

# Reactive Oxygen Species (ROS) detection in planetary regoliths, soils and ices with the OxR device

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## Abstract

Human presence on Moon and Mars requires oxygen gas production and healthy living conditions. O<sub>2</sub> may exist in regoliths of solar bodies as Reactive Oxygen Species (ROS). We propose a device (OxR, Oxygen Release), that indirectly measures ROS (superoxide radical, O<sub>2</sub><sup>•</sup>, and peroxides, O<sub>2</sub><sup>2-</sup>) by quantitatively measuring released O<sub>2</sub> by their conversion. A larger version of the OxR can sustainably extract O<sub>2</sub> gas, since ROS are expected to continuously form due to cosmic radiation ('Oxygen farming' concept). Other health-toxic ROS such as hydroxyl radical, •OH, can be also measured. The OxR device will be used to select the least toxic sites for the astronauts, and guide where organic markers of extraterrestrial life potentially exist on other planetary and icy worlds.

## 1. Introduction

Intense irradiation of planetary surfaces from the Sun's UV rays and from cosmic rays, as well as from the fine fracturing of minerals when bombarded by micrometeorites, is a continuous process that induces the formation of Reactive Oxygen Species (ROS). Mineral ROS can be present as metal combinations of superoxides (O<sub>2</sub><sup>•</sup>), such as KO<sub>2</sub> and NaO<sub>2</sub>, and peroxides (O<sub>2</sub><sup>2-</sup>), such as Na<sub>2</sub>O<sub>2</sub>, K<sub>2</sub>O<sub>2</sub>, MgO<sub>2</sub>, and CaO<sub>2</sub>. All release H<sub>2</sub>O<sub>2</sub> upon H<sub>2</sub>O-wetting combined with certain metal catalysis. Hydroxyl radicals (•OH) also belong to this group of ROS chemicals, and can be released upon H<sub>2</sub>O-wetting of the planetary soils or regoliths.

The oxygen release has been firstly observed to exist in the Martian soils during the Viking Label release biological experiment. This oxygen gas is now attributed to an abiotic process that is caused by the presence of ROS in the regolith materials, and not from putative microorganisms in the Martian soil [1]. Experiments on desert soils from Atacama show that ROS can be produced by photochemical reactions from the Sun's light [2]. Perchlorate salts, now known to be present on Mars, also a result of the same physical phenomenon [3].

The existence of ROS species in planetary soils and regoliths is proposed to be used as an indication of the absence of biosignatures in the surface soils of planets. This is because ROS are highly reactive with organics, disintegrating them and destroying any evidence of a biosignature, given they are extremely toxic to the organisms. This necessity justifies additionally the construction of a miniaturised oxygen release detection device (OxR) which can detect ROS in planetary soils and regoliths, as well as ices. Consequently, soils with ROS are not appropriate samples to search for life or its traces, and it also constitutes a strong selection condition of whether to collect a sample, for such purpose, in sample return missions, such as NASA's Mars 2020.

Furthermore, the scaling up of such an OxR device and its incorporation on a robotic vehicle, could be used to scavenge the oxygen gas induced release from regoliths that are rich in ROS. To achieve oxygen gas volumes that can support respiration of astronauts for a full working day, the utilisation and processing of a larger volume of soil is required. It

is estimated that this is possible when processing the top cm of soil from an area of a hectare of the Martian surface. The lunar surface is expected to be more efficient in oxygen production, but we do not have enough data to proceed to any estimations, therefore simulant soils must be prepared.

The same area can be utilised at regular intervals, most possibly for ever. This is because the processed soil can be immediately released at the same areas, and reactivated by the sun's rays and cosmic rays, allowing its continuous processing. This introduces the concept of 'oxygen farming', a novel concept for ensuring the human presence on other solar bodies. Further to using the oxygen for respiration, bigger installations might allow the production of oxygen gas in higher volumes, which can be used as fuel. The whole process is of very low energy consumption, which might be covered with solar panels. Parallel process of large areas might cover all the oxygen requirements of a small community of astronaut workers.

## 2. Reactive Oxygen Species (ROS) in the Solar System

On Earth, the production of ROS in soils is typically associated with the relatively high abundance of O<sub>2</sub> in the atmosphere [2]. However, in other solar system environments, or space environments beyond our solar system, where gaseous O<sub>2</sub> exists only in trace amounts (e.g., on Mars [4], Earth's Moon [5],[6], Europa [7], Saturn's rings [8], and interstellar clouds [9]), or even in planetary environments lacking gaseous O<sub>2</sub>, still ROS can be produced by many well-known natural processes. For example, in environments containing H<sub>2</sub>O, CO and/or CO<sub>2</sub> [10] and on the Moon (presumably on Mars as well), ROS can be generated by the interaction of H<sub>2</sub>O ice with cosmic rays [11].

When ·OH is considered, experiments indicate that Lunar (and presumably Martian) dust can generate it via the Fenton reaction. This is demonstrated on Lunar simulants [12] and on Fe-rich silicate minerals [13]. Additionally, freshly fractured Lunar regolith besides ·OH can produce large amounts of H<sub>2</sub>O<sub>2</sub> and other ROS [14], which are considered to play a crucial role in Lunar dust toxicity [15]. Although none of the curated Apollo mission Lunar samples exist in a state that fully preserves the reactive chemical surface aspects (i.e., ROS) that would be expected to be present on the lunar surface. For example, freshly ground Lunar soil has been shown to produce ·OH upon contact with H<sub>2</sub>O [16].

On Mars, reactive O<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>-</sup> can form through the release of ROS via scattering of CO<sub>2</sub> ions from solid surfaces. The produced oxygen is preferentially ionised by charge transfer from the surface over the predominant atomic oxygen product [10]. ROS (e.g., ·OH) may also be produced by Martian regolith via silicate abrasion during dust storms [17] (e.g., by mechano-radical production [18]). Moreover, silica fracturing generates surface free radicals such as -SiO<sub>2</sub>·, -SiO<sub>3</sub>· and -Si<sup>+</sup>-O<sub>2</sub><sup>-</sup> which can generate ·OH when in contact with H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> [19]. Silica dust toxicity has been verified on mammalian cells [20] and can pose serious health hazard to astronauts (e.g., upon inhalation) during future missions to Moon and Mars.

Beyond Moon and Mars, complex interactions between Saturn and its satellites Titan and Enceladus can cause the generation and transport of oxygen from the latter to the former [21],[24]. Ice water from Enceladus south polar plumes can be radiolytically oxidised to H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, by energetic particles from Saturn's radiation belts (mostly electrons). Such ROS emanating from this radiolytic gas-driven cryovolcanism can be continuously accumulated deep in the icy regolith [21]. Concurrently, H<sub>2</sub>O molecules escaping from Enceladus' plumes should be split by magnetospheric plasma (protons, H<sub>2</sub><sup>+</sup>, water group ions) into neutral and charged particles (O<sup>+</sup>), which can enter Titan's atmosphere and be captured by fullerenes (hollow carbon atom shell, e.g., of C<sub>60</sub>). Exogenic keV O<sup>+</sup> ions could become free oxygen within those fullerene aerosols, and eventually fall free onto Titan's surface. Such process could be driven by cosmic ray interactions with aerosols at all heights and can eventually drive pre-biotic chemistry [24]. It has been suggested that ice-covered worlds require an external source of oxidants to maintain biological viability [23]. Hand et al. [22], have proposed that oxidants produced by UV and ionizing radiation on the surface of icy worlds, such as Europa, can be carried down to the water column to react with reduced species to provide a source of redox energy [22].

## 3. The OxR device

### 3.1. The Viking biological experiment

The observation that the Viking Mars mission biological experiment released oxygen gas fully justifies the development of a sensor instrument to detect ROS. In 1976, the Viking Lander performed biological experiments designed to detect extant life in the Martian regolith. The reactivity of the Martian regolith was first indicated by the release of O<sub>2</sub> in the Gas Exchange Experiment (GEX), combined with possible life-driven decomposition of organics, contained in a culture media used in the Labelled Release (LR) experiment [25],[26],[27]. In the GEX, up to ~770 nmoles O<sub>2</sub> was produced from 1 cm<sup>-3</sup> regolith sample upon humidification or wetting. The persistence of O<sub>2</sub> release from samples that were heated to 145°C for 3 hrs and then cooled, prior to wetting or humidification, ruled out a biological explanation of the GEX results [28],[25].

In the Viking LR (Labelled Release) experiment, up to ~30 nmoles  $^{14}\text{C}$  labelled gas, presumed to be  $\text{CO}_2$ , was released after regolith samples ( $0.5\text{ cm}^{-3}$ ) were wetted with an aqueous solution containing  $^{14}\text{C}$ -labelled organics [29],[30]. The release of  $^{14}\text{C}$ -labelled gas in the LR experiment was eliminated by heating the sample to  $160^\circ\text{C}$  for 3 hrs and then cooling prior to the addition of the culture media with the labelled organics, an indication that  $^{14}\text{C}$ -labelled gas was derived from the nutrients upon contact with soil ROS. These results lead to the conclusion that the Martian surface material contains more than one type of reactive oxidants [25]. Metal salts of the ROS  $\text{O}_2^{\cdot-}$  were among the earliest proposed explanations for the thermally stable agent responsible for  $\text{O}_2$  release in the GEX. In the case of the LR experiment, peroxides were among the earliest explanations proposed for the thermally liable agent responsible for  $^{14}\text{CO}_2$  release.

In addition to the possible presence of metal salts of  $\text{O}_2^{\cdot-}$ , it has been proposed that  $\text{O}_2^{\cdot-}$  is generated on Martian dust and regolith surfaces by a UV-induced mechanism. This was based on the generation of  $\text{O}_2^{\cdot-}$  by UV-exposure of the regolith under simulated Mars atmosphere [31]. Such mechanism for  $\text{O}_2^{\cdot-}$  has also been shown with Mars analogue Mojave and Atacama Desert regolith [2].

### 3.2. Technology and design of the OxR device

The OxR device is a novel device, designed to be of small footprint and fully automated, which measures ROS in planetary soils and regoliths. It is a temperature- and pressure-controlled system that is based on microfluidic technologies, with reagent reconstitution and delivery parts [32]. Currently at Technology Readiness Level (TRL) 3 is built in the lab (Figure 1), but the intention is to reach TRL 4 or 5.

A main component of the device is the integrated solid-state optical sensing  $\text{O}_2$ -electrode with an ultralow detection limit (1 ppb) which measures the oxygen that is released and dissolved in the water after its reaction with the ROS that is present on the mineral surfaces of the soils. To investigate ROS in detail, we have used pure mineral powders and dusts of rock regolith simulants (i.e., anorthosites or basaltic powders), which we have synthesised and irradiated in the lab, and we plan to use Lunar meteorites and Lunar rocks. We have also implemented a spectrofluorometer sensor to measure  $\cdot\text{OH}$  concentration.

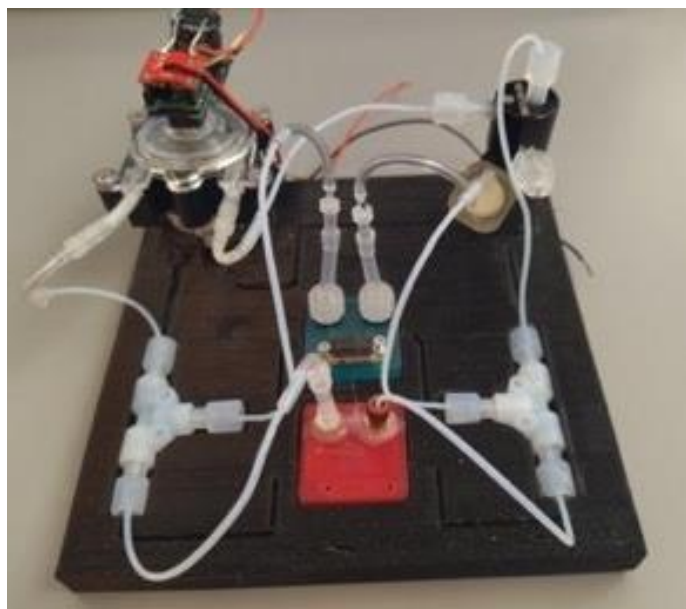


Figure 1: Test breadboard of the fluidic circuit made with 3D printing and with modified OEM devices and parts. A peristaltic pump on the top left, electronically controlled by the SuperModified® V3.0 controller from Zero One Mechatronics LTD, the sample holder on the top right with a filter to permit the soil powder to enter the fluidic circuit, and two micro-electro-valves (green and red in the middle) to isolate the first fluidic circuit for the first stage oxygen release and  $\cdot\text{OH}$  measurement, and the second fluidic circuit where the second release of oxygen will be measured.

The OxR device is also designed so that it can be used to identify ROS on other planetary and icy worlds, such as, Titan, Europa, Enceladus. Considering habilitation of Mars, the use of ROS will serve to identify soils for crop

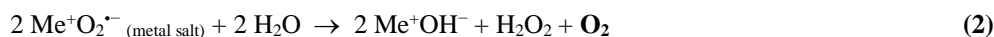
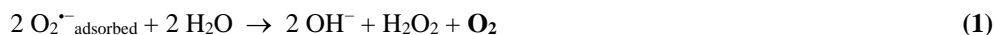
cultivation or to select areas where humans can settle down. Moreover, the OxR device can monitor in spaceships toxic ROS development that is induced by cosmic radiation on the metal frames/walls, or in the food and water storage tanks. Terrestrial applications again include agriculture, especially on arid or overcultivated areas, or those affected by climate change. ROS is very well known to exist in mining areas, since it is naturally produced on the surfaces of some minerals; it is toxic to employees and therefore it should be monitored.

### 3.3. Oxidant chemistry in soils

ROS can exist in diverse forms. In planetary and terrestrial regolith,  $O_2^{\cdot-}$  can exist as adsorbed ( $O_2^{\cdot-}_{ads}$ ) [2] or as metal (Me) salts ( $Me^+O_2^{\cdot-}$ ) such as  $KO_2$  and  $NaO_2$  [33], and as ionic complexes with metals ( $Me^{n+}-O_2^{\cdot-}$ ) of certain minerals and oxides [34],[35].

Metal peroxides can exist as salts of metals with  $O_2^{2-}$  bonding either as  $Me^{2+}O_2^{2-}$  (e.g.,  $CaO_2$ ,  $MgO_2$ ) or  $Me^+O_2^{2-}$  (e.g.,  $Na_2O_2$ ,  $K_2O_2$ ). Metal peroxides can also exist as hydroperoxides ( $MeO_2H$ ; e.g., of  $Ti^{4+}$ ,  $Zr^{4+}$ ,  $Ce^{4+}$ ) [36]. The presence of  $Mg^{2+}$ ,  $Ca^{2+}$ ,  $K^+$ ,  $Na^+$  ions on Lunar [37] and on Martian regolith (measured with the Phoenix Mars Lander Wet Chemistry Lab [38], [39], [40]), may provide the counter ions needed for stabilization as metal salts of  $O_2^{\cdot-}$ ,  $O_2^{2-}$ , and  $O_2H^{\cdot-}$  in the regolith.

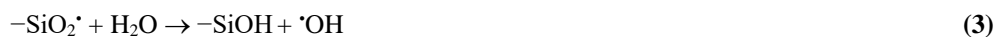
Examples of how metal salts of  $O_2^{\cdot-}$  or hydro/peroxides ( $O_2H^{\cdot-}/O_2^{2-}$ ) can undergo aqueous decomposition at neutral pH, releasing  $O_2$  and  $H_2O_2$ , are given in the following chemical equations:



Besides  $O_2^{\cdot-}$  generation on Martian dust and regolith surfaces by a UV-induced mechanism under simulated Martian atmosphere [31],  $O_2^{\cdot-}$ —together with  $H_2O_2$  and  $\cdot OH$ —is also generated by a photo-induced electron transfer with Mars analogue Mojave and Atacama Desert regolith [2]. Here, sunlight radiation-induced generation, by soils, of unpaired electrons that convert  $O_2$  to  $O_2^{\cdot-}$ , which can be initially adsorbed on the surface of soils and stabilized in the long term as metal  $O_2^{\cdot-}$  and  $O_2^{2-}$ . These, then, can be converted (via dismutation and hydrolysis, respectively) to  $H_2O_2$ , which can be converted subsequently to  $\cdot OH$  in the dark by reaction with reduced soil transition metals.

A second route of  $\cdot OH$  generation may involve a single electron abstraction from  $H_2O$  or  $OH^-$  released by photo-excited  $TiO_2$  [2]. Indeed, ROS can be also produced by photo-excitation of  $TiO_2$  and  $ZnO$ , oxides found on Moon and Mars, i.e., in [41] and [42], due to their small band-gap energies, which for  $TiO_2$  (rutile) it is 3.0 eV (or 413.3 nm), 3.3 eV (or 375.0 nm) for anatase [43], and for  $ZnO$  it is 3.1 (399.9 nm), 3.2 (387.5 nm), and 3.3 (375.7 nm) eV [44].

Another  $O_2^{\cdot-}$ ,  $H_2O_2$  and  $\cdot OH$  generation mechanism involves  $H_2O$ -wetting of  $\gamma$ -radiolysed perchlorate (in Martian soil salt analogues, under a  $CO_2$  atmosphere), which also generates oxychlorine species such as chlorite ( $ClO_2^-$ ). Subsequent  $ClO_2^-$  UV-photolysis generates—among other oxychlorine species—hypochlorite ( $ClO^-$ , e.g.,  $NaClO$ ), the UV-photolysis of which produces  $\cdot OH$  [3] with the involvement of  $H_2O$  or  $OH^-$ , and protonated superoxide radical  $HO_2^{\cdot}$ . Additionally, surface free radicals  $-SiO_2^{\cdot}$  and  $-Si^{\cdot}-O_2^{\cdot-}$  are known to be produced on fractured silica in the presence of oxygen, and they generate  $\cdot OH$  upon reaction with  $H_2O$  (and  $H_2O_2$ ) [19]. An example for the formation of free radical from fractured silica is given in the following chemical reaction:



Therefore, the measurement of released  $O_2$  can be used for the direct identification of the metal ROS  $O_2^{\cdot-}$  and  $O_2^{2-}$ , and of  $\cdot OH$ —an indirect inference of the presence of photo-excited/radiolysis-generated minerals. The necessary  $H_2O$  molecules for *in situ* generation of  $\cdot OH$  might be present in areas where ice (e.g., on Mars) can provide increased humidity levels.

### 3.4. Assays for regolith $O_2^{\cdot-}$ , $O_2^{2-}$ , $\cdot OH$

Given the poorly understood nature and distributions of ROS in Lunar and Martian regolith, there is a need for the development of flight instruments for their specific identification and quantification. The only flight instrument previously built for the non-specific, qualitative *in situ* determination of oxidants in general, was the Mars Oxidant Experiment (MOX) instrument [45] as the US contribution to the failed Soviet Union's Mars-96 mission. That

instrument would have exposed materials-sensors to the Martian regolith and monitored their reaction with oxidants over time. New developments allow the detection of ROS such as  $O_2^{\cdot-}$ ,  $O_2^{\cdot-}$ , and  $\cdot OH$  [46], [2], [3].

Assays are important chemical means to assist the above purpose. For  $O_2^{\cdot-}$  and  $O_2^{2-}$  we have previously developed an enzymic assay [3], which functions in two steps for oxygen release: (a) the superoxide dismutase (SOD)-catalysed dismutation of 1 mole  $O_2^{\cdot-}$  to  $\frac{1}{2}$  mole  $O_2$  and  $\frac{1}{2}$  mole  $H_2O_2$ , and (b) the catalase (CAT)-catalysed decomposition of 1 mole  $H_2O_2$  (formed by the first step-dismutated  $O_2^{\cdot-}$ , and/or by the inorganic hydro/peroxide hydrolysis reactions) to  $\frac{1}{2}$  mole  $O_2$ , which is measured as further increase of the first step  $O_2$  measure.

Complementing the extension of the enzymic to the inorganic assay, the inclusion of a non-fluorescent terephthalic acid (TPA) in the water, added in the first step, constitutes the simple assay procedure that will measure the fluorescent 2-OH-TPA generated by the reaction of  $\cdot OH$  with TPA. Specifically, the 1:1 stoichiometric reaction of  $\cdot OH$  with TPA produces 2-OH-TPA, which can be measured fluorometrically at excitation of 315 nm and induced fluorescence at 425 nm [2].

### 3.5. Steps of $O_2$ release from $O_2^{\cdot-}$ and $O_2^{2-}$ and their quantification, together with $\cdot OH$ , by the inorganic OxR assay

The first step for oxygen gas release involves mixing the regolith with water, which will dismutate  $O_2^{\cdot-}$  to  $O_2$  and  $H_2O_2$ . Concurrently,  $H_2O_2$  will be also released from the hydrolysis of any present metal  $O_2^{2-}$  (see reaction 1). Released  $O_2$  is recorded until a constant concentration plateau is reached. Inclusion of the  $\cdot OH$ -probe TPA (at 300  $\mu M$ ) as an aqueous solution will result in trapping the regolith generated  $\cdot OH$  as 2-OH-TPA, which is measured fluorometrically. As already mentioned, this measurement involves an excitation source at 315 nm, and induced fluorescence peaks at 425 nm.

The second step of oxygen gas release follows after the concentration of released  $O_2$  in the first step reaches a plateau. At that time, to the aqueous mixture the CAT-mimetic  $MnO_2$  is added (e.g., as suspended  $MnO_2$  nanoparticles), which will catalyse the conversion to  $O_2$  of the  $H_2O_2$  released earlier in the first step, as well as the  $H_2O_2$  released from the hydrolysis of peroxides. This last step is terminated when the released  $O_2$  also shows a plateau as dissolved oxygen into the water solution. Figure 2 details the two steps and the reactions taking place.

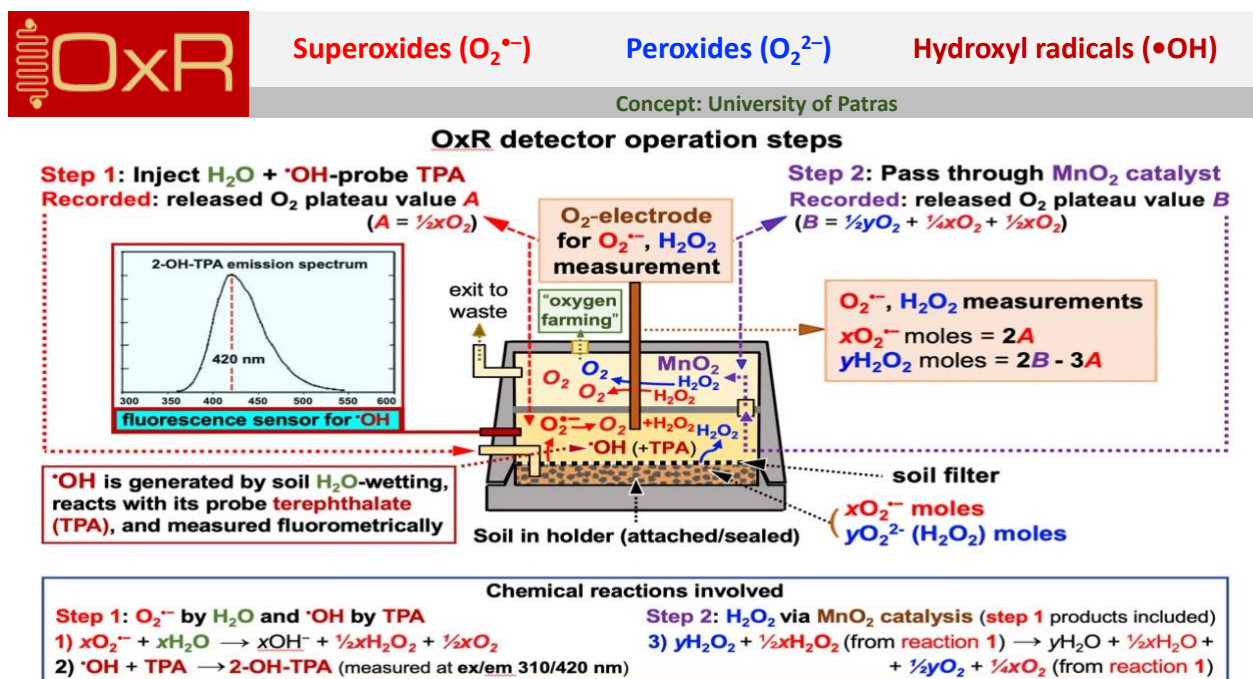


Figure 2: A graphic explaining in detail the chemical steps and measurement of the oxygen gas release and of the  $\cdot OH$  concentration.

#### 4. Moon and Mars regolith and soil simulants

The unavailability of real planetary samples to test and calibrate the instrument for quantitative O<sub>2</sub> and ROS concentration measurements justifies the development of regolith and dust simulants from terrestrial materials. The materials that can be used to perform the task include pure minerals, analogue terrestrial rocks, synthesised simulants, existing curated simulants, lunar meteorites, and returned samples of Lunar dusts (when provided upon request).

Simulants and analogue samples are of increasing importance in space exploration and space utilisation. Mimetic or analogue rocks with mineralogy, chemistry, texture, and other physical or geometrical properties which are similar to planetary regolith are the only resource to perform experiments prior to applying those when we land on a planet. They are also used to test analytical instruments or to calibrate their operation, to test mechanical and electronic parts of vehicles and of different devices, even to test the processes for ISRU purposes. During a mission, simulated (synthesized samples from natural terrestrial raw materials) or analogue samples (natural terrestrial samples that have been collected from certain areas of the Earth of similar petrological and geochemical environments) are frequently analysed by replica instruments to better predict the rock compositions on the explored planet. This is often done under simulated atmospheres, as well.

For this work, it is important to synthesise well-referenced Lunar and Martian simulants. Preparing the simulants in the lab, it allows full control of the constituent rocks or minerals. It is also important to start this evaluation by firstly controlling the ROS production on pure minerals or bulk rocks and estimate the efficiency of each of them. Then, the cumulative efficiency will be compared to the rock mixtures resulting from them.

It has been already mentioned that grinding and generally mechanical treatment of minerals leaves free bonds to their surfaces. Further activation can be performed by irradiation with UV lamps. To assess the potential of oxygen ISRU we have synthesised Lunar and Martian simulants with good figures of merit compared to the Apollo Lunar samples and the Martian Rocknest samples (Figure 3; manuscript under preparation).



Figure 3: The first Martian and Lunar simulants produced for evaluating the device.

Additional objectives require the repetitive reactivation of the powders in order to estimate the the number of cycles that reactivation can be performed, as well as the activation efficiency of each cycle. Other reasons to justify the synthesis of our own simulants include:

- Experiments must be performed on pure mineral phases, prior to the synthetic rocks that result from their mixing. It is pertinent that materials must be well-characterised and known as single, pure phases. Different minerals have different re-activation efficiencies in ROS and oxygen production; this is required to be



estimated.

- Simulant mixtures must be exactly known in the proportion of their mineral components. It is pertinent to investigate if the effect is additive, while assisting in the better prediction of other compositions that will be identified in the future. Acquisition of prepared commercial simulants are useful only for comparison and as reference materials.
- Precise knowledge of humidity and possible organic content of the samples is required.
- The atmospheric oxygen that is adsorbed on the surface of the mineral grains must be controlled, preferably reduced. Therefore, soil and regolith simulant preparation must be either performed in vacuum or in inert gases, in order to minimise background signal coming from adsorbed oxygen from the terrestrial atmosphere. Preliminary experiments have shown the significance of this objective.

## 5. ISRU of oxygen

### 5.1. Estimated oxygen production from Martian and Lunar regolith for developing human life support systems

According to the Viking life experiments [25], [26], [27], one cm<sup>3</sup> of Martian soil released 770 nmoles of oxygen gas. In normal terrestrial conditions (STP – Standard Temperature and Pressure) and according to the ideal gas equation, this corresponds to  $1.72 \times 10^{-5}$  litres of oxygen gas. Assuming that only the upper 1 cm of the regolith is scooped from the surface of Mars and processed, one hectare of area is expected to release **1724.8 litres** of O<sub>2(gas)</sub>, or about **8200 litres** of breathing air.

In addition to the released component discussed above, perchlorates (ClO<sub>4</sub><sup>-</sup>) can also constitute an additional source of oxygen release, adequate for human consumption [47]. It has been also estimated in that the daily consumption of oxygen for one astronaut per day is about **550 litres**, which can be released by microbial dissociation of 60 kg of Martian regolith [47]. The air respiration requirement of humans is generally difficult to estimate, but according to [48], the oxygen consumption, explicitly occurring in the human lungs, is measured to be in the order of 11 ml/min. This constitutes only 5% of the oxygen requirements of the full human body, thus, a human consumes **316.8 l/day** of oxygen gas. This is not too low compared to the previously mentioned value of 500 l/day for an astronaut, probably performing some work. This suggests that with the right life support technologies, we can produce oxygen that can support at least one Martian resident for a full day. These values are estimated, resulting from scavenging an area of one hectare and processing of about 1.5 tone of regolith. There is currently no estimate for the Moon.

Concluding, it is important to mention that the two above sources of oxygen are clean, providing ready to breath oxygen gas, and they do not alter the constitution of the regolith or leave behind toxic substances, passivating the soils from major toxic materials and allowing their use for agricultural and construction purposes.

### 5.2. Activation of regolith through irradiation

The combined long-term irradiation of the regolith (i.e., alpha particle irradiation, UV) over the ‘geological’ time has activated the materials in depths (bulk property) of several meters. Short-term irradiation, however, is rather a surface process, in the range of a few tenths of microns in a single full day of 24 hours and differs for the different materials, grain size, water content [49]. Therefore, oxygen production from the Lunar or Martian regolith mostly depends on the irradiation of a certain area for its re-activation, rather than the volume of the material in large depths. This requirement reduces significantly energy demand for excavation and transport of large masses of regolith. Concepts must be developed on how to perform ISRU, i.e., if the daily reshuffling of only the top surface layer of the regolith is required or another technology will be used (Figure 4).

The above descriptions and calculations suggest that simulants should be of high fidelity, that is, very close approximates of the planetary samples. The role of meteorites and their study, as well the role of a real Lunar regolith, are vital. Experiments have to be performed on pure minerals, and mineral mixtures, and be compared with natural materials, such as meteorites or Apollo lunar regolith.

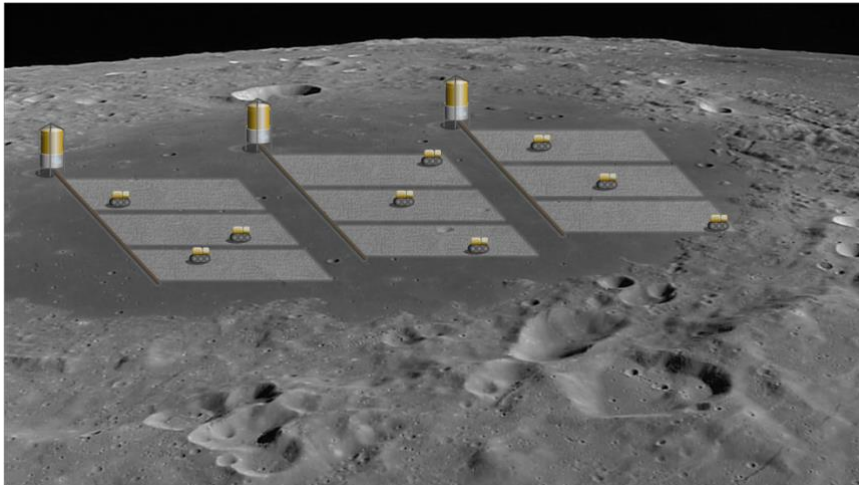


Figure 4: ISRU concept for oxygen gas ‘farming’.

## 6. Conclusions

This paper describes preliminary designs and concepts on a miniaturised, portable or wearable instrument that is capable of measuring Reactive Oxygen Species (ROS) from the oxygen gas they release when they react with water. These reactions occur instantly, without the need for an energy source. Multiple steps of these reactions not only produce additional volumes of oxygen, but they also recover the reacting water, significantly minimising its consumption. With the use of hypersensitive oxygen gas detectors, the required sample to perform a measurement is in the range of a couple of grams. Using specific assays,  $\cdot\text{OH}$  can be also measured, an additional toxic chemical present in the soils (terrestrial or extraterrestrial). The purpose of this instrument is to select planetary environments appropriate for settlements and other work activities, such as ISRU. Also important is that it can be used to identify soils and regolith that are appropriate for sampling and possibly sample return in missions that relate to the search of life, either as extant life or extinct through putative biosignatures. For example, the presence of ROS excludes these samples from further investigations because ROS are highly reactive and any life or any organic molecule is destroyed.

The sole production of ultra-pure oxygen gas during water-ROS reactions renders possible the concept of ‘oxygen farming’. According to this concept, the energetic radiation of the sun as well as the continuous fracturing of rocks due to micrometeorite impacts forms ROS on the upper layers of planetary soils, regoliths, and ices. By wetting these soils with water, oxygen gas is rapidly produced and can be scavenged. These soils can be redeposited on the surface again, and reactivated by the same natural mechanisms. Periodic processing of the same areas results in oxygen ISRU operations, which also demand extremely low energy consumption. It is envisaged that mobile vehicles with the appropriate large-scale OxR reactor and a storage chamber can periodically scan larger areas of the planetary surfaces and accumulate the released oxygen in appropriate chambers. First estimations come from the oxygen that is released and measured during the Viking life detection experiment, as well as from preliminary experiments. Both conclude that processing of the very first top cm layer of one hectare of the Martian surface, the oxygen that is produced can support at least one astronaut for a full day of operations. This process does not alter the soils in any way, or pollutes them, on the contrary it neutralises them from ROS (if further irradiation is precluded) making them compatible for possible agricultural purposes or to build settlements. These operations can apply also on Earth, for example in areas where mining or agricultural activities have been intense.

Currently, the device is at TRL level 3 (Technology Readiness Level), and through the OxR project it is aimed to achieve at least TRL 4 or 5 and be tested in the field.

## Disclaimer

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