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# X-ray fluorescence for Moon exploration and exploitation

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**Abstract**

X-ray Fluorescence (XRF) is a spectroscopic method that allows detection and measurements of the amount of any atoms heavier than Na. XRF spectrometers are used in wide range of application and are paramount instruments for planetary science since the beginning of space exploration. Improvements of detectors and electronics allowed to improve capabilities of such planetary instruments. Up to now, all the XRF space instruments have used radioisotopes sources as excitation sources. The only exception is the very last PIXL instrument sent on Mars by NASA on-board Perseverance, which uses an X-ray tube.

We propose to use XRF for three different instruments for the exploration and exploitation of the Moon.

The first instrument will be placed on a rover for geological survey; this instrument will used pyroelectric X-ray generator as an excitation source. We reached an energy resolution of 121.17 eV using a Silicon Drift Detector and we have reduced measurement fluctuation from 25.2% to 3.7% thanks to renormalization process. The current development of this first instrument has reached a Technology Readiness Level of 6 (full-scale model demonstration in relevant environment).

The second instrument will be used by astronauts in a handheld version and will use a miniature X-ray tube. The device will allow rapid sampling of rocks to allow the best choice of samples for earth return. The device will use machine learning and will present results on simple way to tell astronauts if a sample is worth collecting. The current Technology Readiness Level of this second instrument is 4 (Functional verification).

The third instrument will be used to monitor the Oxygen production unit from lunar regolith. Oxygen extraction is taking place using a method called molten salt electrolysis, involving placing regolith in a metal basket with molten calcium chloride salt to serve as an electrolyte, heated to 950°C. At this temperature, the regolith remains solid. But passing a current through it causes the oxygen to be extracted from the regolith and migrate across the salt to be collected at an anode. As a bonus, this process also converts the regolith into usable metal alloys. XRF will be used to follow the concentration of atoms involved in the process and therefore to monitor the oxygen production. The current TRL level of this third instrument is 3 (Proof of concept).

**Keywords:** X-ray, fluorescence, Pyroelectric, Oxygen, Moon, Geology

**Acronyms/Abbreviations**

EDXRF: Energy Dispersive X-Ray Fluorescence
FFC: Fray-Farthing-Chen-Cambridge Process
FWHM: Full Width Half Maximum
ISRU: In-Situ Resource Utilization
PXG: Pyroelectric X-ray generator
ROI: Region Of Interest
TRL: Technology Readiness Level
SDD: Silicon Drift Detector
XRF: X-Ray Fluorescence

## 1. Introduction

Portable X-ray fluorescence (XRF) spectrometers are used in wide range of application and are paramount instruments for planetary science since the beginning of space exploration. Improvements of detectors and electronics allowed to improve capabilities of such planetary instruments. We propose to use XRF for three different instruments. The first instrument will be placed on a rover for geological survey, the second one will used by astronauts in a handheld version and the third one will be used to monitor the Oxygen production unit from lunar regolith.

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The first and third one would use a pyroelectric X-ray generator (PXG) and the second one will use a miniature X-ray tube.

## 2. XRF rover instrument using PXG

Up to now, all the XRF space instruments have used radioisotopes sources as excitation sources. The only exception is the very last PIXL instrument sent on Mars by NASA on-board Perseverance, which uses an X-ray tube.

Because in space the weight and power consumption are critical parameters, we propose to use a lightweight PXG as X-ray excitation source for XRF process. The XRF photons are detected using a Silicon Drift Detector (SDD), custom electronic readout, special algorithm and renormalization process.

### *2.1 Pyroelectric X-ray generator*

A PXG consists of a pyroelectric crystal, a metallic target, and an electric heater (Fig.1). The spontaneous polarization of the pyroelectric crystal depending on temperature accelerates electrons to emit X-rays in a pressure of <1 Pa [1]. Crystal cooling provides X-rays emitted from the crystal due to positive electric polarization of -Z surface while the heating provides X-rays from the metallic target.

We have developed the PXG for X-ray sources of X-ray fluorescence analysis on the planetary surface [2–6]. The crystal with the metallic target combinations of a $LiNbO_3$ crystal with a Mo target and a $LiTaO_3$ with a Cu target will be employed for an effective XRF analysis of light elements such as Mg, Al, and Si, and relatively heavy elements such as Ca, Ti, and Fe, respectively [6]. Typical time profiles of temperature change and X-ray counts, and energy spectra obtained from the PXG with the Cu target are shown in Fig.2. An X-ray emission from the PXG is available as needed, which avoids an unnecessary exposure during developments as well as an X-ray tube. Comparing to an X-ray tube, the simple structure of PXG without a high voltage power supply allows to achieve characteristic features of a small size of TO-8 like metal package, a light weight of ~50 g and a low power consumption of ~1.0 W typically.

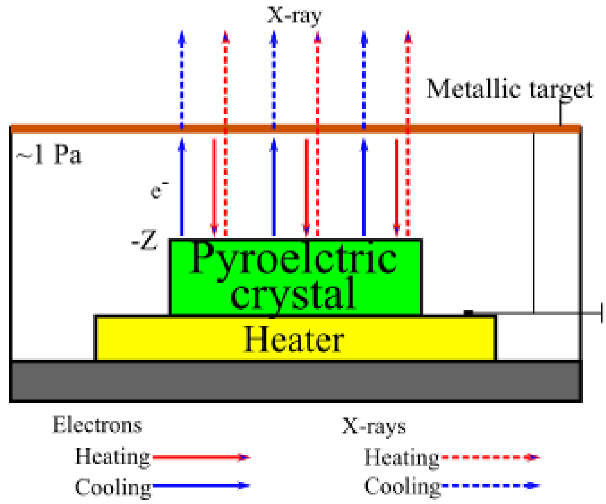


Fig. 1. Schematic drawing of the PXG.

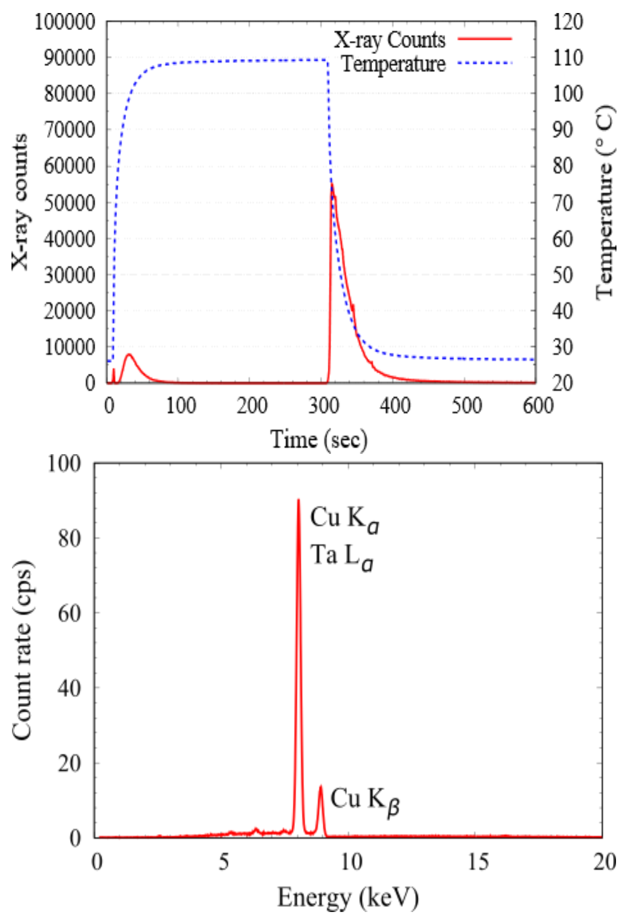


Fig. 2. (Upper) Typical time profiles of PXG X-ray count with temperature change. (Bottom) Typical PXG energy spectra. These results are obtained by the $LiTaO_3$ with the Cu target.

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*2.2 Electronic readout and data treatment*

XRF signals are detected by state-of-the-art semiconductor detector used in Energy Dispersive X-Ray Fluorescence (EDXRF): Silicon Drift Detector (SDD). The detector electronic readout is designed to meet space requirements: size reduction, weight, vacuum compatibility, radiation hardening… The current development is also an opportunity to improve energy resolution. The achieved resolution has been measured on the Full Width Half Maximum (FWHM) of the Mn $K_\alpha$ peak at 5.89 keV of a $^{55}Fe$ radioisotope source (Eckert & Ziegler Model IECB15940) with enclosure of the SDD thermalized at 10°C. The resolution measured is 121.17 eV [7].

In portable XRF, excitation source fluctuations, whatever the cause, can be an issue. As we are using pulsed PXG, variation within a pulse and inter-pulses variations are problematic. A process is introduced to monitor the total source emission during a measurement and normalize the measured spectrum for the total fluence of the source. The normalization factor is obtained by monitoring the fluorescence of a known reference sample in the field of view of the instrument. An Indium thin wire is used as reference to monitor the intensity of its $L_\alpha$ line at 3.28 keV. As anorthosite is representative of lunar soil, we used a pressed pellet anorthosite standard to do ten successive measurements using simultaneously two Amptek COOL-X PXG (one unmodified and one with Mo target instead of Cu). The intensity of the Ca $K_\alpha$ line at 3.69 keV of anorthosite sample was measured ten times during 12 minutes. The relative standard deviation of the ten measurements, using the two PXG sources simultaneously without renormalization was 25.2% and with normalization, it was reduced to 3.71%.

As our instrument will be used in space (i.e. Moon or Mars probe), a concern is about the peak's Region Of Interest (ROI) definitions. The ROI width can be affected by the thermal environment because temperature can affect SDD resolution [8]. Besides, induced space radiation aging of electronic components can also affect the position of the peak because radiation can modify the amplifiers' parameters [9] (i.e. gain). The peak's width of a given fluorescence line can also be modified due to radiation induced noise in electronic [10]. A peak search algorithm [11] is therefore used to define the best ROI for a given peak with a calibration. This could be implemented in flight with a filter wheel on-board the instrument. The wheel would have several reference samples that would be used to re-run the algorithm to optimize ROI even with aging instrument in space ionizing radiation environment. The wheel reference samples could be synthetic samples of anorthosite with increasing content of atoms of interest for lunar geology. The procedure is tested with samples of anorthosite with added amount of Mn (0.2%; 0.5%; 1%, 2% and 5%). The algorithm is used with renormalized spectrum as explained previously. The best ROI found with the algorithm has allowed to obtained a perfect linear calibration ($r^2=1$) as illustrated on Fig. 3. For higher concentration, a quadratic curve should be use to take into absorption or possible count reduction due to pileup.

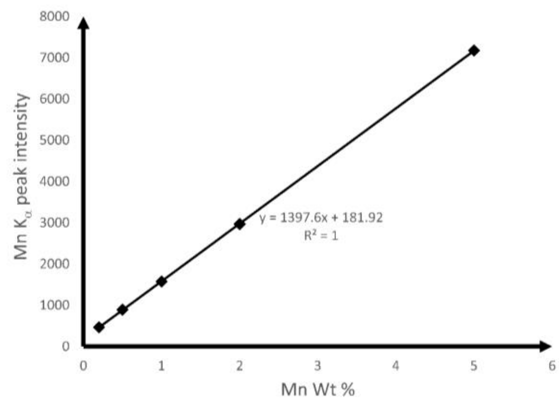


Fig. 3. XRF peak selection algorithm efficiency tested on anorthosite samples with increasing content of Mn

## 3. Handheld instruments for astronauts

For astronauts, the drawback of using a PXG is the measurement time. PXG excitation flux will induce measurement time of several minutes to achieve good measurement on low concentration sample. It would be difficult to ask astronaut to hand the instrument if front of a sample for several minutes. A solution could be to ask the astronauts to place the device on a holder and a leave it alone during the measurement but this would reduce the advantage of manned space mission Vs robotic mission. Thanks to their extensive training, astronauts will be more efficient at visually selecting rock to analyse and short measurement time would allow to improve productivity of manned mission. Therefore, we propose to build a version of the current instrument that would use a miniature X-ray tube as an excitation source. As X-ray tube have a far higher flux than PXG, the measurement time would be reduced to a few seconds. A handheld instrument of this type would allow astronauts to samples a lot of rocks. We have already [12] build a TRL 4 (functional verification on working prototype) version as illustrated on Fig. 4.

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Fig. 4. Handheld instrument with miniature X-ray tube

We still have to improve the technology level of the current handheld instrument using X-ray tube to meet space environment (size reduction, weight, vacuum compatibility, radiation hardening…), but the most important point to improve is the software (machine learning) and user interface for astronauts. Despite their extensive training, astronauts are not geologist and spectroscopist; a rough XRF spectrum will probably be useless for astronauts on the Moon. We must build a simple user interface to inform the astronauts if a given sample is worth bringing back to earth for detailed analysis. The device and its interface must also be suitable to be used with gloves of a spacesuit. Preliminary contacts have been established with ESA European Astronaut Centre (EAC) for a possible interface design and test.

## 4. In-Situ Resources Utilization (ISRU) process monitoring

For long-duration human exploration and habitation to be safe and sustainable, the extraction, refinement, and utilisation of local resources will be essential. Returning to the lunar surface and using it as a test bed to learn how to utilise off-Earth resources is currently a goal of many agencies and industrial players worldwide [13]. Lunar regolith is the most abundant and ubiquitous resource on the lunar surface and exists as a layer of unconsolidated rock, mineral and glass 3-10 metres thick across the entire lunar surface. This material contains approximately 40-45 wt% oxygen, which is a critical resource for life support and propellant. Additionally, many useful metals are present in significant quantities in lunar regolith, such as silicon, aluminium, and iron; the future refinement of these materials from the by-product of oxygen extraction processes presents an important opportunity to reduce the reliance on construction component materials from Earth.

As one of the most valuable and sought-after resources, various oxygen extraction methods have been proposed. Hydrogen and carbothermal reduction are the most well-researched of such processes [14]. Reduction of iron oxides with hydrogen requires temperatures of ~900 °C and utilises a low-risk solid-gas interaction, but only yields 2-3 wt.% oxygen and is heavily dependent on feedstock composition. Carbothermal reduction affords higher yields (10-20 wt.%) but requires temperatures of ~1600 °C and the handling of molten regolith. Similarly, molten regolith electrolysis requires high temperatures and the handling of molten regolith but presents the distinct advantage of higher oxygen yields and simultaneous production of iron-silicon alloys [15].

The Fray-Farthing-Chen (FFC)-Cambridge Process, invented in the late 1990s as a direct electrochemical method for producing titanium, has potential as an efficient process for the production of both oxygen and useful metals from lunar regolith. The lunar regolith is placed in a bath of molten calcium chloride salt at ~900 °C, and a current is passed through the system to extract the oxygen from the solid regolith material. In the terrestrial metallurgy industry, a carbon-based anode facilitates the removal of oxygen in the form of carbon dioxide and carbon monoxide. The use of an inert anode can produce oxygen directly, which would be important for a processing plant operating on the lunar surface. The cathodic and anodic processes are described in Fig. 5. In this process, the salt acts as a non-consumable supporting electrolyte. The FFC process has been demonstrated to be able to extract almost all of the oxygen within lunar regolith simulants, and has also been shown to be effective at temperatures well below 900 °C [16,17]

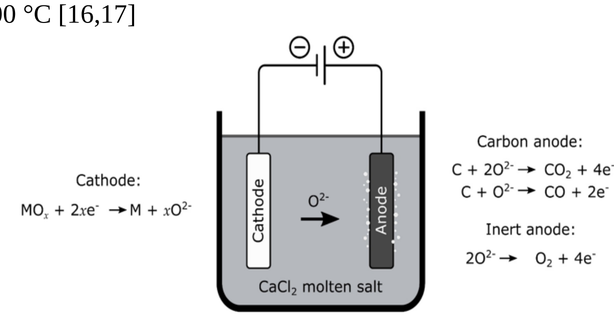


Fig. 5. A schematic of the FFC molten salt electrolysis.

Multiple payloads have been proposed to demonstrate ISRU processes on the lunar surface. Following these demonstration activities, pilot plants producing meaningful quantities of oxygen and metal are the likely next step. For any extractive process operating on the Moon, accurate monitoring and of the rate of extraction and product material formation will be essential. Assessment of the regolith feedstock prior to reduction will also be necessary to properly understand the influence that the unique material properties of lunar regolith may have on the process parameters.

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XRF instruments have been used to assess the chemical composition of regolith in multiple previous lunar and Martian missions. In the context of ISRU processes, it is a highly promising option for both the compositional analysis of the regolith starting material, and the compositional analysis of the semi-reduced or fully reduced metallic by-product. Fig. 6 shows the XRF signal (with renormalization and peak definition algorithm) Vs the content for Fe.

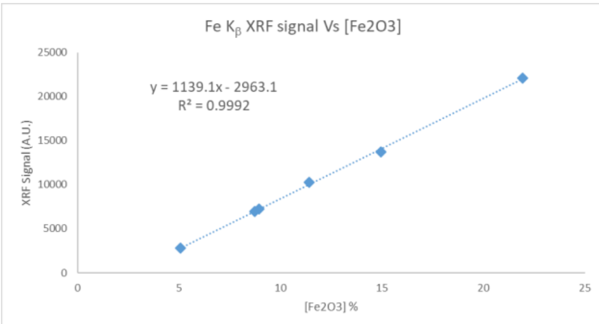


Fig. 6. XRF signal Vs $Fe_2O_3$ content

The same measurements have been done for other atoms and give the following correlation coefficients.

| Atom measured | Correlation coefficient $R^2$ |
|---|---|
| Fe | 0.9992 |
| Ca | 0.9768 |
| Ti | 0.9991 |
| Cr | 0.9975 |
| Al | 0.9929 |
| Mg | 0.9774 |

Assessment of the changes in peak intensity could also allow for the inference of reduction stage and oxygen content, thereby making XRF an interesting option for in-situ process monitoring. An example of lunar regolith simulant and the metallic product resulting from oxygen extraction via the FFC molten salt electrolysis process is shown in Figure 7, representing the range of material that will need to be accurately characterised in situ to allow for proper process monitoring.

Fig. 7. The metallic product (right) produced from lunar regolith (left, regolith simulant)

## 5. Conclusions

State-of-the-art X-ray detector, adapted electronic readout, renormalization procedure and software treatment allow lightweight accurate EDXF instrument with world record energy resolution for planetary exploration (manned or robotic geological survey) and exploitation (In-Situ Resources Utilization).
allow for proper process monitoring.

## 6. Acknowledgement

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