



Review

A review of the handheld X-ray fluorescence spectrometer as a tool for field geologic investigations on Earth and in planetary surface exploration



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ABSTRACT

X-ray fluorescence (XRF) spectroscopy is a well-established and commonly used technique in obtaining diagnostic compositional data on geological samples. Recently, developments in X-ray tube and detector technologies have resulted in miniaturized, field-portable instruments that enable new applications both in and out of standard laboratory settings. These applications, however, have not been extensively applied to geologic field campaigns. This study investigates the feasibility of using developing handheld XRF (hXRF) technology to enhance terrestrial field geology, with potential applications in planetary surface exploration missions. We demonstrate that the hXRF is quite stable, providing reliable and accurate data continuously over a several year period. Additionally, sample preparation is proved to have a marked effect on the strategy for collecting and assimilating hXRF data. While the hXRF is capable of obtaining data that are comparable to laboratory XRF analysis for several geologically-important elements (such as Si, Ca, Ti, and K), the instrument is unable to detect other elements (such as Mg and Na) reliably. While this limits the use of the hXRF, especially when compared to laboratory XRF techniques, the hXRF is still capable of providing the field user with significantly improved contextual awareness of a field site, and more work is needed to fully evaluate the potential of this instrument in more complex geologic environments.

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1. Introduction

X-ray fluorescence (XRF) spectroscopy is a well-established analytical technique for determining the chemical composition of a sample. For decades, XRF instruments have been used in laboratory settings to investigate samples for geochemical, industrial, and archaeological applications with great success (von Hevesy, 1932; Shaw, 1952; Parrish, 1956; Norrish and Hutton, 1969; Norrish and Chappell, 1977; Jenkins et al., 1995; Jenkins, 1999; Beckhoff et al., 2006; etc.). Recently, however, several XRF manufacturers have recognized the merits of increasing the mobility of XRF instrumentation for initial applications in fields such as industry and mining. By miniaturizing this technology, companies like Innov-X, ThermoScientific, and Bruker (among others) have made it possible to collect compositional information *in situ*. While groups in other scientific fields have recognized the merits of deploying handheld XRF (hXRF) instruments in the field (Potts et al., 1995; Shrivastava et al., 2005; Markey et al., 2008; Potts and West, 2008; Phillips and Speakman, 2009; Shackley, 2010; Liritzis and Zacharias, 2010; Zurfluh et al., 2011; Margui et al., 2012; etc.), these instruments are not commonly used in the geological sciences. There is, however, precedent for obtaining valuable *in situ* geochemical data while conducting field geologic traverses. Alpha Particle X-ray Spectrometers (APXS) have flown on three Mars rover missions; Pathfinder, MER (Mars Exploration Rovers), and MSL (Mars Science Laboratory) (Rieder et al., 1997, 2003; Brückner et al., 2003; Gellert et al., 2009). The discoveries made by APXS have been abundant (*i.e.* Squyres et al., 2004; Ming et al., 2006; among many others) and this technology has proven invaluable in providing real-time geochemical contextual information for each of the Mars rover landing sites. This kind of rapid, *in situ* geochemical analysis has the potential to be of equivalent high value to terrestrial field geologists, as well as to the next generation of planetary surface explorers.

While laboratory analyses will remain the standard for providing the highest quality data possible, these measurements can be costly, and require intensive sample preparation and analysis time. There is therefore a niche in the community for the use of hXRF technology in that it can provide rapid, *in situ* data to the user to inform them about the composition of samples at their field site. The user can also deploy the hXRF to triage samples, allowing them to select a sample suite tailored to their field and scientific objectives for return for future laboratory work. By deploying the hXRF in the field, the field geologist can streamline field operations, gain a real-time geochemical understanding of a field site, select which samples to collect, save time and money on laboratory analyses, and potentially minimize future return trips to the field site.

Before recommending that the hXRF be added to a field geologist's toolbox, however, it is crucial to understand just what the capabilities and limitations are of hXRF instrumentation. This report reviews the utility of the hXRF based on an examination of the accuracy and precision of this technology as well as its limitations and best deployment practices in an effort to evaluate its utility in field geologic applications. It is important to consider that this instrument will not be a substitute for laboratory analyses, and this study therefore investigates what capabilities hXRF spectroscopy can bring to geologic field science. We use a selected suite of

fine-grained terrestrial sample standards to calibrate this technology in a geologically-relevant environment and demonstrate that hXRF instruments can be valuable field geologic tools.

We also note that portable instruments that can be used easily in the field have great utility both in terrestrial applications (especially in remote locations where return trips are especially costly) and in a planetary exploration context (where sample return could be highly constrained). The results of this work therefore have implications for both terrestrial field geology, in reviewing the utility of the hXRF as a valuable and reliable tool for field campaigns, as well as planetary surface exploration, where the hXRF can provide *in situ* geochemical information on a timescale appropriate for human spaceflight (Young et al., 2011, 2012, 2014, 2015).

1.1. The development of hXRF technology

In order to miniaturize XRF technology, changes from the original bench-top or laboratory instrument configurations were made in both X-ray tube and detector technology. These changes introduce advantages as well as analytical challenges that we identify below.

Sample preparation: Extensive sample preparation is not required for hXRF Energy Dispersive Spectroscopy (EDS) analysis, enhancing the practicality of deploying this instrument in the field. This contrasts with laboratory sample preparation (where samples are powdered and mixed to achieve a uniform sample composition and then pressed with a binder or fused into a wafer) required for wavelength dispersive spectroscopic XRF analysis (Jenkins et al., 1995, Jenkins, 1999; Beckhoff et al., 2006).

Power: The handheld, battery-powered instruments are generally less than 4 W (versus the 50–100 W of power required to operate laboratory instruments), making the instruments safe to handle but also decreasing the signal, and in turn lowering the precision of the instrument. This study evaluates whether the precision of the hXRF is sufficient for field operations.

Limits of low beam energies: Due to the lower beam energies associated with the handheld configuration, the returning secondary X-rays also have lower energies, making it more challenging to detect and measure the lighter elements.

Detector size and type: Silicon drift detectors, used in hXRF technology, have large surface areas and better resolutions than their alternatives (*i.e.* Si-PIN and CdTe detectors), meaning that they can differentiate between the broader X-ray peaks as well as detect and measure lower energy X-rays (Longoni et al., 1998; Strüder et al., 1998).

1.2. Instrument introduction

The data presented in this study were collected using an Olympus Innov-X DELTA Premium Handheld XRF Analyzer. Weighing roughly four pounds, the instrument is equipped with a rechargeable Li-ion battery, a large-area silicon drift detector (with a resolution of approximately 185 eV), and a 4 W Rh anode X-ray tube that provides the excitation source. The specific X-ray tube geometry and variable excitation source configuration allows for analysis of a large range of the periodic table. Due to the low beam

energies however, these measurements are not as precise as those that can be produced using a laboratory XRF, though we demonstrate that this does not affect the utility of the instrument in a field setting. These low energies also mean that the signals for light elements – specifically those lighter than Mg – preclude accurate detection and measurement with this system but again, as we will demonstrate, this only slightly limits the value of field applications of the hXRF. Noble gasses are also not measurable, nor are actinides heavier than Pu. This will be further discussed in the following sections.

There are multiple deployment options for the hXRF. The instrument was originally developed for use in industry and mining, meaning that its dominant deployment mode is handheld. Each unit is designed for a natural and straightforward interface with a human user in the field. The low weight, user interface design, and instrument configuration lends the instrument to easy field operations. However, most hXRF manufacturers also offer benchtop technology for repetitive analyses in a laboratory setting. As we collected all data for this calibration study in the laboratory on sample standards, we dominantly used the benchtop configuration.

2. Methods

2.1. Sample calibration

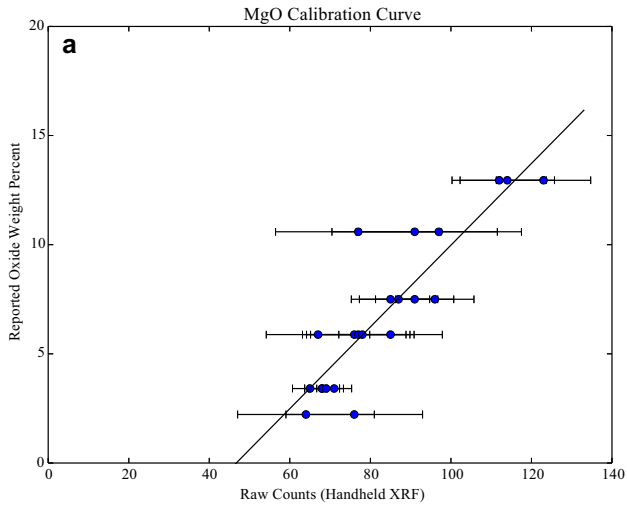
Per the recommended protocol provided by the instrument manufacturer, we monitored internal instrument stability by measuring Fe K- α counts on a 316 stainless steel coin every day of use. However, standard hXRF models are traditionally used in industry and mining rather than in rigorous geologic analysis, meaning that their calibration algorithms for conversion from raw count data to oxide weight percent data were built from materials with compositions not relevant to most geologic field settings. For this reason we sought to calibrate the instrument against a set of relevant sample standards to determine the instrument's ability to provide useful geochemical data. In order to understand the instrument's capabilities, and calibrate this instrument using a specific set of standards, we analyzed a suite of well-characterized samples and created a set of calibration curves for the major element oxides (except for Na₂O, which is too light to be detected using most commercially-available hXRF models). Our standard samples were loaned from Dr. Richard Morris' Spectroscopy and Magnetism lab, which houses all standards for the Mars rover instruments tested at NASA's Johnson Space Center. The standard sample suite comprises five relatively unaltered, fine-grained, massive volcanic rocks ranging from andesitic composition to Si-undersaturated basalts. We chose fine-grained and homogenous samples with few obvious heterogeneities (i.e. large phenocrysts or vesicles) to accommodate the relatively large analysis footprint for the hXRF (8 mm², the size of the instrument's proline window). Selecting samples that minimized these geochemical heterogeneities allowed us to isolate whether the instrument itself had any signal inconsistencies. In addition, we collected our standard data on smooth, cut surfaces to minimize surface effects. The sample standards analyzed include HWHL100 (Hawaiian basalt from Hualai volcano), CP-5 (Columbia River basalt), BPNTX1 (basalt from Pilot's Knob, Texas), WIME101 (basalt from Mellen Quarry, Mellen, Wisconsin), and TMGNV5 (andesite from Table Mountain, Goodsprings, Nevada). There is precedent for including these samples in evaluating geologic analytical techniques as Anderson et al., (2011) used all five of these samples in their effort to evaluate how to improve the accuracy of laser induced breakdown spectroscopy (LIBS) analyses. We were provided with detailed compositional information for each sample, data that were obtained at Franklin and Marshall College using a 9:1 Li₂B₄O₇-sample flux-fusion

procedure to prepare glass disks and a Philips 2404 XRF spectrometer equipped with a 4 KW Rh X-ray tube (Boyd and Mertzman, 1987). As these traditional sample preparation techniques that homogenize each sample were used to obtain the laboratory data, these data represent bulk composition measurements. Similarly, we homogenized the data taken for the calibration curves in two ways: 1) the instrument window, as stated above, is 8 mm², meaning that each individual data point is averaged over that area on each sample's surface, and 2) we took several analyses on each sample standard (3–5 per sample), resulting in coverage of a large area on each sample's surface. Again, as the samples chosen had minimal vesicularity and phenocryst content, we were able to compile a representative geochemical fingerprint of each of the five sample standards selected in this study.

Using the techniques discussed above, we collected data on this sample suite of terrestrial volcanic standards and constructed linear calibration curves for each major element oxide (MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, MnO, and Fe₂O₃) using the energy spectrum built from the emitted raw counts measured with the hXRF and measured element oxide content reported from the laboratory XRF. These curves, and their linear regressions, are shown in Fig. 1a–i. We note that we measured the total FeO as Fe₂O₃ because the sample standards being analyzed were initially characterized as standards for Mars surface analyses, with Fe₂O₃ representing the standard in this field. Operating the instrument using the *Innov-X* software's two-beam mining mode, we empirically determined that, in the case of these fine-grained rocks, a 60-s analysis time was sufficient to provide reasonably accurate data (typically < 3% accuracy), and still be operationally manageable for different field configurations. Output for each 60-s analysis included the energy spectrum of the returning secondary X-ray. For each element of interest, we generally used the maximum number of counts from the energy peak representing that element's K- α emission. (For broad emission peaks, we instead averaged the values forming the peak.) Using these calibration curves, we were able to calculate weight percent oxide for each major element on all raw count data for all future analyzed samples. As shown in Fig. 1a–i, there are discrepancies in the quality of these calibration curves. At present, calibration curves for SiO₂, CaO, TiO₂, and K₂O show that the hXRF is able to calculate reasonably precise values when compared to laboratory values. The calibration curves for P₂O₅, MnO, and Fe₂O₃ are poorer, but we believe a major cause is the restricted range of MnO and Fe₂O₃ in the standard suite. The greater dispersion of data in the P₂O₅ calibration exercise is likely due to the low concentrations of this oxide in all five sample standards, resulting in poor counting statistics. Future work will include expanding the range of samples used to calibrate for these less concentrated elements.

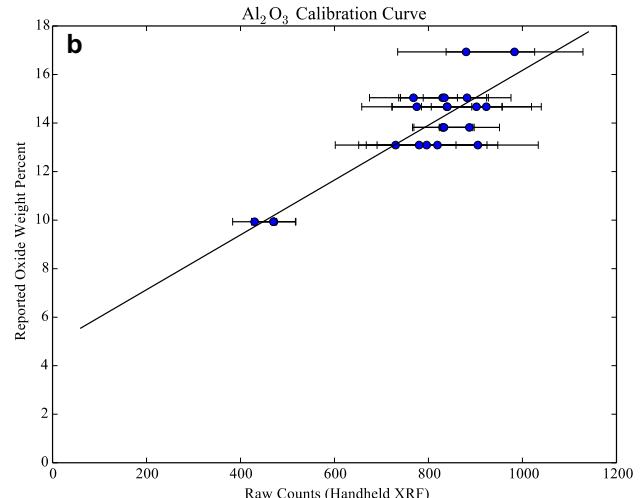
2.2. Physical deployment of instrument

While hXRF instruments are typically designed for field deployment, multiple instrument configurations are possible. The nominal field configuration allows the user to carry the instrument either in hand, in a carrying case, or even in a belt-mounted holster for easy access. When a sample of interest is identified, the hXRF must be placed so that the detector window at the front of the instrument is flush with the sample (Fig. 2b). If the instrument is not completely flush with the surface, there is the possibility for errant X-rays that do not interact with the sample to escape into the area surrounding the front of the instrument. For this reason, the user should be sure to handle the instrument in its nominal, recommended mode (Fig. 2b) and not put any body part directly next to where the instrument is touching the sample. The second configuration, and the one in which we collected the majority of the



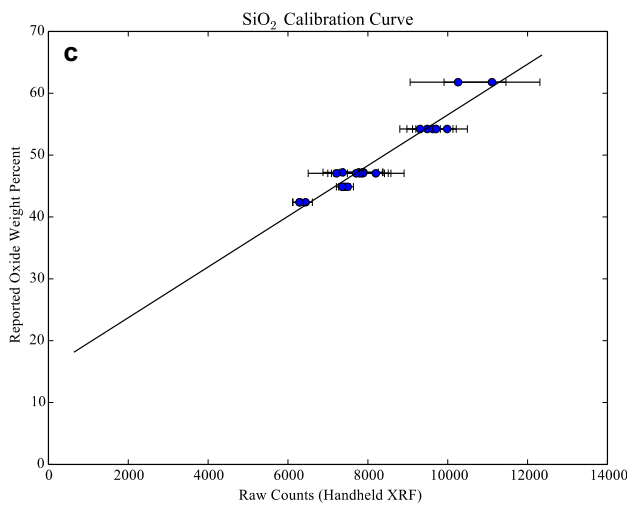
Equation for the line: $y = 0.19x - 8.74$

$R^2 = 0.78$



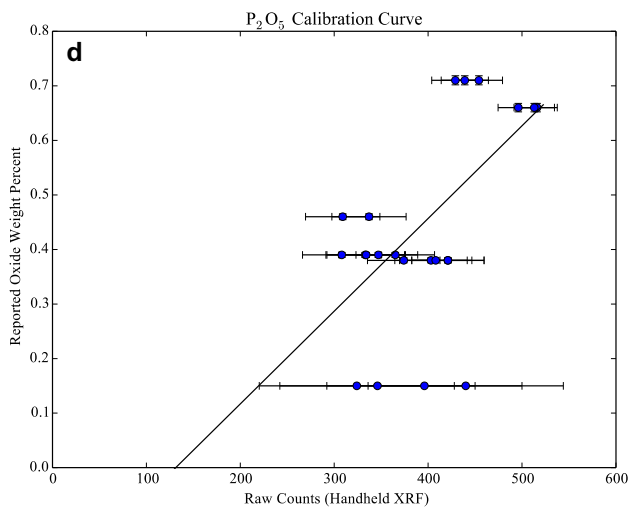
Equation for the line: $y = 0.01x + 4.87$

$R^2 = 0.76$



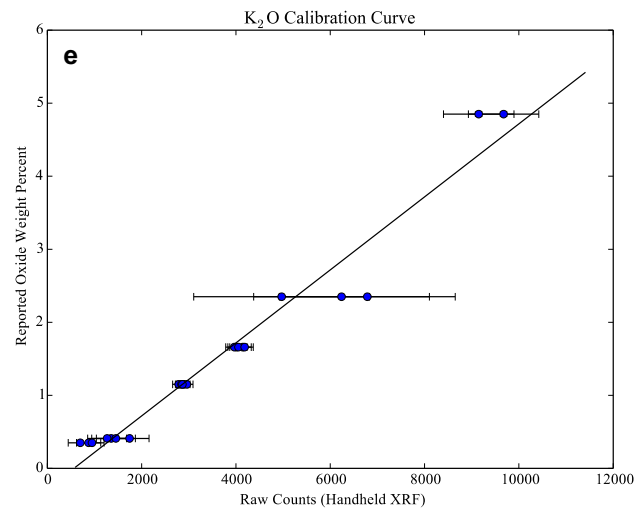
Equation for the line: $y = 0.0041x + 15.52$

$R^2 = 0.94$



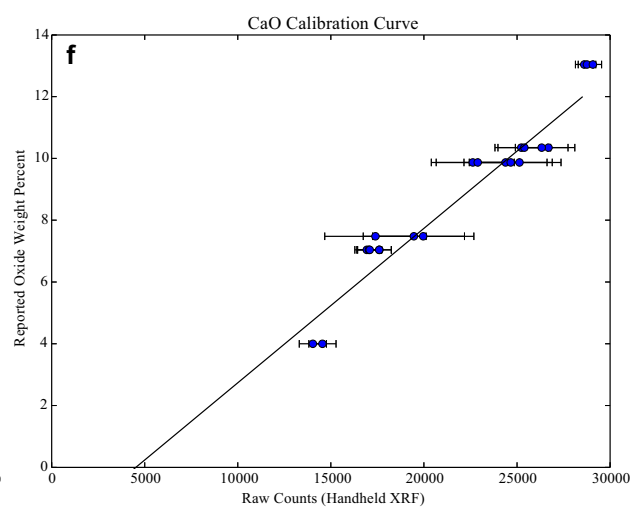
Equation for the line: $y = 0.0017x - 0.22$

$R^2 = 0.32$



Equation for the line: $y = 0.0005x - 0.28$

$R^2 = 0.96$



Equation for the line: $y = 0.0005x - 2.26$

$R^2 = 0.94$

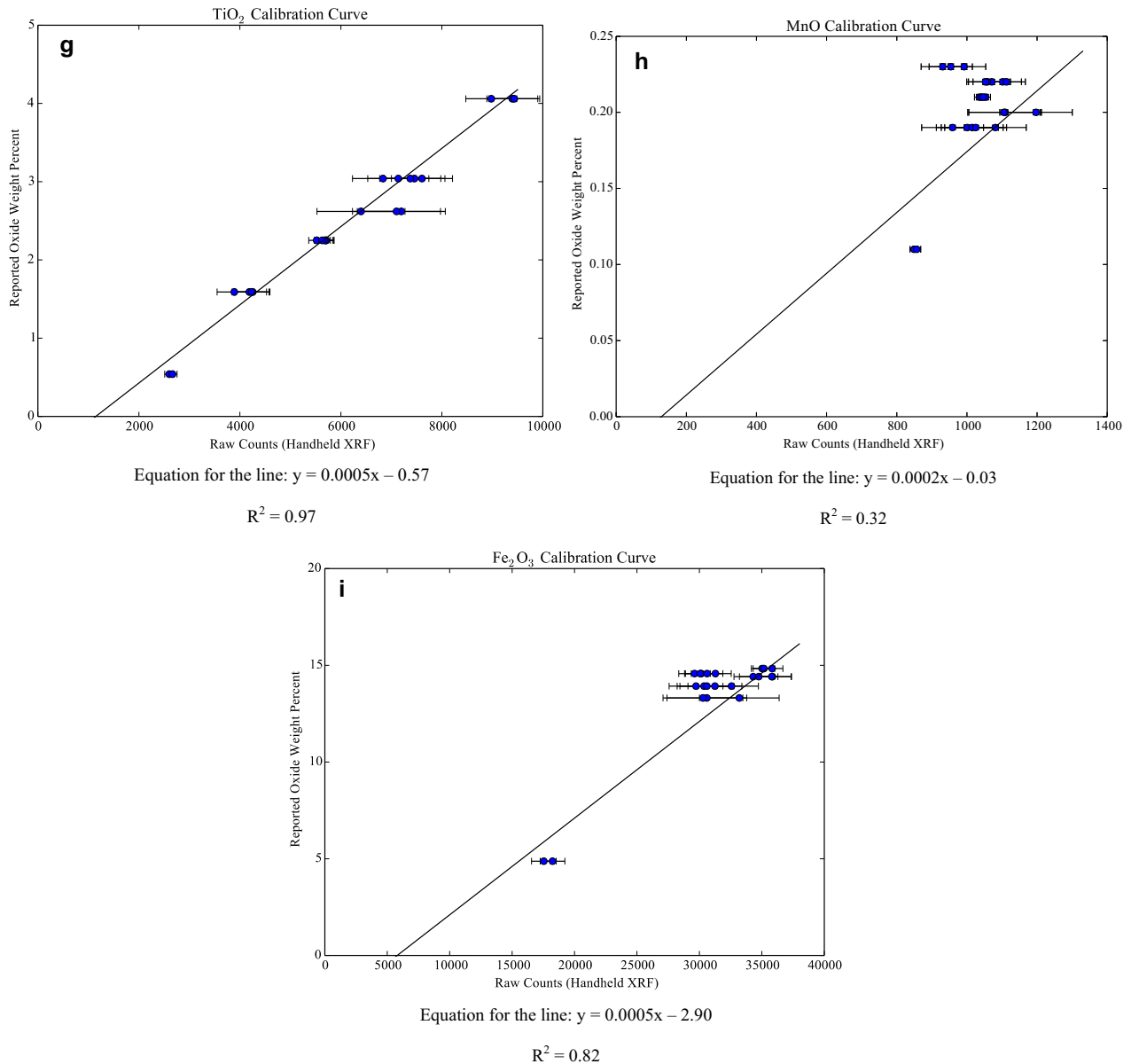


Fig. 1. (continued).

data for this study, involves mounting the instrument in a housing case designed by the instrument manufacturers (Fig. 2a). The compartment on top is intended for sample placement and radiation containment. The sample must again be closely aligned to the detector sample window to allow for a direct X-ray path into the detector through the prolene window. The lid of the compartment is then closed, allowing for containment of any errant X-rays that do not make it to the detector. A cable is connected from the hXRF to a nearby computer, from which the user can control the triggering and data management screens. Regardless of the deployment mode, instrument conditions such as beam firing times, testing mode, etc. can all be manipulated at will by the user (we kept the settings identical for all data collection in this study). The

user can also view and export any and all data from this computer. After the 60 s of data collection are complete, the user can open the compartment and either modify the sample's presentation to the instrument's window or switch samples entirely. The third and final configuration tested is mounting the hXRF in a glovebox, simulating planetary exploration test conditions found in Evans et al. (2013) and shown in Fig. 2c.

3. Data

After calibrating the hXRF, we tested these calibration curves in a number of ways to evaluate its flexibility in a number of geologically-relevant scenarios.

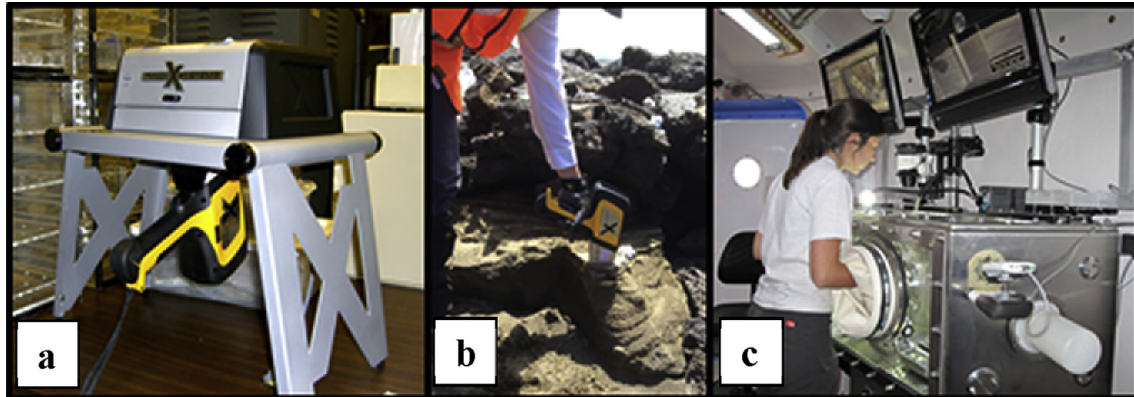


Fig. 2. Different deployment modes of the hXRF. a) Laboratory deployment in the housing provided by the manufacturer. All data presented in this study were collected using this mode. b) Field deployment. c) Deployment in a geologic glovebox in a NASA analog mission. The hXRF is mounted to the left side of the glovebox for sample analysis during a planetary exploration mission.

3.1. Effects of sample preparation

The above calibration curves were based on the best possible sample surface and instrument geometries: smooth uniform surfaces enabling complete contact between the instrument and the sample surface. However, field applications present less ideal and more variable sample surface geometries, making sample presentation an issue that will affect data quality. The miniaturization of the X-ray tube and detector technologies have resulted in challenges in detecting lower energy X-rays. To lessen the challenges of detecting these lower energy elements, minimizing the distance between the detector (and therefore the polyene window) and the sample of interest is crucial. Sample surface heterogeneities introduced, for example, when breaking off a sample in the field with a rock hammer, have the same effect of increasing the instrument working distance. Sawed samples present the ideal case of a perfectly smooth sample for presentation to the instrument window. However, this amount of sample preparation is not possible in a field setting. It is therefore important to understand the implications of varying surface roughness on data quality. In order to illustrate this effect, we show data collected from the laboratory XRF as well as data we collected using the hXRF, but the hXRF data are shown in two groupings: for surfaces that are sawed, and for rough surfaces (though all data was collected on fresh surfaces with no weathering or alteration products) (Fig. 3a–e).

3.2. Instrument stability

After investigating the effects that sample preparation has on hXRF data quality, we evaluated instrument stability over time by collecting data on our established set of sample standards on five separate dates over two years. We analyzed all five terrestrial sample standards over the course of two years (specifically, data were collected in July 2010, November/December 2010, June 2011, July 2012, October 2012). We converted raw counts for each major element (Mg, Al, Si, P, K, Ca, Ti, Mn, and Fe) measured on the hXRF into oxide weight percent using the calibration curves shown in Fig. 1. These data are shown in Table 1.

3.3. Testing on lunar samples

As an independent test of the hXRF on other well-characterized samples that were not part of the sample standard suite, we collected data on a suite of seven Apollo Lunar samples that have

been set aside as a laboratory test collection (Allen et al., 2010) at the NASA JSC Lunar Experiment Laboratory. We compared the hXRF data to those obtained by standard, laboratory-based geochemical analysis by several investigators and compiled in the Lunar Sample Compendium (Meyer; Accessed March 2014), shown in Table 2. Note that we converted the measured Fe_2O_3 to FeO to compare with the published literature. By collecting raw count data for each major element (again, except for Na) for these seven basalt samples, converting these data to weight percent oxide using our empirically derived calibration curves, and comparing these calculated values to values reported in the literature, we conducted an independent test on both the instrument's accuracy and the applicability of the calibration curves shown in Fig. 1. All of the data we collected on the lunar reference suite are shown in Table 2. Though more detailed information on the petrography of each lunar sample discussed here can be found in the references mentioned here, basic petrography is stated in Table 2. It should be noted that, due to the strict operational requirements introduced when working with the returned lunar samples, we did not have as much control over selecting precise measurement sites as with the terrestrial samples. The implications of this, as well as the implications of the complex petrology of these samples, are discussed below. However, all analyzed lunar samples had flat, sawed surfaces, meaning that the samples were flush with the instrument window during analysis.

References for Table 2: Meyer, Lunar Sample Compendium; Compston et al., 1971; Cuttitta et al., 1973; Duncan et al., 1973; Maxwell et al., 1970; Rhodes et al., 1976; Rose et al., 1973; Ryder and Schuraytz, 2001; Taylor et al., 1972; and Willis et al., 1971. Phenos = phenocrysts. Oliv = olivine. Plag = plagioclase. Pyx = pyroxene. Cpx = clinopyroxene. Note: the negative values in the table are likely due to the low concentrations of this element in the measured samples.

4. Discussion

Based on our evaluation of the hXRF instrument, we can identify key attributes of the technology and begin to frame ways that it can be used in the field to the advantage of geologists. Our findings are discussed below.

The Handheld XRF instrument is a remarkably stable instrument. Table 1 shows the average weight percent oxide for each major element calculated on only sawed surfaces from each of the five standards on each of the five data collection dates (July 2010, November/December 2010, June 2011, July 2012, and October 2012). When we compared these values both to one another and to

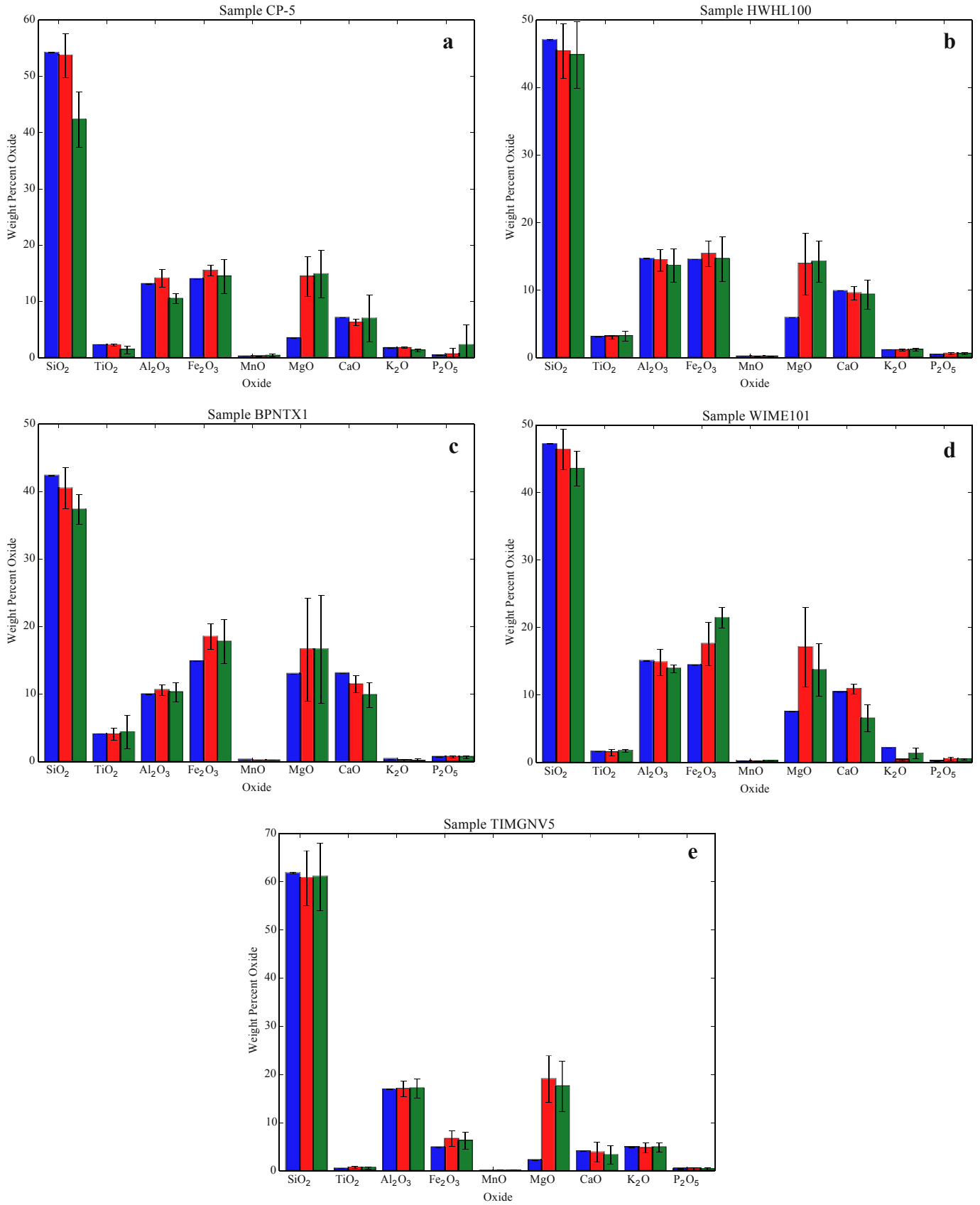


Fig. 3. a) Sample CP-5: Sawed versus Rough. b) Sample HWHL100: Sawed versus Rough. c) Sample BPNTX1: Sawed versus Rough. d) Sample WIME101: Sawed versus Rough. e) Sample TIMGNV5: Sawed versus Rough. Plots showing comparisons for the nine major elements of interest. Data from the laboratory XRF (blue), hXRF on sawed surfaces (red), and hXRF on rough surfaces (green) are compared. Error bars represent $\pm 2\sigma$. If the error bars are not visible, the error is too small for that point to be visible.

Table 1
Comparison for five major data collection dates. Errors represent $\pm 2SE$.

Element oxides	Date of Data Collection					Lab XRF Oxide Wt%
	Sample: CP-5					
	Summer 2010	Winter 2010	Summer 2011	Summer 2012	Winter 2012	
SiO ₂	51.57 ± 4.26	54.54 ± 3.20	54.43 ± 3.58	54.28 ± 2.61	53.55 ± 2.39	54.23 ± 0.09
TiO ₂	2.12 ± 0.18	2.20 ± 0.25	2.27 ± 0.16	2.22 ± 0.15	2.16 ± 0.18	2.25 ± 0.00
Al ₂ O ₃	13.33 ± 1.81	14.29 ± 1.83	14.39 ± 0.92	14.26 ± 1.17	14.16 ± 1.03	13.09 ± 0.03
Fe ₂ O ₃	15.29 ± 1.02	15.62 ± 1.13	15.84 ± 0.56	15.37 ± 0.66	15.09 ± 0.78	13.92 ± 0.02
MnO	0.22 ± 0.04	0.24 ± 0.19	0.22 ± 0.02	0.22 ± 0.02	0.22 ± 0.01	0.22 ± 0.00
MgO	13.74 ± 3.06	15.24 ± 3.77	13.89 ± 3.43	15.16 ± 2.88	13.81 ± 3.42	3.41 ± 0.01
CaO	6.04 ± 0.38	6.26 ± 0.77	6.47 ± 0.49	6.33 ± 0.33	6.15 ± 0.44	7.04 ± 0.01
K ₂ O	1.74 ± 0.11	1.74 ± 0.14	1.78 ± 0.14	1.74 ± 0.13	1.71 ± 0.12	1.66 ± 0.01
P ₂ O ₅	1.02 ± 1.96	0.59 ± 0.47	0.40 ± 0.06	0.47 ± 0.05	0.61 ± 0.11	0.39 ± 0.00
	n=10	n=11	n=10	n=10	n=9	
Sample: BPNTX1						
SiO ₂	39.29 ± 2.54	40.73 ± 3.40	41.13 ± 3.16	40.71 ± 2.78	40.45 ± 2.58	42.37 ± 0.07
TiO ₂	4.45 ± 1.89	3.96 ± 0.43	4.10 ± 0.29	4.00 ± 0.28	3.88 ± 0.20	4.06 ± 0.00
Al ₂ O ₃	10.48 ± 1.05	10.62 ± 0.99	10.55 ± 0.80	10.64 ± 0.76	10.65 ± 0.64	9.93 ± 0.03
Fe ₂ O ₃	19.49 ± 2.07	18.61 ± 2.05	18.51 ± 1.70	18.18 ± 1.15	18.00 ± 1.56	14.83 ± 0.02
MnO	0.19 ± 0.01	0.19 ± 0.02	0.19 ± 0.01	0.19 ± 0.02	0.19 ± 0.01	0.23 ± 0.00
MgO	14.95 ± 1.75	18.44 ± 9.75	21.85 ± 3.18	14.40 ± 3.26	14.08 ± 2.87	12.95 ± 0.02
CaO	11.27 ± 2.09	11.51 ± 1.73	11.70 ± 0.61	11.51 ± 0.86	11.28 ± 0.86	13.04 ± 0.02
K ₂ O	0.05 ± 0.27	0.18 ± 0.16	0.14 ± 0.05	0.15 ± 0.07	0.15 ± 0.04	0.35 ± 0.00
P ₂ O ₅	0.75 ± 0.23	0.69 ± 0.12	0.62 ± 0.07	0.71 ± 0.09	0.66 ± 0.11	0.66 ± 0.01
	n=9	n=9	n=10	n=14	n=9	
Sample: WIME101						
SiO ₂		46.23 ± 2.47	47.53 ± 1.20	44.87 ± 2.09	45.15 ± 1.85	47.20 ± 0.09
TiO ₂		1.51 ± 0.17	1.61 ± 0.19	1.51 ± 0.13	1.47 ± 0.11	1.59 ± 0.00
Al ₂ O ₃		14.82 ± 1.04	15.03 ± 1.00	14.19 ± 0.87	14.49 ± 0.88	15.04 ± 0.05
Fe ₂ O ₃		18.01 ± 1.08	18.04 ± 0.92	17.38 ± 1.09	17.40 ± 1.05	14.41 ± 0.01
MnO	No Data Collected	0.21 ± 0.01	0.21 ± 0.01	0.21 ± 0.01	0.21 ± 0.01	0.21 ± 0.00
MgO		16.62 ± 4.12	19.81 ± 4.72	14.60 ± 1.86	14.66 ± 3.86	7.50 ± 0.02
CaO		10.66 ± 0.46	11.20 ± 0.32	10.76 ± 0.33	10.61 ± 0.66	10.35 ± 0.01
K ₂ O		0.34 ± 0.21	0.35 ± 0.08	0.33 ± 0.12	0.35 ± 0.09	2.18 ± 0.01
P ₂ O ₅		0.58 ± 0.16	0.39 ± 0.06	0.58 ± 0.10	0.64 ± 0.10	0.15 ± 0.00
		n=11	n=14	n=7	n=8	
Sample: TMGNV5						
SiO ₂		60.29 ± 3.27	63.69 ± 5.58	59.50 ± 4.38	59.00 ± 4.11	61.79 ± 0.12
TiO ₂		0.79 ± 0.10	0.56 ± 0.09	0.70 ± 0.19	0.71 ± 0.16	0.54 ± 0.00
Al ₂ O ₃		16.70 ± 1.16	17.80 ± 1.70	16.91 ± 1.27	16.50 ± 1.54	16.93 ± 0.05
Fe ₂ O ₃		7.63 ± 0.44	5.79 ± 0.60	6.67 ± 1.36	6.86 ± 1.28	4.87 ± 0.00
MnO	No Data Collected	0.16 ± 0.01	0.17 ± 0.03	0.16 ± 0.02	0.16 ± 0.01	0.11 ± 0.00
MgO		21.42 ± 4.36	19.83 ± 5.05	17.49 ± 2.14	17.37 ± 1.31	2.22 ± 0.00
CaO		4.95 ± 0.24	2.85 ± 0.32	3.85 ± 1.90	4.18 ± 1.78	4.00 ± 0.00
K ₂ O		4.42 ± 0.19	5.33 ± 0.45	4.75 ± 1.00	4.60 ± 1.01	4.85 ± 0.03
P ₂ O ₅		0.55 ± 0.27	0.36 ± 0.06	0.41 ± 0.15	0.64 ± 0.08	0.46 ± 0.01
		n=7	n=8	n=8	n=6	
Sample: HWHL100						
SiO ₂	45.26 ± 1.67	46.69 ± 2.44		42.09 ± 2.48	46.49 ± 1.56	47.06 ± 0.09
TiO ₂	3.01 ± 0.10	3.12 ± 0.27		2.87 ± 0.20	3.08 ± 0.26	3.04 ± 0.00
Al ₂ O ₃	14.63 ± 0.55	14.64 ± 1.89		13.41 ± 1.06	14.76 ± 0.62	14.67 ± 0.04
Fe ₂ O ₃	15.24 ± 0.45	15.85 ± 2.34		14.44 ± 1.25	15.42 ± 1.08	14.57 ± 0.01
MnO	0.19 ± 0.01	0.19 ± 0.04	No Data Collected	0.18 ± 0.01	0.20 ± 0.02	0.19 ± 0.00
MgO	13.68 ± 2.73	14.57 ± 6.18		13.40 ± 4.67	13.24 ± 1.94	5.88 ± 0.01
CaO	9.82 ± 0.30	9.64 ± 1.20		8.93 ± 0.45	9.73 ± 0.47	9.87 ± 0.01
K ₂ O	1.12 ± 0.06	1.11 ± 0.14		1.04 ± 0.11	1.13 ± 0.12	1.15 ± 0.01
P ₂ O ₅	0.59 ± 0.05	0.60 ± 0.11		0.52 ± 0.08	0.64 ± 0.08	0.38 ± 0.00
	n=8	n=13		n=7	n=7	

the laboratory-reported values, we demonstrated the ability of the hXRF to provide data consistent with laboratory-reported values. There is negligible instrument drift over the two years in which we collected data, demonstrating the reliability of the hXRF, and its potential application in remote locations and longer field campaigns where the instrument must continue to provide consistently accurate data without the ability to repair the instrument or update any software. One of the sources of error is likely due to location of the sampling spots over time – we did not precisely map analysis

locations on each sample, so repetitive XRF analysis spots (the 8 mm² footprint of the instrument) are at different locations on the same sample. There are slight geochemical inconsistencies at that resolution throughout each sample that will most likely show up, however slightly, in the XRF data, which helps explain at least some of the variance shown in Table 1. It should be noted that the analytical uncertainty associated with hXRF work is typically one-two orders of magnitude higher than the reported lab values for most elements.

Table 2

Data for Apollo lunar samples. Laboratory data is compared to handheld XRF data.

Laboratory versus handheld XRF data for Apollo returned samples							
Sample number	70,215,312	15556,11	12,002,492	14,310,220	12052,26	15555,62	10017,30
Rock type	Mare basalt	Vesicular basalt	Olivine basalt	Feldspathic basalt	Pigeonite basalt	Olivine basalt	Ilmenite basalt
Petrology	Fine-grained, porphyritic	Medium-grained, small olv phenocrysts	Medium-grained, porphyritic	Fine-grained, phenos of plag and pyx	Porphyritic, phenos of oliv and cpx	Medium-grained, phenos of oliv and pyx	Fine-grained, vesicular, poikilitic
SiO ₂ – hXRF	40.58	36.89	41.62	46.72	46.53	42.45	42.56
SiO ₂ – Reported	38.46	45.7	43.56	47.14	46.13	45.21	40.78
TiO ₂ – hXRF	12.83	2.44	2.44	1.1	3.4	1.56	9.38
TiO ₂ – Reported	12.48	2.62	2.6	1.23	3.35	1.73	11.71
Al ₂ O ₃ – hXRF	10.91	9.6	9.52	19.01	11.68	11.44	12.03
Al ₂ O ₃ – Reported	9.01	9.48	7.87	20	9.95	10.32	8.12
FeO – hXRF	13.18	14.52	18.12	7.21	16.56	17.91	11.27
FeO – Reported	17.51	19.50	19.49	7.53	18.63	18.14	17.83
MnO – hXRF	0.19	0.24	0.27	0.14	0.24	0.27	0.17
MnO – Reported	0.29	0.28	0.28	0.12	0.28	0.25	0.22
MgO – hXRF	6.7	5.3	11.1	7.83	6.98	10.45	9.7
MgO – Reported	7.91	8.17	14.88	7.88	8.07	11.2	7.65
CaO – hXRF	10.64	8.22	8.12	14.22	11.11	9.37	10.52
CaO – Reported	10.94	10.56	8.26	12.29	10.89	9.96	10.55
K ₂ O – hXRF	–0.11	–0.13	–0.12	0.43	–0.02	–0.08	0.28
K ₂ O – Reported	0.05	0.05	0.05	0.49	0.07	0.05	0.3
P ₂ O ₃ – hXRF	0.34	0.29	0.28	0.65	0.38	0.34	0.44
P ₂ O ₃ – Reported	0.1	0.07	0.11	0.34	0.08	0.05	0.13

Another finding is that sample preparation (or lack of sample preparation) is a factor in the way the data are gathered and used. When the instrument is used in field settings where time and resources are limited (in a traditional terrestrial field geology scenario or on a planetary surface), the operational constraints require minimal sample preparation. Fig. 3 shows the laboratory XRF data compared with hXRF data collected on both rough and sawed faces of the same sample standards. Despite the analytical uncertainty introduced by data collection on surfaces with more complicated geometry, these data can be used in a qualitative way for a rough idea of the sample's geochemistry. We argue that, in conditions where fresh but uncut surfaces are the only option, the hXRF is still valuable in enhancing contextual awareness real-time in the field. When the user is deciding which surface to present to the instrument, the flattest and most homogenous surface should be analyzed, assuming that this surface is fresh and representative of the sample as a whole (i.e. no large phenocrysts, weathering products, vesicles, etc.).

Field geologists explore an area of interest in part through careful examination of the lithology of all rock units found at that site. Weathering processes can have a dramatic effect on the surfaces of these units, chemically altering the surface composition through interaction with rainwater and snowfall. It is important when exploring an area that the geologist examines the fresh, unweathered face of a target rock to ensure proper sample interrogation. This problem was recognized in the rover missions to Mars and was mitigated by the Rock Abrasion Tool (RAT) on the Mars Exploration Mission rovers, Spirit and Opportunity. To enable examination of fresh rock surfaces, each rover was equipped with a RAT, designed to drill underneath the thick layer of dust that coats most exposed rocks on the surface of Mars (Bartlett et al., 2005).

A similar approach of simple surface preparation by an abrasive tool or some other method would enable more quantitative applications of the hXRF tool (unless research goals are aimed at investigating weathering rinds and surfaces). Furthermore, an easy-to-deploy surface abrasion tool could create a more even surface, in addition to removing dust and surface weathering products. A sample characterized by a high degree of surface

topography will not allow the user to ensure that the sample is flush with the instrument's window, effectively increasing the distance between the sample and the detector, and decreasing the potential signal that is received by the detector.

Under ideal circumstances (flat surfaces, homogenous sample, data reduction using calibration curve based on similar rock types) the hXRF can provide data for several geologically-important elements that are comparable to laboratory XRF instruments. Our tests on the Apollo sample suite provided fairly accurate analyses of the samples (Table 2). The analyses were acquired using the same parameters (60 s on a flat surface, no other preparations), and in accordance with the laboratory rules for using the samples. What inconsistencies are present in the data are likely due to the high degree of compositional heterogeneities and the complex petrology common in lunar samples available for analysis. When compared to the relatively homogenous terrestrial sample standards selected for this study, the lunar samples analyzed here are remarkably complex. Analyses were completed on whichever sawed, flat surfaces already existed on the Apollo samples, meaning that there was not much flexibility in the precise locations where hXRF data could be taken. Despite the less-than-ideal analysis conditions, the hXRF was fairly accurate in determining the chemistry of these extraterrestrial samples, at least in the elements shown to be most robust with the calibration curves discussed above.

Though the hXRF is able to dependably measure some geologically-important elements (such as Si, Ca, Ti, and K), the instrument is still unable to detect other important elements reliably (i.e. Mg, Na). This limits the usefulness of the instrument when compared to laboratory techniques. Despite this fact, the technology still represents a considerable advancement in the ability of field scientists to gain an *in situ* geochemical understanding of a site of interest, as the elements detected reliably by the instrument are sufficient to gain an initial understanding of the terrain as well as to assist the user in triaging samples for follow-up laboratory analysis.

Our assessment of the hXRF indicates that it holds significant potential as a geochemical tool both for terrestrial field geologists and for astronauts on future planetary surface exploration

missions. Our data (Table 2) demonstrate that this instrument provides rapid, although at present limited, diagnostic geochemical data on samples collected during exploration traverses on the Moon. We believe, based on our tests, that if the Apollo astronauts had used this instrument in the field, they would have gained real-time contextual awareness for their geologic surroundings, which could have altered their traverse activities and samples selected for return to Earth.

Future studies will evaluate the instrument's applicability across a greater range of sample compositions, not just homogenous basalts. We are also testing ways to collect data on non-volcanic samples, including coarse grained samples, alteration products and regolith. Another future study will examine the effect the hXRF would have on a simulated planetary surface mission with pre-designed traverse plans.

The data shown in Table 2 also illustrate the amount of variation for each major element. While some element oxides (i.e. SiO₂, TiO₂, and even Al₂O₃) are fairly reliable when compared to laboratory values, other element oxides (such as MgO, K₂O, and P₂O₅) vary from the laboratory values to a greater degree. The spread in measured MgO amounts is most likely related to the fact that Mg detection is at the edge of currently available hXRF instrument capabilities. The variance in MnO, K₂O, and P₂O₅ relates directly to the small concentrations contained in these basaltic samples, so that small analytical differences in measurements using our hXRF result in a greater ratio. Future work will include studies on samples with a greater distribution of these oxides.

5. Conclusions

Though prior industrial and other scientific applications of handheld XRF systems have proven successful (Potts et al., 1995; Potts and West, 2008; Phillips and Speakman, 2009; Liritzis and Zacharias, 2010; Zurfluh et al., 2011), these instruments are rarely used by field geologists. Our work shows that hXRF is a viable method for producing basic geochemical analyses during field mapping exercises with results that are generally comparable with laboratory XRF results for most elements, albeit with lower precision. Measurements made on fresh outcrop surfaces take about 60 s and yield results that can help inform lithologic correlations during fieldwork. When desirable, some on-site sample preparation (such as breaking and smoothing fresh surfaces) can improve the precision and accuracy of hXRF results. Handheld XRF data may be especially valuable for determining which samples to collect for further geochemical or geochronological analysis. For example, rapid high-grading of volcanic rocks with relatively high K₂O contents prior to collection may substantially improve the quality of subsequent ⁴⁰Ar/³⁹Ar geochronologic studies of collected samples.

In the future, small portable or handheld XRF instruments could prove extremely useful for missions of scientific exploration in the inner Solar System. Such instruments on missions that employ rovers could transmit geochemical data back to Earth for adaptive traverse planning, and could inform sample collection and archiving for future return to Earth. Rapid contact analysis by hXRF may be especially desirable for use by astronaut geologists given the tight time constraints of extravehicular activity (Hodges and Schmitt, 2011).

Despite the promise of hXRF technology for use in field geologic investigations, this technology should still be regarded as a work in progress. Possible beneficial technological advances include an expansion of the number of elements that can be analyzed, beyond the four of ten elements (Si, Ca, Ti, and K) in a standard whole-rock analysis that today can give the most reliable results, as well as increases in detection limits and improvements in analytical precision. Sodium, for example, is too light to precisely measure with

current hXRF instrumentation, and our data demonstrate that it is difficult to reliably measure Mg, a key element in classifying basalts. Commercial manufacturers of hXRF instruments are refining their products and we anticipate that future instrument development iterations will be guided by the needs and operational experiences of an expanding scientific user base. In addition to challenges with analyzing lighter element, commercial hXRF models have other characteristics that limit their immediate utility to field geologists. As discussed above, they are calibrated using materials not relevant to geologists. Additionally, their user interfaces are not designed for specific use in field geology, meaning that it can be difficult to very rapidly interpret geochemical data in the field. Our team is currently working on developing new technologies for *in situ* geochemical analysis to mitigate some of these issues that arise with buying commercially available units. Future work will center on these challenges and attempt to mitigate them through new and emerging technology.

Our tests focused on major element compositions of predominantly fine-grained basaltic rocks. More work is required to define operational parameters appropriate for a wider range of lithologies. For example, in more porphyritic rocks, more work is needed to determine how many analysis spots on a surface would, when averaged, produce values comparable to bulk-rock analysis. In addition, we know little as yet regarding the best practice for measuring trace elements. Future work will focus on refining sampling protocols that benefit from hXRF instrumentation. This will include developing algorithms for quickly ingesting the data outputs from the hXRF and reducing them to produce reliable geochemical fingerprints for a variety of rock types in real time. Our instrument's software interfaces were developed for industrial applications and did not directly yield meaningful data such as geochemical classification. The data we collected were time consuming to reduce, and the procedure would be too inefficient for large quantities of samples, especially in real-time. Having demonstrated that sample preparation and presentation have an important effect on the quality of hXRF data, we suggest that hXRF technological advances co-evolve with the development of integrated sample preparation tools – perhaps similar to the Rock Abrasion Tool on the Mars Exploration Rovers. With these instrument and operational improvements, the use of handheld, field-friendly geochemical tools can revolutionize terrestrial field geology and become critical tools for future planetary field explorers. Our work has provided the first comprehensive look at the hXRF as a valuable tool for both terrestrial and planetary field geology, investigating strengths, weaknesses, and best practices for deploying the instrument. We will continue to perform both laboratory calibration work on an expanded set of lithologies as well as conduct field evaluations of this technology for future integration with planetary surface exploration missions.

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References

- Allen, C., Sellar, G., Nunez, J.I., Winterhalter, D., Farmer, J., 2010. Lunar reference suite to support instrument development & testing. In: 41st Lunar and Planetary Science Conference. Abstract 1457.
- Anderson, R.B., Morris, R.V., Clegg, S.M., Bell III, J.F., Wiens, R.C., Humphries, S.D., Mertzman, S.A., Graff, T.G., McInroy, R., 2011. The influence of multivariate analysis methods and target grain size on the accuracy of remote quantitative chemical analysis of rocks using laser induced breakdown spectroscopy. *Icarus* 215, 608–627.
- Bartlett, P.W., Carlson, L.E., Chu, P.C., Davis, K.R., Gorevan, S., Kusack, A.G., Myrick, T.M., Wilson, J.J., 2005. Summary of rock abrasion tool (RAT) results pertinent to the Mars Exploration Rover science data set. In: 36th Lunar and Planetary Science Conference. Abstract 2292.
- Beckhoff, B., Kannigieser, B., Langhoff, N., Wedell, R., Wolff, H., 2006. *Handbook of Practical X-ray Fluorescence Analysis*. Springer, New York.
- Boyd, F.R., Mertzman, S.A., 1987. Composition and structure of the Kaapvaal lithosphere, southern Africa. *Magmat. Process. Physicochem. Princ.* 1, 13–24.
- Brückner, J., Dreibus, G., Rieder, R., Wänke, H., 2003. Refined data of Alpha Proton X-ray Spectrometer analyses of soils and rocks at the Mars Pathfinder site: implications for surface chemistry. *J. Geophys. Res.* 108, 8094.
- Compston, W., Berry, H., Vernon, M.J., Chappell, B.W., Kaye, M.J., 1971. Rubidium-strontium chronology and chemistry of lunar material from the Ocean of Storms. In: *Proceedings of the 2nd Lunar Science Conference*, vol. 2, pp. 1471–1485.
- Cuttitta, F., Rose Jr., H.J., Annell, C.S., Carron, M.K., Christian, R.P., Ligon Jr., D.T., Dwornik, E.J., Wright, T.L., Greenland, L.P., 1973. Chemistry of twenty-one igneous rocks and soils returned by the Apollo 15 mission. In: *Proceedings of the 4th Lunar Science Conference*, vol. 2, pp. 1081–1096.
- Duncan, A.R., Erlank, A.J., Willis, J.P., Ahrens, L.H., 1973. Composition and interrelationships of some Apollo 16 samples. In: *Proceedings of the 4th Lunar Science Conference*, vol. 2, pp. 1097–1113.
- Evans, C.A., Calaway, M.J., Bell, M.S., Young, K.E., 2013. GeoLab – a habitat based laboratory for preliminary examination of geological samples. *Acta Astronaut.* 90, 289–300.
- Gellert, R., Campbell, J.L., King, P.L., Leshin, L.A., Lugmair, G.W., Spray, J.G., Squyres, S.W., Yen, A.S., 2009. The alpha particle X-ray spectrometer (APXS) for the Mars Science Laboratory (MSL) Rover Mission. In: 40th Lunar and Planetary Science Conference. Abstract #2364.
- Hodges, K.V., Schmitt, H.H., 2011. A new paradigm for advanced planetary field geology developed through analog experiments on Earth. In: Garry, W.B., Bleacher, J.E. (Eds.), *Analogues for Planetary Exploration*, pp. 17–31. Geological Society of America Special Paper 483.
- Jenkins, R., 1999. *X-ray Fluorescence Spectrometry*, second ed. Wiley-Interscience, New York.
- Jenkins, R., Gould, W.R., Gedcke, D., 1995. *Quantitative X-ray Spectrometry*, second ed. Marcel Dekker, Inc., New York.
- Liritzis, I., Zacharias, N., 2010. Portable XRF of archaeological artifacts: current research, potentials and limitations. In: Shackley, M.S. (Ed.), *X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology*. Springer, New York, pp. 109–142.
- Longoni, A., Fiorini, C., Leutenegger, P., Sciuti, S., Fronterotta, G., Strüder, L., Lechner, P., 1998. A portable XRF spectrometer for non-destructive analysis in archaeometry. *Nucl. Instrum. Methods Phys. Res. Sect. A Accel. Spectrom. Detect. Assoc. Equip.* 409, 407–409.
- Margui, E., Hidalgo, M., Queralt, I., Van Meel, K., Fontas, C., 2012. Analytical capabilities of laboratory, benchtop and handheld X-ray fluorescence systems for detection of metals in aqueous samples pre-concentrated with solid-phase extraction disks. *Spectrochim. Acta Part B At. Spectrosc.* 67, 17–23.
- Markey, A.M., Clark, C.S., Succop, P.A., Roda, S., 2008. Determination of the feasibility of using a portable X-ray fluorescence (XRF) analyzer in the field for measurement of lead content of sieved soil. *J. Environ. Health* 70, 24–29.
- Maxwell, J.A., Peck, L.C., Wijk, H.B., 1970. Chemical composition of Apollo 11 lunar samples 10017, 10020, 10072, and 10084. In: *Proceedings of the Apollo 11 Lunar Science Conference*, vol. 2, pp. 1369–1374.
- Meyer, C., Lunar Sample Compendium, <http://curator.jsc.nasa.gov/Lunar/lsc/index.cfm> (Accessed March 2014).
- Ming, D.W., Mittlefehldt, D.W., Morris, R.V., Golden, D.C., Gellert, R., Yen, A., Clark, B.C., Squyres, S.W., Farrand, W.H., Ruff, S.W., Arvidson, R.A., Klingelhöfer, G., McSween, H.Y., Rodionov, D.S., Schröder, C., de Souza Jr., P.A., Wang, A., the Athena Science Team, 2006. Geochemical and mineralogical indicators for aqueous processes in the Columbia Hills of Gusev crater, Mars. *J. Geophys. Res.* 111, E02S12. <http://dx.doi.org/10.1029/2005JE002560>.
- Norrish, K., Chappell, B.W., 1977. X-ray fluorescence spectrometry. *Physical Methods in Determinative Mineralogy*, pp. 201–272.
- Norrish, K., Hutton, J.T., 1969. An accurate X-ray spectrographic method for the analysis of a wide range of geological samples. *Geochim. Cosmochim. Acta* 33, 431–453. [http://dx.doi.org/10.1016/0016-7037\(69\)90126-4](http://dx.doi.org/10.1016/0016-7037(69)90126-4).
- Parrish, W., 1956. X-ray spectrochemical analysis. *Phillips Tech. Rev.* 17, 269–286.
- Phillips, S.C., Speakman, R.J., 2009. Initial source evaluation of archaeological obsidian from the kuril islands of the Russian Far East using portable XRF. *J. Archaeol. Sci.* 36, 1256–1263.
- Potts, P.J., Webb, P.C., Williams-Thorpe, O., Kilworth, R., 1995. Analysis of silicate rocks using field-portable X-ray fluorescence instrumentation incorporating a mercury (II) iodide detector: a preliminary assessment of analytical performance. *The Analyst* 120, 1273–1278.
- Potts, P.J., West, M., 2008. *Portable X-ray Fluorescence Spectrometry: Capabilities for In Situ Analysis*. The Royal Society of Chemistry, Cambridge.
- Rhodes, J.M., Hubbard, N.J., Weismann, H., Rodgers, K.V., Brannon, J.C., Bansal, B.M., 1976. Chemistry, classification, and petrogenesis of Apollo 17 mare basalts. In: *Proceedings of the 7th Lunar Science Conference*, pp. 1467–1489.
- Rieder, R., Economou, T., Wanke, H., Turkevich, A., Crisp, J., Brückner, J., Dreibus, G., McSween Jr., H.Y., 1997. The chemical composition of martian soil and rocks returned by the mobile alpha proton X-ray spectrometer: preliminary results from the X-ray mode. *Science* 278, 1771–1774.
- Rieder, R., Gellert, R., Brückner, J., Klingelhöfer, G., Dreibus, G., Yen, A., Squyres, S.W., 2003. The new Athena alpha particle X-ray spectrometer for the Mars Exploration Rovers. *J. Geophys. Res.* 108, 8066.
- Rose Jr., H.J., Cuttitta, F., Berman, S., Carron, M.K., Christian, R.P., Dwornik, E.J., Greenland, L.P., Ligon Jr., D.T., 1973. Compositional data for twenty-two Apollo 16 samples. In: *Proceedings of the 4th Lunar Science Conference*, vol. 2, pp. 1149–1158.
- Ryder, G., Schuraytz, B.C., 2001. Chemical variation of the large Apollo 15 olivine-normative mare basalt rock samples. *J. Geophys. Res.* 106, 1435–1451.
- Shackley, M.S. (Ed.), 2010. *An Introduction to X-ray Fluorescence Spectrometry for Archaeologists*. In *X-ray Fluorescence Spectrometry (XRF) in Geoarchaeology*. Springer, New York, pp. 7–44.
- Shaw, C.H., 1952. Chemical analysis by X-rays. *Ohio J. Sci.* 52, 134–145.
- Shrivastava, P., O'Connell, S., Whitley, A., 2005. Handheld X-ray fluorescence: practical application as a screening tool to detect the presence of environmentally-sensitive substances in electronic equipment. In: *Proceedings of the 2005 IEEE International Symposium on Electronics and the Environment*, pp. 157–162.
- Squyres, S.W., Arvidson, R.E., Bell III, J.F., Brückner, J., Cabrol, N.A., Calvin, W., Carr, M.H., Christensen, P.R., Clark, B.C., Crumpler, L., Des Marais, D.J., d'Uston, C., Economou, T., Farmer, J., Farrand, W., Folkner, W., Golombek, M., Gorevan, S., Grant, J.A., Greeley, R., Grotzinger, J., Haskin, L., Herkenhoff, K.E., Hviid, S., Johnson, J., Klingelhöfer, G., Knoll, A.H., Landis, G., Lemmon, M., Li, R., Madsen, M.B., Malin, M.C., McLennan, S.M., McSween, H.Y., Ming, D.W., Moersch, J., Morris, R.V., Parker, T., Rice Jr., J.W., Richter, L., Rieder, R., Sims, M., Smith, M., Smith, P., Soderblom, L.A., Sullivan, R., Wänke, H., Wdowiak, T., Wolff, M., Yen, A., 2004. The opportunity Rover's Athena science investigation at Meridiani Planum, Mars. *Science* 306, 1698–1703.
- Strüder, L., Lechner, P., Leutenegger, P., 1998. Silicon drift detector – the key to new experiments. *Naturwissenschaften* 85, 539–543.
- Taylor, S.R., Kaye, M., Muir, P., Nance, W., Rudowski, R., Ware, N., 1972. Composition of the lunar uplands: chemistry of Apollo 14 samples from Fra Mauro. In: *Proceedings of the 3rd Lunar Science Conference*, vol. 2, pp. 1231–1249.
- von Hevesy, G., 1932. *Chemical Analysis by X-rays and Its Applications*. McGraw-Hill, New York.
- Willis, J.P., Ahrens, L.H., Danchin, R.V., Erlank, A.J., Gurney, J.J., Hofmeyr, P.K., McCarthy, T.S., Orren, M.J., 1971. Some interelement relationships between lunar rocks and fines, and stony meteorites. In: *Proceedings of the 2nd Lunar Science Conference*, vol. 2, pp. 1123–1138.
- Young, K.E., Evans, C., Allen, C., Mosie, A., Hodges, K.V., 2011. In-situ XRF measurements in lunar surface exploration using Apollo samples as a standard. In: 42nd Lunar and Planetary Science Conference. Abstract #2121.
- Young, K.E., Evans, C., Hodges, K.V., 2012. Evaluating handheld X-ray fluorescence (XRF) technology in planetary exploration: demonstrating instrument stability and understanding analytical constraints and limits for basaltic rocks. In: 43rd Lunar and Planetary Science Conference. Abstract #2628.
- Young, K.E., Bleacher, J.E., Evans, C.A., Arzoumanian, Z., Gendreau, K., Hodges, K.V., 2014. The integration of handheld technologies into planetary surface exploration. In: *Annual Meeting of the Lunar Exploration Analysis Group (2014)*. Abstract #3043.
- Young, K.E., Bleacher, J.E., Evans, C.A., Rogers, A.D., Ito, G., Arzoumanian, Z., Gendreau, K., 2015. Examining volcanic terrains using in situ geochemical technologies; implications for planetary field geology. In: 46th Lunar and Planetary Science Conference. Abstract #1658.
- Zurfluh, F.J., Hofmann, B.A., Gnos, E., Eggenberger, U., 2011. Evaluation of the utility of handheld XRF in meteoritics. *X-ray Spectrom.* 40, 449–463.