmic elements locked into solids, liquids and gases.

Processes in the early solar system were far more complicated than they are today. In the mainly gaseous disc, from which the solar system evolved, gravity dragged matter towards its centre. That eventually ignited nuclear fusion of hydrogen to form our star. More remote from its gravitational pull vortices aggregated dust into bodies known as planetesimals that in turn accreted to larger protoplanets. Solar gravity dragged gas from the inner solar system leaving rocky protoplanets, whereas gas was able to be attracted to the surface of what became the gas giants where their gravity outweighed that of the far-off Sun. This was complicated by a sort of Milankovich Effect on steroids in which protoplanets continuously changed their orbits and underwent collisions. The best known of these was between the protoEarth and a Mars-sized body that formed the Earth-Moon system, both bodies having deep [magma oceans](#) as a result of the huge energy focussed on them by the collision. What may have happened to the protoplanet that became Earth before the Moon-forming collision has been addressed by three geoscientists at the University of California Los Angeles and the Carnegie Institution for Science Washington DC, USA (Young, E.D. *et al.* 2023. Earth shaped by primordial H₂ atmospheres. *Nature*, v. 616, p. 306–311; DOI: 10.1038/s41586-023-05823-0 [PDF request to: eyoung@epss.ucla.edu]).



A thick hydrogen-rich atmosphere's interacting chemically with a protoplanet (left). A possible later stage (right) where iron oxide in the magma ocean of the Early Hadean after Moon formation oxidises a hydrogen atmosphere to form surface water (Credit: Sean Raymond 2023, Fig 1)

The focus of the work of Edward Young, Anat Shahar and Hilke Schlichting is directed at the possibility that the Earth-forming protoplanets originally retained thick hydrogen atmospheres. They use thermodynamic modelling of the equilibrium between hydrogen and silicate magma oceans that had resulted from the energy of their accretion. The authors' main assumption is that insufficient time had elapsed during accretion for the protoplanets to cool and crystallise: a distinct possibility because loss of accretionary heat by thermal radiation would have been 'blanketed' by actively accreting dust and gas in orbit around the growing protoplanets. Effectively, the equilibrium would have been chemical in nature: reactions between highly reducing hydrogen and oxidised silicate melts or even vaporised rock evaporated from the very hot surface. The authors suggest that protoplanets bigger than Mars (0.2 to 0.3 times that of Earth) could retain a hydrogen-rich atmosphere long enough for the chemical reactions to come to a balance, despite high temperatures. There would have been no shortage of hydrogen at this early stage in solar system evolution: perhaps as much as 0.2% percent the mass of the Earth surrounding a protoplanet about half its present size.

Two outcomes may have emerged. Reaction between hydrogen and anhydrous silicates could produce H₂O in amounts up to three times that currently in the Earth's oceans, some locked in the magma ocean, some in the dense atmosphere. A by-product would have been iron oxide, giving the current mantle its oxidising properties known from the geochemistry of basaltic magmas. Hydrogen might also have dissolved in molten iron alloys, thereby contributing to the nascent core. That second outcome would help explain why the modern core is less dense than expected for iron-nickel alloy, both solid and liquid. In fact densities calculated by geophysicists from the speeds of seismic waves that have travelled through the core are 5 to 10% percent lower than expected for the alloy. So the core must contain substantial amounts of elements with low atomic numbers.

Several other possibilities have been suggested to account for Earth's abundance of water. Two popular ideas are comets arriving in the 'settled' times of the Hadean or by original accretion of hydrous chondrite meteorites, whose hydrogen isotope proportions match those of ocean water. Hydrogen as the light element needed in the core is but one possibility along with oxygen, sulfur and other 'light' elements. Also, the oxidising potential of the modern mantle may have resulted from several billion years of wet lithosphere being subducted. To paraphrase Sean Raymond (below), 'other hypotheses are available'!

See also: Raymond, S.N. 2023. Earth's molten youth had long-lasting consequences. *Nature* (News & Views), v. 616, p. 251-252; DOI: 10.1038/d41586-023-00979-1 [PDF request to: rayray.sean@gmail.com]

Relics of the Moon-forming impact?

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An artist's impression of the collision between Theia and the proto-Earth. (Credit: Hernán Cañellas, Nature)

Close to the core-mantle boundary (CMB) there are two extensive zones up to 10 km thick in the lower mantle. They have seismic-wave speeds that are much lower than expected at such depths: hence their being termed large low-velocity provinces (LLVPs). Seismic velocities being inversely proportional to the density of the material through which such waves travel, these zones have anomalously high density. The LLVPs have remained enigmatic since they were first discovered. Some have suggested that they are relics of dense [subducted banded iron formations](#) (see also: [Curiously low-velocity material at the core-mantle boundary](#); March 2005) or simply [piles of subducted slabs](#) with an eclogite component that have gradually accumulated through Earth's long history of plate tectonics. An alternative is that LLVPs may be connected to geochemical evidence for a heterogeneous lower mantle and perhaps are relics of Earth's earliest history.

The Moon-forming event about 4,500 Ma ago (for more information search the [Planetary Science annual logs index](#)) that probably involved a collision between the proto-Earth and another, Mars-sized planet – dubbed 'Theia' – is an alternative explanation for LLVPs. Maybe they are chunks of that planet that became embedded in the early Earth's mantle. Many geochemical approaches to such an obvious origin are inconclusive, however. The latest attempt to model the processes involved in such a planetary truck crash using computer simulation does suggest that LLVPs may indeed be relics of Theia material that sank through the molten mass that became Earth's mantle after the collision (Yuan, Q. *et al.* 2023. [Moon-forming impactor as a source of Earth's basal mantle anomalies](#). *Nature* v. **623**, p. 95–99; DOI: 10.1038/s41586-023-06589-1).

Qian Yuan of the California Institute of Technology, and colleagues from China, USA and the UK based their approach on geochemical anomalies in plume related ocean-island basalts. These included distinctly non-terrestrial isotopic proportions of the noble gases neon and xenon, similar to those in lunar basalts., which in turn are more iron-rich than most basalts and thus 2-3% denser. The initial assumption in their modelling was that during the collision fragments of Theia peppered the magma ocean that became Earth upper mantle. These were thoroughly mixed in this molten zone as it convected before solidifying. But melts derived from some of the fragments could have penetrated the solid mantle below 1400 km depth as blobs, to retain their chemically anomalous integrity. Being dense, the blobs could slowly sink to accumulate at the CMB to form the two LLVPs. An animation of the processes revealed by Yuan *et al.*'s modelling [can be viewed here](#).

See also: Oza, A. 2023. [Strange blobs in Earth's mantle are relics of a massive collision](#). *Nature* v. **623**; DOI: 10.1038/s41586-023-06589-1