Oxygen: making molecules for a mission to the Moon and Mars

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We humans can literally thank our lucky stars for those heavier elements needed to create DNA, specifically carbon, hydrogen, nitrogen, oxygen, phosphorous and sulphur (CHNOPS), forged inside the nuclear furnaces of dying stars that implode leaving behind supernova remnants (Bailey, 2020). Since the first cosmic whiff and most distant detection of O jettisoned by the galaxy MACS1149-JD1 ~13.28 billion years ago at a time when the universe was less than 2% of its current age (Hashimoto *et al.*, 2018), this element has become synonymous with life. With the advent of oxygenic photosynthesis, atmospheric levels of the diatomic oxygen (O_2) molecule (two Os glued together with a double covalent bond sharing 2 pairs of valence electrons) increased rapidly during the Proterozoic aeon of the Precambrian period, with each O_2 'pulse' sparking an explosion in Earth's biota, heralding the emergence of complex multicellular life, aerobic respiration and cephalisation. Indeed, the human brain stands as clear testament to our reliance on this precious gas and inherent vulnerability to failure when supply is cut off given its voracious appetite in the face of little to no O_2/glycogen reserves (Bailey, 2019). In short, we are all 'obligate neurobes'! But don't take this gas for granted since atmospheric O_2 levels have started to wax and wane from the 20.93 % (ambient PO_2 of 150 mmHg) that we've come to enjoy over the last ~100 million years or so (Berner *et al.*, 2007). Indeed, conservative estimates based on parabolic modelling (Livina *et al.*, 2015) predict that within ~3,600 years, living at sea-level will feel as uncomfortably hypoxic as if we were atop a ~5,340 m mountain, equivalent to the highest habitable elevation that humans can 'endure' here on Earth (Bailey, 2019). Complete depletion has been predicted to occur within ~4.4 millennia, a sobering prospect that seems to have escaped public attention given current preoccupation with rising levels of that other gas, carbon dioxide (CO_2), the flipside of the climate coin. Hence the need to consider alternative sources of O_2 is important if we are to continue to sustain life here on Earth, or indeed beyond.

This challenge has taken on new significance as humans plan extended missions to the lunar surface and beyond with a crewed mission to Mars anticipated as early as the 2030s; the next frontier in our quest to becoming a spacefaring, multiplanetary species. Of all the planets in the solar system, Mars most closely resembles Earth, yet the journey to and habitation on the Red Planet poses unique physiological challenges. Astronauts will have to cope with the combined stresses of space radiation, altered gravity, isolation/confinement and closed environments (Patel *et al.*, 2020) for up to 1,000 days on a planet located anywhere from ~55 to 400 million km from Earth (dependent on the position of the planets in their orbits). Even the average temperature on Mars exceeds -60°C (Trainer *et al.*, 2019), a full 20°C lower than the coldest temperature ever recorded on the summit of Mt. Everest, which incidentally is a third of the height of Mars' Olympus Mons volcano (21,229 m)!

But most important of all, there is next to no atmospheric O_2. The first in-situ measurements were recently performed via quadrupole mass spectrometric sampling of air from the Gale Crater over the course of three Mars years (equivalent to nearly six Earth years) aboard NASA's Curiosity rover. Data confirmed that the lion's share of the Martian atmosphere is made up of CO_2 (95.1%), followed by nitrogen (2.59%), argon (1.94%) with O_2 (0.16%) coming in fourth ahead of carbon monoxide (0.06%) (Trainer *et al.*, 2019). Although way less than that required to support life, the unpredictable behaviour of O_2 given seasonal fluctuations of up to 30% continues to baffle scientists, implying that something is generating it before quickly destroying it.

And humans will need a fair share of O_2 to survive their sojourn. Conservative estimates indicate that around a (metric) ton of O_2 will be required to keep a crew of 4 astronauts alive on Mars for a year (see Figure 1C for calculations). And that's just the "lemon next to the pie". While putting boots on Mars won't be easy, bringing them back will prove way more (O_2) expensive. Mission models suggest that in excess of 30 tons of (liquid) O_2 will be needed to provide sufficient propellant to slip the albeit less surly bonds of Martian gravity (0.38g). This represents ~78% of the propellant mass in a methane/O_2 propulsion system (Hecht & Hoffman, 2016) (Figure 1C). This payload would translate into ~400 tons in Earth orbit, requiring anywhere between 4-5 heavy lift launches (Hecht & Hoffman, 2016). Hence, the supply of O_2 is not an insignificant hurdle that needs to be overcome so that humans and rockets alike can 'breathe' easy.

So how do we get around this? One potential solution lies in harvesting O_2 'in-situ' via high-temperature solid oxide electrolysis (SOXE) of Mars' number one constituent gas, CO_2 that would otherwise prove fatal to humans at the prevailing concentration. This would dramatically reduce mission logistics and costs, increase self-sufficiency and reduce risks to the crew by avoiding the need to lug O_2 all the way from Earth's deep(er) gravitational well. And here's where the 'Mars Oxygen In Situ Resource Utilisation Experiment' known affectionately as 'MOXIE' (Figure 1A) (Meyen *et al.*, 2016) comes in. It is the combined brainchild of the Massachusetts Institute of Technology and NASA, and a technological descendant to the 'oxygenator' used by Mark Watney in Andy Weir's Hollywood movie, The Martian. Dubbed the 'mechanical tree', this golden box no bigger than a car battery was shipped aboard NASA's Perseverance rover (that was also the first to give us sound on Mars!). This time last year, it managed to wring out 5.37 g of O_2 for the first time on Mars; only enough to sustain ~10 min worth of an astronaut's pedestrian activity, yet proof-of-concept support for the technology. Now there's a race on to further improve O_2 extraction efficiency not only from the atmosphere but also from ice and rock through the tweaking of electrocatalysts including perchlorate brine electrolysis of Martian regolith (Gayen *et al.*, 2020) and alternative approaches focused on 'plasma'-driven electro- and photo-catalytic technologies.

But there's still a long road ahead with the fine-tuning and upscaling of technologies required to supply sufficient O_2 to support human exploration of Mars. With Artemis missions, NASA will land the first woman and first person of colour on the Moon with an orbital outpost, while making sufficient O_2 to preserve human life and establishing the necessary infrastructure to travel into deep space. In support, up to 96 % of the O_2 locked up inside solid lunar regolith simulant was recently extracted via solid-state electrochemical reduction of metal oxides (Lomax *et al.*, 2020) (Figure 1B). Capitalising on this discovery, the European Space Agency through partnerships with industry, have just announced plans to build the first experimental payload that will crunch up moondust to make air on the Moon for our astronauts. An important first step towards the next giant leap for (wo)mankind, from the Moon to Mars. Per adua ad astra!

Author contributions

DMB conceived the idea and wrote the first draft of the manuscript with input from JDC. DMB edited and revised the manuscript. DMB and JDC approved the final version submitted for publication.

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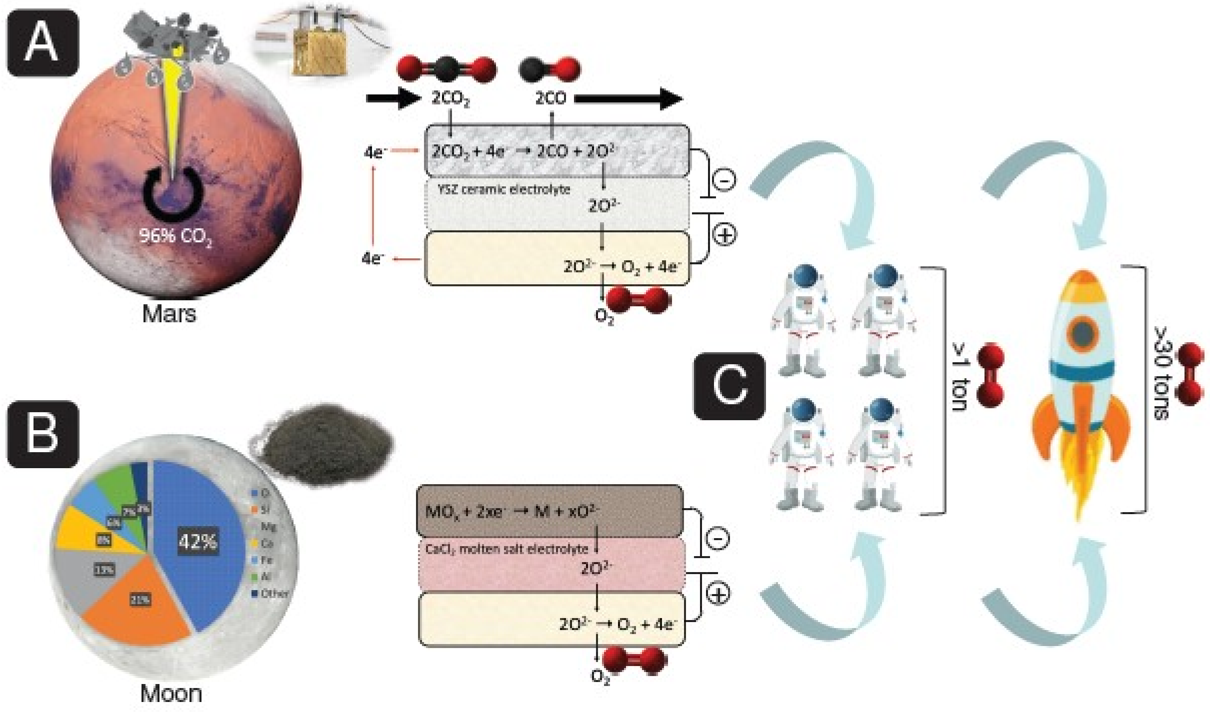

Figure 1. Man-made oxygen for life and lift-off

A. Carbon dioxide (CO_2) is the primary constituent gas in the Martian atmosphere. The Mars Oxygen In Situ Resource Utilisation Experiment (MOXIE) aboard NASA's Perseverance rover incorporates a custom-designed solid oxide electrolysis (SOXE) stack comprised of scandia-stabilised zirconia electrolytes with ceramic anodes and cermet (ceramic-metallic composite) cathodes. Since the atmosphere on Mars is almost ~167 times thinner than here on Earth, CO_2 is compressed before being fed to the electrolysis unit. Here it flows over the catalysed cathode under an applied electric potential prior to being electrolysed. Carbon monoxide (CO) is vented while oxygen ions are driven through the SOXE to the anode, where they are oxidised evolving breathable O_2 gas at a rate proportional to current ($\dot{n} = \frac{I}{4F}$) where I is SOXE stack current and F is Faraday's constant (96,485 Coulombs/mole of electrons). The O_2 yield is 1g per 2.75 g of CO_2 consumed (Meyen *et al.*, 2016). B. Oxygen is the most abundant element found in lunar regolith (40-45 % by mass) locked up as oxides taking the form of minerals and amorphous glass. Up to 96% of the O_2 can be extracted (from JSC-2A simulant, shown as powder inset) by direct electro-deoxidation via the Metalysis-Fray, Farthing, Chen (FFC)-Cambridge process using an O_2-evolving doped tin oxide anode. The metal oxide (MO_x) is reduced to the corresponding metal in molten salt with an O_2 yield of 42 wt% per kg of regolith simulant. C. The O_2 needs for a sojourn to Mars are substantial to support human respiration and as propellant for the return trip home. Assuming basal oxygen consumption of 0.316 $L.min^{-1}$ for a 1.90 m tall astronaut (Scott *et al.*, 2020), this would equate to 664, 358 L (crew of 4 astronauts over a year) or 29,659 moles O_2 (664, 358 L × 1/22.4 L) equivalent to 949 kg of O_2 (molar mass of O_2 = 32 g). Note that these are conservative estimates and do not include the additional energetic demands of being more physically active due to work and/or training. A recent estimate, albeit not underpinned by any supporting calculations, indicates that each crewmember (assuming an average body mass of 82 kg) will require 0.89 kg/day of O_2 (Ewert & Stromgren, 2019) (compared to 0.65 kg/day using the above basal calculation). This would translate into ~37% greater mass of O_2 required (0.89/0.65 × 949 = 1,299 kg of O_2). More than 30 tons of (liquid) O_2 will be required as propellant assuming it represents ~78% by mass in a methane/O_2 propulsion system (Hecht & Hoffman, 2016). These calculations highlight the importance, if not indeed obligatory requirement, for In Situ Resource Utilisation for a return trip to Mars, with the capacity to save tens of billions of pounds.