Development of an ultra-miniaturised XRD/XRF instrument for the in situ mineralogical and chemical analysis of planetary soils and rocks: implication for archaeometry

Article *in* Rendiconti Lincei. Scienze Fisiche e Naturali · October 2015

DOI: 10.1007/s12210-015-0477-3

CITATIONS
2

READS
239

17 authors, including:

Lucia Marinangeli
Università degli Studi G. d'Annunzio Chieti e Pescara
218 PUBLICATIONS **2,562** CITATIONS
SEE PROFILE

Loredana Pompilio
Università degli Studi G. d'Annunzio Chieti e Pescara
52 PUBLICATIONS **227** CITATIONS
SEE PROFILE

A. Baliva
Università degli Studi G. d'Annunzio Chieti e Pescara
40 PUBLICATIONS **503** CITATIONS
SEE PROFILE

Sergio Billotta
National Institute of Astrophysics
24 PUBLICATIONS **196** CITATIONS
SEE PROFILE

Rend. Fis. Acc. Lincei
DOI 10.1007/s12210-015-0477-3

GEOSCIENCES AND CULTURAL HERITAGE

Development of an ultra-miniaturised XRD/XRF instrument for the in situ mineralogical and chemical analysis of planetary soils and rocks: implication for archaeometry

Lucia Marinangeli[1] · Loredana Pompilio[1] · Anonio Baliva[1] · Sergio Billotta[2] · Giovanni Bonanno[2] · Maria Chiara Domeneghetti[3] · Anna Maria Fioretti[4] · Oliva Menozzi[1] · Fabrizio Nestola[5] · Eugenio Piluso[6] · Monica Pondrelli[7] · Vasco La Salvia[1] · Maria Carla Somma[1] · Fabio Tateo[4] · Paolo Petrinca[8] · Carlo Di Giulio[8] · Anna Chiara Tangari[1]

Received: 12 January 2015 / Accepted: 14 September 2015

Abstract An ultra-miniaturised (mass 1.5 kg; volume $\sim 22 \times 6 \times 12$ cm^3) instrument which combines X-ray diffraction and fluorescence has been developed for the mineralogical and chemical characterization of Martian soils/rocks and was included in the ExoMars-Pasteur payload. The simultaneous in situ acquisition of elemental and mineralogical information would significantly improve any robotic missions and may unravel doubtful points regarding the mantle composition, crustal evolution and resource potential. The instrument employs a fixed reflection geometry to fulfil the diffraction principle which can be applied to unprepared sample as well. The instrument basically consists of a radioisotope as source of X-rays and a CCD-based detection system. This is the first successful diffraction experiment using a radioisotope since the early tests in the 60s. For terrestrial application the radioisotope can be easily replaced with a cathodic tube. The reduced dimension as well as the possibility to perform non-destructive analysis makes it suitable for terrestrial applications, particularly in the archaeometry field. We are envisaging an X-ray tomographer to map the mineralogical and elemental composition of an artefact (i.e., painting, pottery) directly on the object without sample preparation. Nowadays, X-ray radiography or computer tomography are becoming standard techniques widely used and accepted by art historians, archaeologists, curators and conservators as these methods enable information about the manufacturing process and the condition of an object without touching the artefact or even taking original sample material.

Keywords Planetary instrument · Mineralogy · Diffraction · Fluorescence · Archaeometry

This contribution deals with topics considered in the session, "Archaeometry and cultural heritage: the contribution of geosciences" held during the conference "The future of the Italian geosciences, the Italian geosciences of the future", organized by the Società Geologica Italiana and the Società Italiana di Mineralogia e Petrologia, Milano, 10–12 Sept, 2014.

✉ Lucia Marinangeli
lucia.marinangeli@unich.it

[1] DiSPUTer, Università G. d'Annunzio, VIA dei Vestini 31, 66013 Chieti, Italy

[2] INAF-Osservatorio Astrofisico di Catania, Via Santa Sofia, 78, 95123 Catania, Italy

[3] Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, Via Ferrata 1, 27100 Pavia, Italy

[4] CNR - Istituto di Geoscienze e Georisorse, Via G. Gradenigo 6, 35131 Padua, Italy

[5] Dipartimento di Geoscienze, Università di Padova, Via Gradenigo 6, 35131 Padua, Italy

[6] Dipartimento di Biologia, Ecologia e Scienze della Terra (DIBEST), Università della Calabria, Via Pietro Bucci, 87036 Arcavacata Di Rende (CS), Italy

[7] IRSPS-Università G. d'Annunzio, Viale Pindaro 42, 65127 Pescara, Italy

[8] OMICA srl, Via P.G.A. Filippini 144, 00144 Rome, Italy

1 Introduction

The search for life inside and outside our solar system has fostered the interest of a growing scientific community around the investigation of space. As a consequence, a large variety of instruments have been proposed and developed so far, to acquire all the information required to address this problem. Nevertheless, the search for life passes through the unambiguous assessment of the existence of prolonged periods of standing water (or at least

Published online: 27 October 2015

other fluids) at the surface or in the subsurface. At the present, we have no evidence of liquid water occurring at the surfaces of terrestrial planets in our solar system. However, many geomorphological evidences suggest that the occurrence of standing water bodies has characterized at least part of the history of Mars, thus encouraging us to pursue the goal of finding signatures of past life in the Martian environment. In order to have an understanding of the processes that occurred at the Martian surface and were responsible for its evolution, the scientific research must unravel several physical parameters at the landing site, as the chemical composition of the surface and subsurface. This requirement is critical to have an understanding of both the past environmental conditions and the processes that modified the original conditions. In addition, having an understanding of the composition of Mars will certainly improve our knowledge of the origin and evolution of the whole solar system.

The role of composition, in terms of chemistry and mineralogy of the surface and subsurface, is fundamental to develop further assumptions on the evolution of the present Martian environments. Therefore, several investigations, both from remote and in situ observations, have been carried out so far. However, one of the most promising technique for assessing the mineralogical and chemical composition of the rocks, the XRD (X-rays diffraction)/XRF (X-rays fluorescence) spectroscopy, has been implemented only in the last NASA rover Curiosity mission (Blake et al. 2012; Bish et al. 2014; Vaniman et al. 2014).

The X-ray diffractometer (XRD) is the routine instrument used in every earth science laboratory to provide the mineralogical composition of rocks. XRD produces unequivocal results because it is based on the recognition of the geometrical properties of the crystal lattice. This kind of investigation is an extremely useful tool to define the textural and petro-mineralogic characteristics of rocks and soils during in situ investigation.

X-ray diffraction technique in various geometrical configurations (relative to source-sample-detector positions) is often used in laboratories for textural, petrographic, mineralogical and physical–chemical purposes on various types of crystalline materials such as powders, single crystals or thin sheets. The different geometrical configurations to obtain Bragg's diffraction are justified by the large number of applications and resolutions required.

These data can be integrated with those simultaneously obtained by elemental analysis (XRF), to determine the exact chemistry of rock components and to add constraints for quantitative mineralogical analyses. The XRD and XRF data can be acquired simultaneously by the instrument and separated trough appropriate software instructions.

In the frame of the ESA ExoMars mission, an innovative and advanced concept of combined XRD and XRF instrument has been developed (Marinangeli et al. 2007) and gathers the experience achieved in Europe for the design miniaturisation in the space industries. The instrument prototype consists of a radioisotope (^{55}Fe) as source of X-rays, a collimator and a CCD-based detection system. The instrument is built following a fixed reflection geometry to minimize the sample handling or to allow non-destructive analyses.

The numerous archaeometric analysis which have been used till today both for scientific research and for diagnostic purposes are mostly invasive methodologies and needs quite complicated protocols, mainly because of the choice of representative samples. The main protocols have mostly a petrographic approach, through thin section analysis, which are at the moment used in combination with chemical and/or mineralogical analyses (EDS analysis, SEM, XRD and so on), involving very different labs and specialists, often not integrating the data and mainly giving results aiming at research but not suitable for direct diagnostic purposes.

With the increasing issues concerning a proper conservation and valorization of the archaeological heritage in Italy and throughout the Mediterranean Basin, it is now necessary to plan a more integrated non-invasive methodology, allowing different typologies of analysis closely useful both for diagnostic and research purposes. Such approach could support not only the archaeologists and the geo-archaeologists, but also restorers, architects, project managers of the cultural heritage. The interaction among geologists, archaeologists, geo-archaeologists, architects and restorers in using this new technique guarantees a high quality of this multidisciplinary project, as well as a wider context of fields of application.

The close collaboration with archaeologists working in Italy, as well as in Egypt, Libya, Albania, France and Cyprus, also provides a wide range of sample cases, as well as a complete view of the archaeological finds and monuments which could be suitable for the analysis using the prototype, also allowing the possibility to understand the costs in each typology of sample case of application.

Several attempts to make portable XRD/XRF instruments for archaeometry have been pursued in the last decade; Nakai and Abe (2012) provide a detailed description of different apparatus and highlight the main strengths of this combined technique in the archaeometry field. An important Italian effort in developing an XRD/XRF instrument has been described by Pifferi et al. (2009) and Plescia and Ingo (2005).

We present the main findings of our space prototype development, MARS-XRD, and the potential future development for in situ non-destructive archaeometry.

1.1 The MARS-XRD space prototype

The MARS-XRD prototype was built in 2006 under the European Space Agency (ESA) ExoMars project (Vago et al. 2013) and further grant of the Italian Space Agency (ASI). The prototype consists of an X-ray source that irradiates the surface of the specimen and a detection system placed on a circumference (radius 12 cm) at the other side of the specimen where it "sees" the irradiated surface (Fig. 1). The configuration chosen for MARS-XRD is a fixed reflection mode which provides enough versatility and robustness to be easy applicable for in situ analysis even without sample preparation. Technical information on the prototype are shown in Table 1.

The industrial phase based on ESA funding was concluded at the beginning of 2007 and allowed the development of the first prototype based on the MARS-XRD concept (Marinangeli et al. 2007). The team included the University of Leicester for the detector development and the Technical University of Delft for scientific support while the overall instrument design, assembly and integration were under the responsibility of Thales Alenia Space Italia in Milan.

The design of the MARS-XRD breadboard follows a reflection configuration concept defined on the relative source-sample-detector positions and consists of the following main subsystems (Fig. 2):

- A collimator holding a ^{55}Fe capsule as source of X-rays;
- A sample-holder;
- A detector chamber containing n.4 E2 V 42-10 CCDs arranged along a curved ceramic structure of 12 cm radius.

The incoming beam has been collimated with a slit placed at 6 cm from the emitting surface of the source, while a 3 mm pinhole was placed in front of the source (Fig. 3). Further evaluation on the optimization of the collimation system has been performed by Pelliciari et al. (2011) and the new system is under implementation in the prototype.

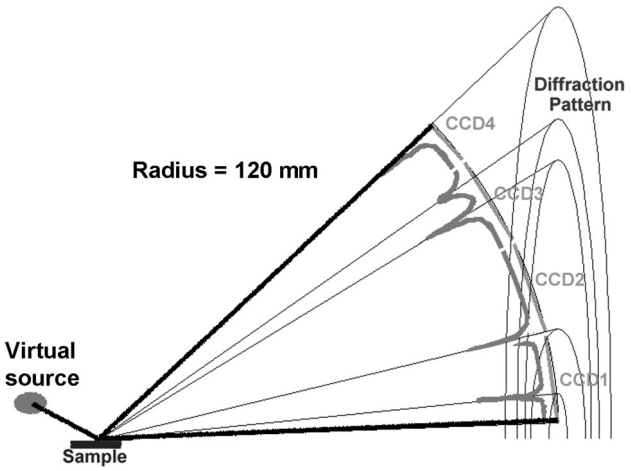

Fig. 1 Concept design of the reflection geometry used for the prototype

The CCDs array is mounted on a Shapal ceramic support, thermally controlled by a multistage Peltier cell (Fig. 4) and encapsulated in an Al chamber maintained under vacuum condition. The cooling system requires a water circuit at 15 °C controlled by a minichiller to assure a working nominal temperature of the CCDs at −50 °C for an optimal S/N ratio.

All subsystems were mounted on translators to maintain a high level of flexibility to adjust the optimum geometrical configuration based on the type of analysed sample.

The ground support equipment also includes the following:

- the main electronics board;
- a PC with software tool for commanding, data visualisation and processing;
- power supplies;
- a vacuum pump;
- a mini-chiller to cool the CCD array.

A few attempts to use an X-ray emitting radionuclide were performed in the late '60s (Preuss et al. 1966, 1967; Bugenis et al. 1968). This experiment was accomplished using a ^{55}Fe source and the capability to obtain diffraction patterns from mineral species has been fully demonstrated. However, due to the lower photon flux emitted by the radionuclide compared to X-ray tubes, this experiment did not meet the requirements for further commercialization and was discontinued. The proven capability of ^{55}Fe to produce diffraction patterns and its high level of monochromatism justifies the selection of this radionuclide as X-ray source for the prototype.

The source has been chosen as result of a trade-off performed analysing the following parameters:

- level of monochromatism—required to obtain a clean diffraction pattern;
- end of life (EOL) flux—which should be compatible with the mission time schedule to assure an appropriate EOL flux during operation;
- energy of emitted radiation;
- acceptable resolving resolution—based on the capabilities to discriminate the number of diffracted peaks of quartz contained in the selected 2-theta range for given wavelength, compared to the lab reference (Cu Kα radiation);
- environmental protection—to avoid contamination in the working environment; thus the short half-life isotopes are preferred.

Table 1 Main parameters of the MARS-XRD prototype

Parameter	Values	Notes
X-ray source	^{55}Fe isotope activity: 2.96 GBq certified emission (June 2006): 36.7E06 $^{s-1}$ × steradian $-^{1}$	Ka emission corresponding to Mn wavelength; supplier QSA-Global
Detector	n. 4 CCD e2v 42-10 active areas: 27.6 × 3.5 mm^2 pixel size: 13 micron	CCDs mounted on a circular ceramic structure of 12 cm radius
Energy resolution	~20 eV	
Measured 2θ range	6–68	
Incoming beam external slit	0.7 × 6 mm	
Collimator length	60 mm	Distance from source emitting surface to external slit
Distance slit-sample	25 mm	
Spot size on sample surface	~20 × 15 mm	

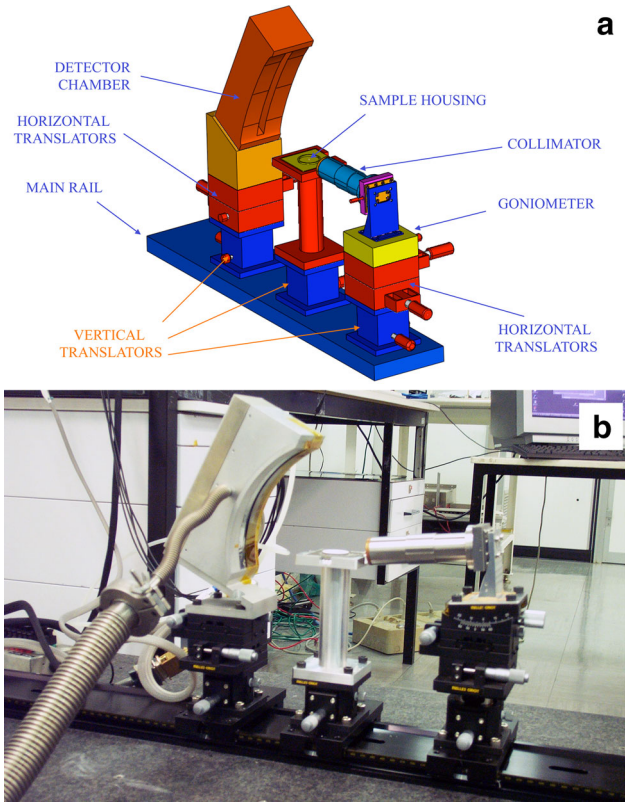

Fig. 2 From design to hardware **a** mechanical design of the main sub-systems; **b** close view of the prototype with the main subsystems: detector chamber (*left*), sample holder (*centre*) and collimated source (*right*)

For planetary exploration purposes as well as in situ open site analyses, the limitation of power resources is a rather critical issue and thus, the use of a self-emitting X-ray source would result in significant power savings. Though this issue is also important for the terrestrial application in terms of portability and miniaturisation, the radioactive power source can be easily replaced with a small cathodic tube. This replacement would not strongly modify either the acquisition chain or the data processing.

A major result of the MARS-XRD breadboard (BB) development and evaluation regards the innovative geometrical arrangement of the instrument and the use of a curved detection system that substitutes the typical goniometer movement of the detector in lab instruments. The breadboard has been evaluated to assess the best XRD configuration for the flight model to test the data handling procedure and the scientific capabilities.

Figure 5 shows the typical geometrical arrangement used for the analysis.

The MARS-XRD breadboard fully demonstrates the feasibility of simultaneous acquisition of fluorescence and diffraction spectra. This makes an instrument like MARS-XRD a complete instrument for in situ rock analysis because it can provide both the mineralogical and the chemical composition of a sample.

The fluorescence spectrum is acquired simultaneously with the diffraction pattern, displayed on the monitor in real time during the analysis and saved as separate files. The spectrum is acquired for each CCD at the same time. It should be considered that the use of the ^{55}Fe wavelength (2.1 Å) produces a systematic broadening of the diffraction peak compared to the Cu wavelength (1.54 Å) commonly used in the lab equipments. The broadening related to the wavelength, affects negatively the real angular resolution of the acquired patterns with MARS-XRD prototype.

A complete measurement cycle consists in the acquisition and integration of data for several hours. XRF and XRD data are acquired simultaneously and the separation of the two types of information is achieved via software. The instrument is able to analyse samples as fine powders or pristine surface with a clean and smooth cut. The latter option is applicable to analyse paintings or ceramics without sample preparation. A number of measurements have been acquired on soils/rocks and compared with

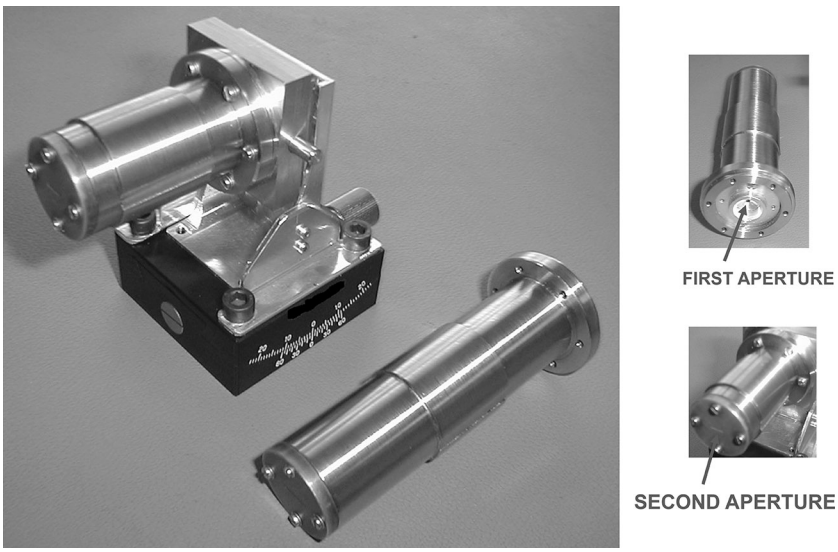

Fig. 3 Details of the collimator used for the prototype testing

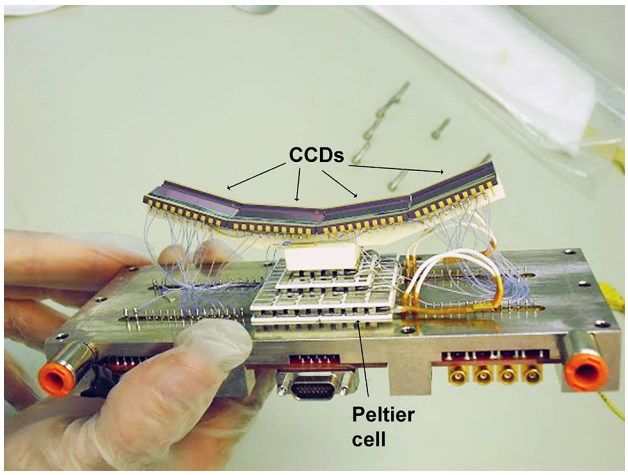

Fig. 4 CCDs array of the detector chamber

measurements acquired using standard commercial instruments to define the instrument detection limits and accuracy. Further tests on pottery as well as a field demo are planned in the next future.

Figure 6 shows a comparison of a XRD pattern of a basalt standard (SRM688) acquired with a lab instrument and the prototype, as well as an XRF spectrum acquired with the prototype. The standard was provided already as fine powder. We did not use the same prepared sample for both analyses; thus there may also be some differences in the XRD pattern due to the different orientation of minerals. The SIEMENS D5000 lab instrument mounted a 1-mm slit either for the incoming and outcoming beam. The prototype was set in the configuration shown in Table 1 and Fig. 5. The duration of the analysis was

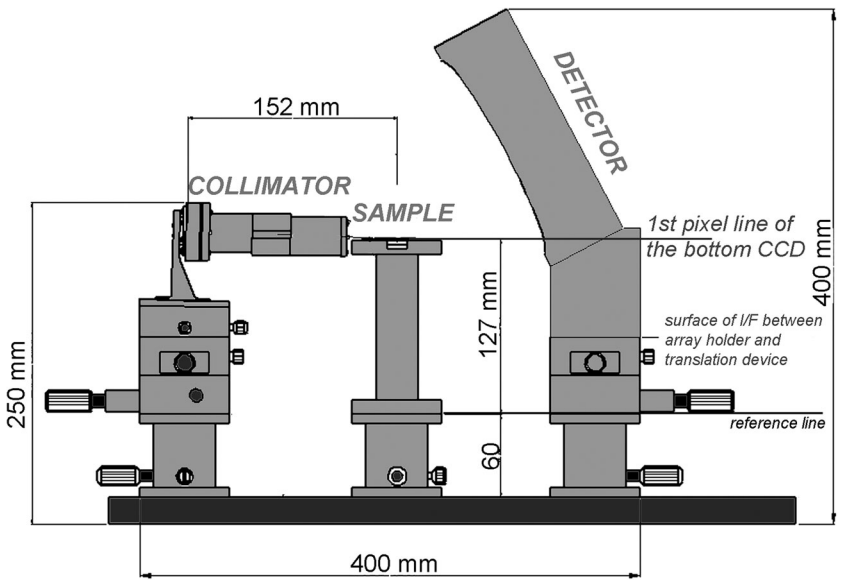

Fig. 5 The geometrical set-up used during the experiment

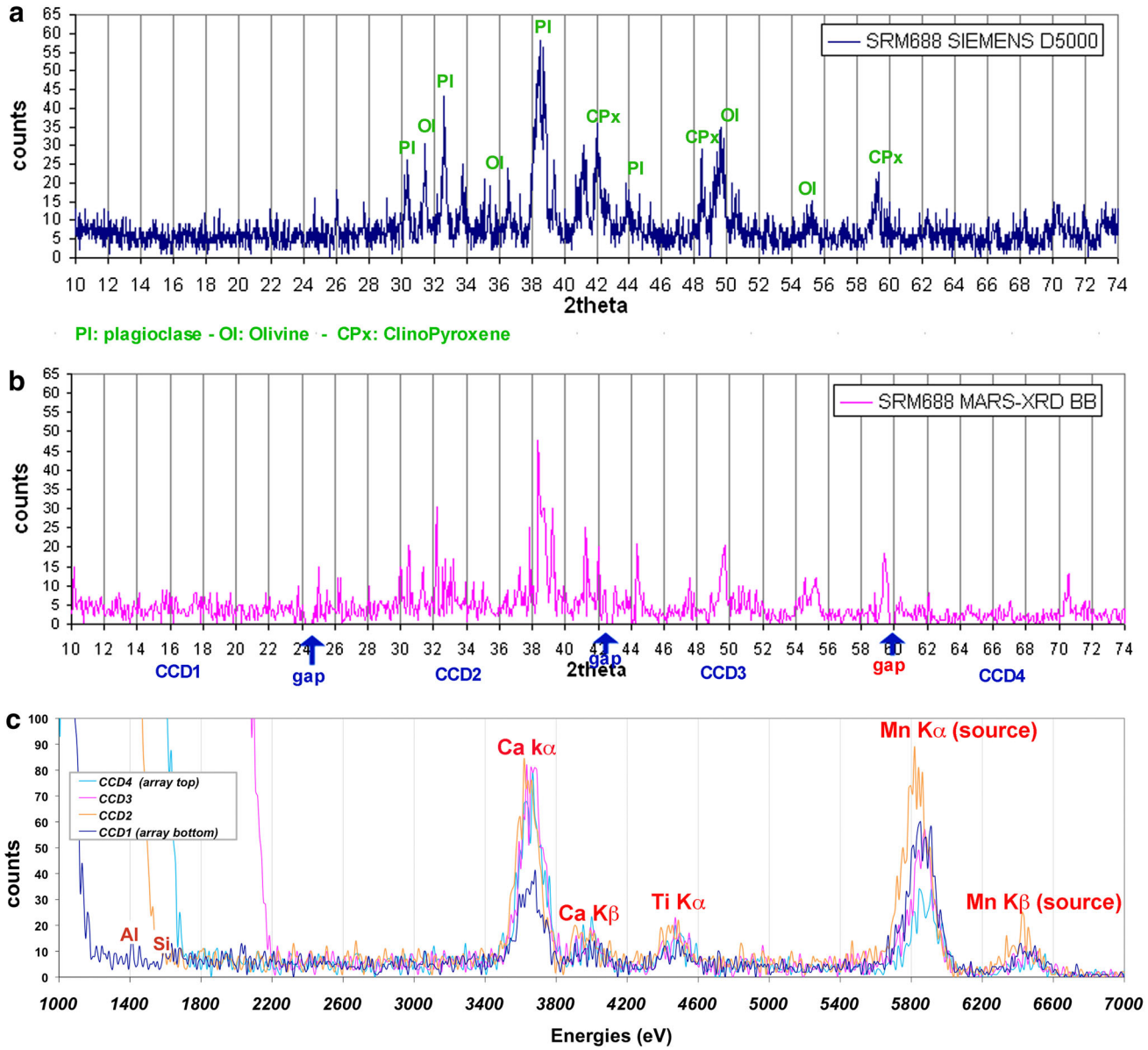

Fig. 6 XRD and XRF acquisition of NIST standard SRM688. **a** XRD pattern acquired with a Siemens D5000 apparatus. **b** XRD pattern acquired with the prototype. **c** XRF spectrum acquired with the prototype

about 1 h for the lab equipment and 4.5 h for the prototype.

The difficulties in analysing the light chemical elements is due to either some unclear high noise level of some of the CCDs and the effect of Mylar® filter plus air absorption. The detection chamber has a 20-µm Mylar foil on the front window to maintain the vacuum inside the chamber. We concluded that the very low transmittance of the Mylar® filter below 2 keV (<1 %) prevented the clear identification of the light chemical elements in the XRF mode, while it does not influence the XRD mode at the 5.9-keV emission of ^{55}Fe.

In order to better understand the capabilities of the concept design in acquiring the XRD and XRF data of non-prepared samples, we also performed some tests with a lab SIEMENS D5000 instrument. The D5000 instrument mounted a 1-mm slit for both the incoming and outcoming beams and the rotation of the sample was stopped. This was necessary to understand the effect of the preferred orientation of the crystals on the unprepared sample, though the overall quality of the diffraction pattern of the powder in this set-up is not as good as nominal performance. We prepared slices of basaltic rocks (A20) collected in the Andes with different surface roughness, the XRD patterns

are shown in Fig. 7. The sample was aligned to the sample-holder using a micrometer to limit the potential out of focusing of the sample. However, some scattering due to the high roughness of the sample was likely responsible for the spikes visible at low 2θ on diffractogram (4) of Fig. 7a, whereas other very intense peaks on diffractogram (4) and (5) of Fig. 7a were likely due to the presence of large plagioclase crystals on the sample surface. Figure 7b shows a reference acquisition acquired with the D5000 instrument with the optimum power supply of the tube and rotating sample.

The comparison of the patterns shown in Fig. 7a indicates that there is a good agreement between the D5000 and prototype measurements with promising outcome for future development.

1.2 Toward an X-ray tomography for archaeometric application

The term 'tomography' nowadays is used for a wide range of 3D imaging methods, not just for those based on radiographic projections. In tomography, the 3D image of an object is obtained in a non-destructive manner by the transmission of the X-ray beam through the sample in several different directions. Investigation of the radiation changes upon interaction with the matter of the sample

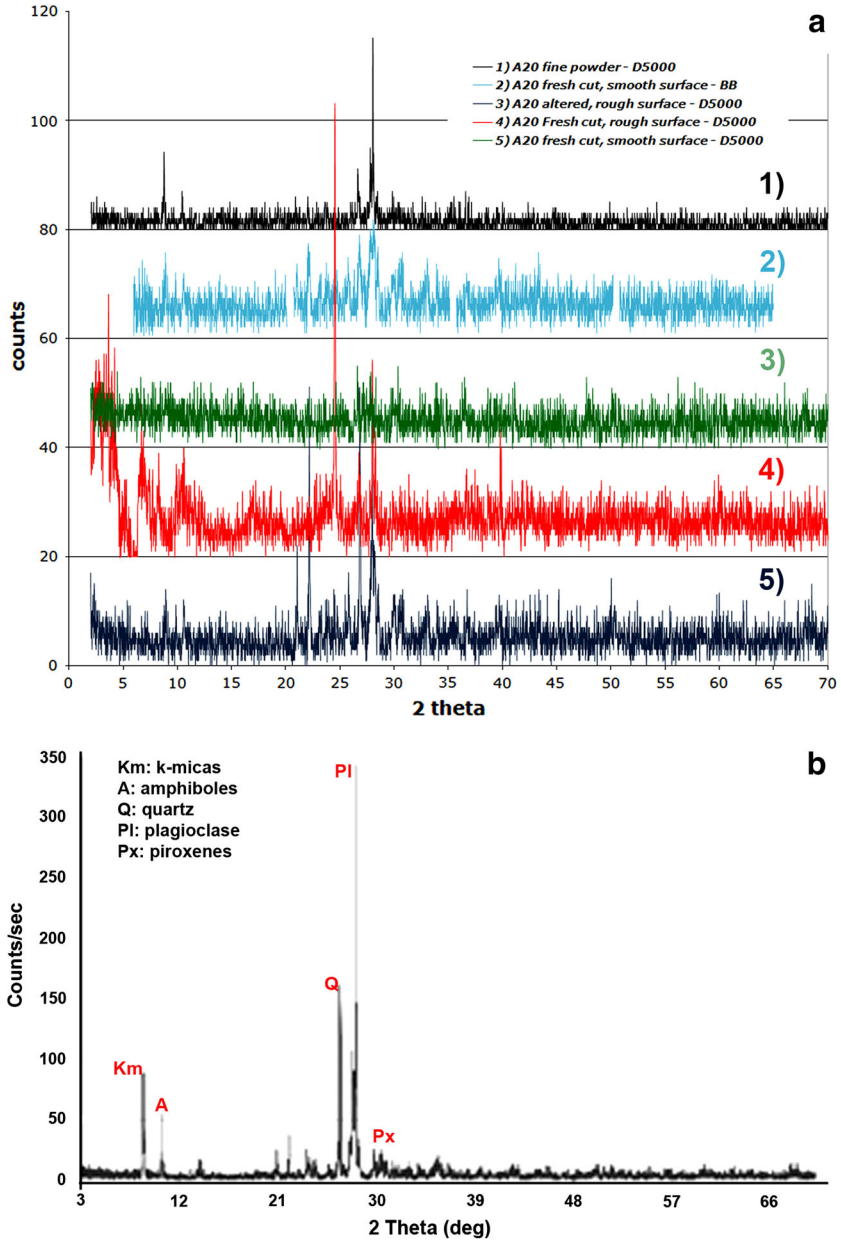

Fig. 7 **a** SIEMENS D5000 XRD patterns (raw data, no filters applied), performed at 20 kV and 5 mA for 12 h, not rotating sample, on slices of sample A20 with different surface roughness and alteration level. The fine powder acquisition was done in the same set up but completed in about 1 h. The lack of strong peaks in pattern (*3*) is likely due to the removal of crystals on the exposed surface of the rocks for weathering processes, whereas the strong peaks in patterns (*4*) and (*5*) are probably due to the presence of large plagioclase crystals on the surface with preferential orientation of the lattice. There is also a surface scattering due to the sample roughness at low 2θ of pattern (*4*). There is good agreement between the acquisition done with the prototype (BB) and the D5000. **b** The reference diffraction pattern of the A20 sample acquired with the D5000 under nominal conditions

allows various physical property changes to be investigated. The physical properties that can be characterized may vary, but the projection requirement assumed states that the signal used for tomographic reconstruction is a monotonic function of a projected physical property. The result of the tomographic reconstruction is a 3D map of the investigated physical property. Tomographic methods that create a 3D image using a more complex signal than a simple projection extend the original meaning of tomography.

Tomography performed using X-ray fluorescent radiation requires to scan the sample sequentially using a small focused beam to avoid the information from different regions of the sample being convoluted irreversibly. Fluorescence tomography is based on the signal produced on an energy-sensitive detector, generally placed in the horizontal plane at some angle with respect to the incident beam caused by photons coming from fluorescence emission. So far, a number of setups have been designed to acquire X-rays fluorescence tomograms of several different sample types. The X-ray imaging and analytical techniques allowed archaeologists to recognize the techniques of manufacture and thus contribute to the overall knowledge of the societies that produced the artefacts, and to the broader understanding of the history of technologies (Tarquini et al. 2012). The authors were able to identify objects in soils with great detail. Applbaum and Applbaum (2005) showed how the X-ray CT imaging, a totally non-destructive research tool, allowed them to view and actually read the inscriptions on the inner tablets from UR III period, which were sealed in clay envelopes. So far X-ray tomographic investigation has been successfully applied to the study of mineral inclusion still trapped in a mineral host phase. Modern X-ray tomography performed to a resolution as high as 0.1–0.3 microns can in fact provide crucial information about mineral phases associations, their spatial distribution and their stress state (i.e., cracking system that cause pressure to be released, see Nestola et al. 2012; Angel et al. 2014, 2015).

In its flight model configuration, the MARS-XRD instrument represents the smallest XRD/XRF instrument ever developed. Based on the experience gained with the space prototype both for the instrument design and data reduction, we propose as evolution of the current prototype for terrestrial application an X-ray tomographer to map the composition of the artefacts. The instrument will be able to work simultaneously both in XRD and XRF modes. To enhance the instrument performance mostly in the XRF spectrum (including the Fe identification) and its portability, we plan to replace the isotopic source with a commercial cathodic tube with Cu target. This change will have limited effect on the data acquisition chain but will increase the weight and power consumption of the apparatus, which is not so critical in terrestrial application.

2 Conclusions

We described the main findings of a space prototype development for a combined XRD and XRF instrument developed under the ESA ExoMars mission framework. The prototype in its final "flight configuration" represents a very high level of miniaturisation with its 1.5 kg mass. Based on this result, we briefly discussed the potential developments of a non-destructive, in situ archaeometric analysis which may be adapted toward an X-ray tomography approach.

The possible applications in the field of the cultural heritage of a non-invasive technique is certainly extremely interesting and particularly important for the Italian context, which includes numerous specific fields, such as archaeological remains and finds, architectonic monuments, artistic paintings, sculptures and other ancient and quite delicate artifact.

Acknowledgements This work has been supported by the Italian Space Agency (ASI) under the contract I/060/10/0. We wish to thank an anonymous reviewer and Mihaela Glamoclija for the detailed and helpful comments. We are grateful to Dott. Fabio Critani for the software development of the prototype.

References

Angel RJ, Mazzucchelli ML, Alvaro M, Nimis P, Nestola F (2014) Geobarometry from host-inclusion systems: the role of elastic relaxation. Am Miner 99:2146–2149

Angel RJ, Alvaro M, Nestola F, Mazzucchelli ML (2015) Diamond thermoelastic properties and implications for determining the pressure of formation of diamond inclusion systems. Russ Geol Geophys J 56(1–2):211–220

Applbaum N, Applbaum YH (2005) The use of medical computed tomography (CT) imaging in the study of ceramic and clay archaeological artifacts from the ancient near east. In: Uda M, Demortier G, Nakai I (eds) X-rays for archaeology. Springer, Netherlands, pp 231–246

Bish D, Blake D, Vaniman D et al (2014) The first X-ray diffraction measurements on Mars. IUCrJ 1:514–522

Blake D, Vaniman D, Achilles C et al (2012) Characterization and calibration of the CheMin mineralogical instrument on Mars science laboratory. Space Sci Rev 170:341–399

Bugenis C, Preuss LE, Toothacker WS (1968) Laboratory Debye-Scherrer camera using an ^{55}Fe source of Mn Kα Xrays. Rev Sci Instrum 39:1754–1755

Marinangeli L, Hutchinson IB, Baliva A et al (2007) An european XRD/XRF instrument for the Exomars mission. In: Lunar and planetary science XXXVIII, Abstract #1322, Lunar and planetary institute, Houston (CD-ROM). http://www.lpi.usra.edu/meetings/lpsc2007/pdf/1322.pdf

Nakai I, Abe Y (2012) Portable X-ray powder diffractometer for the analysis of art and archaeological materials. Appl Phys A 106(2):279–293

Nestola F, Merli M, Nimis P et al (2012) In situ analysis of garnet inclusion in diamond using single-crystal X-ray diffraction and X-ray micro-tomography. Eur J Miner 24(4):599–606

Pelliciari C, Marinangeli L, Critani F, Baliva A, Hutchinson IB (2011) Optimization of the MARS-XRD collimator using converging blades. In: Hudec R, Pina L (eds) EUV and X-ray optics: synergy between laboratory and space II, Proceedings of SPIE, 8076, Cardif

Pifferi A, Campi G, Giacovazzo C, Gobbi E (2009) A new portable XRD/XRF instrument for non-destructive analysis. Croat Chem Acta 82(2):449–454

Plescia P, Ingo GM (2005) Surface monitor: a new instrument for in situ XRD-XRF and optical measurements. In: Denver X-ray conference abstract, Denver

Preuss LE, Toothacker WS, Bugenis CK (1966) Demonstration of X-ray diffraction by LiF using the Mn Kα X-rays resulting from ^{55}Fe decay. Appl Phys Lett 9:159–161

Preuss LE, Toothacker WS, Bugenis CK (1967) Single-crystal X-ray diffraction using photons from two radioactive isotopic sources. J Appl Phys 38:3404–3405

Tarquini O, Colapietro M, Belelli Marchesini B, Pardini G (2012) X-Ray imaging, X-Ray fluorescence and diffraction to study metal archaeological remains from excavations. In: Vezzalini G, Zannini P (eds) Atti del VII Convegno Nazionale di Archeometria-A.I.Ar. Patron Editore, Bologna

Vago J, Witasse O, Baglioni P, Haldemann A, Gianfiglio G, Blancquaert T, McCoy D, de Groot R et al (2013) ExoMars: ESA's next step in Mars exploration. Eur Space Agency Bull 155:12–23

Vaniman DT, Bish DL, Ming DW et al (2014) Mineralogy of a mudstone at Yellowknife Bay, Gale Crater. Mars Sci 343:6169