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Emulation of the Curiosity rover alpha particle X-ray spectrometer with accelerator-based PIXE: Implications for calibration

Erin L. Flannigan, John L. Campbell*

Guelph-Waterloo Physics Institute, University of Guelph, Guelph, Ontario N1G2W1, Canada

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ABSTRACT

A 2.5 MeV broad-beam PIXE system was designed to emulate the alpha particle X-ray spectrometer (APXS) of the Curiosity rover. APXS measurements of the light elements (sodium, magnesium and aluminum) in powdered rock standards showed systematic deviations arising from the rock's violation of the assumption of atomic scale sample homogeneity. These deviations, which are dependent on the iron concentration of the sample, were confirmed with high-accuracy accelerator-based PIXE measurements. Systematically low iron concentrations, not seen in APXS measurements, were present in the PIXE results. These are unlikely to arise due to violation of the homogeneity assumption. Measured particle-size distributions suggest that they are more likely due to the grain size distribution of iron-bearing minerals in the powdered standards. Terrestrial analogs to recently discovered Martian rock types were used to extend the calibration to include high iron and high-alkali samples.

1. Introduction

The alpha particle X-ray spectrometers (APXS) on the Mars rovers Spirit, Opportunity and Curiosity provide elemental analysis of rocks and soils through a combination of particle-induced X-ray emission (PIXE) and X-ray fluorescence (XRF). Six ^{244}Cm sources are arranged in a ring with a collimated silicon drift detector at its centre. The 5.8 MeV alpha particles, reduced to ~5 MeV by passage through a protective titanium foil cover, provide the PIXE excitation, while the XRF is accomplished via the L X-rays that arise from internal conversion of the 42.8 keV transition in the ^{240}Pu daughter. Geochemical reference materials (GRMs) are employed to calibrate these instruments. In the resulting spectra, an example of which is in Fig. 1, the peaks of the lightest elements ($11 \le Z \le 17$) are excited entirely, or almost so, by PIXE, while XRF dominates for the heavier ones ($Z > 26$). For elements such as calcium and titanium, the two processes contribute almost equally. Deduction of element concentrations from these unique spectra requires non-linear least-squares fitting together with conversion of the resulting peak areas to element concentrations through consideration of ion and photon interactions in the sample.

The first approach to deducing concentrations [1] uses the well-known [2] XRF relationships between X-ray yield and concentration for the PIXE branch as well as, obviously, for the XRF branch. This approximation is justified by the observation that the alpha particle range is much larger than the attenuation length of the excited characteristic X-rays, and thus the PIXE interrogation depth is largely determined by the attenuation coefficient of the latter. The ratio between peak count per unit time and concentration, i.e. the sensitivity, is determined. This relationship varies only slowly with atomic number, an advantage which reflects the opposite Z-dependences of the PIXE and XRF cross-sections. A benefit of this approach is that the sensitivity curve can be transferred from one instrument to another through a simple comparison of peak areas. The approach has been used for all APXS spectra from the Mars Exploration Rover (MER) and Mars Science Laboratory (MSL) missions.

A second calibration method [3,4] has been developed by incorporating XRF into the GUPIX code [5,6], which has been widely used by PIXE laboratories for three decades. This code, named GUAPX, takes a “fundamental parameters with standards” (denoted hereafter as FPS) approach, in which the GRMs are utilized differently from the first approach [1]. The spectrum fitting approach differs only in minor ways from that of the first approach but the physics of both XRF and PIXE are treated rigorously in the determination of matrix effects. Values of various instrument parameters have to be determined, either from literature or manufacturer, and also by measurements with a subset of GRMs that are single minerals and therefore constitute homogeneous samples on the distance scale of the alpha particles and X-rays involved. That having been accomplished, concentrations across the entire suite of GRMS (mostly heterogeneous) can be determined and compared with the certified values.

For the light elements excited by PIXE in the Curiosity APXS this comparison revealed systematic departures from unity of the ratio *R*

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* Corresponding author.
E-mail address: icampbel@uoguelph.ca (J.L. Campbell).

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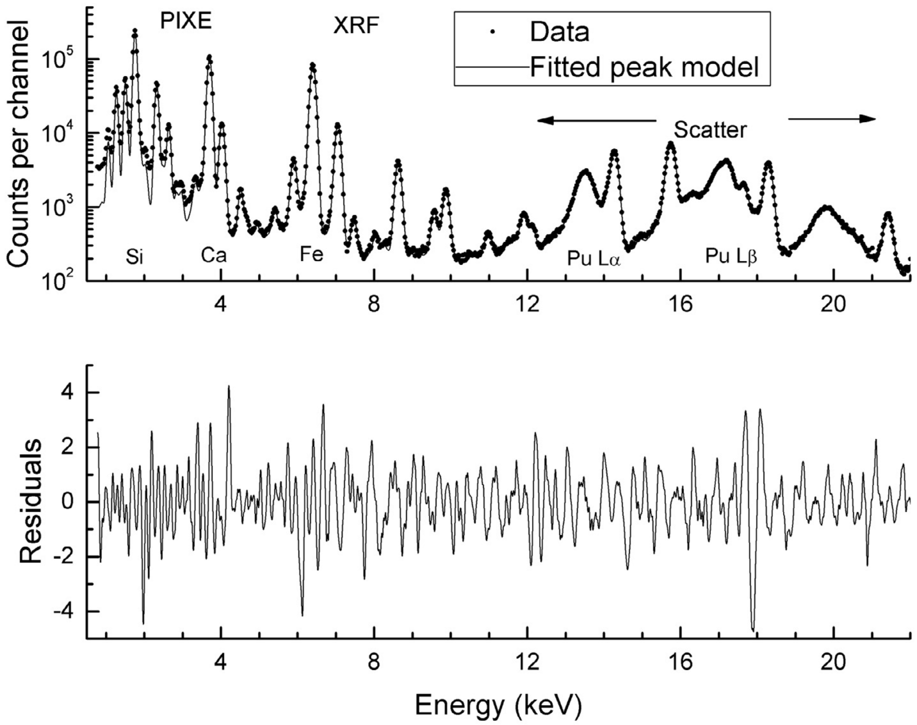

Fig. 1. The APXS spectrum recorded on Sol 704 of the Mars Science Laboratory mission. A digital filter is used to remove the background, which is not shown in the fit, and thus the fit curve shows only the contributing peaks.

between measured and certified concentration [7].

This is not a surprising observation, given that different elements are located in the several different minerals that comprise any rock. The range of alpha particles (see Fig. 2) is such that a given alpha is absorbed within a single mineral. The assumption of homogenous distribution of atoms throughout the entire sample that is inherent in both calibration methods is clearly violated by multi-mineralic rocks. Using widely accepted igneous rock classification schemes, these systematic trends were shown in Ref. [7] to be functions of igneous rock type. However, there remained significant scatter of *R*-value within each rock type, and this is likely due to the effects of grain shape and size.

An improved understanding of these mineralogy-dependent effects has the potential to provide improvements in the analytical accuracy of the APXS. To pursue these issues further and in more depth, we have constructed an accelerator-based PIXE facility that enables us to emulate the 5 MeV alpha particles of the APXS with a 2.5 MeV proton beam. We are not seeking equivalence in terms of using a proton energy that provides velocity matching with the 5 MeV alphas; the required ~1 MeV proton energy would be entirely unsuitable. Instead, our proton energy is chosen to ensure that, as per the alpha particle discussion in the preceding paragraph, the interrogation is for a single mineral. This enables our primary objective, which is to attempt to reproduce the *R*-values of our APXS calibration. It also lays the groundwork for a planned series of studies of particle-size effects, which are more easily carried out with the PIXE system than with the APXS.

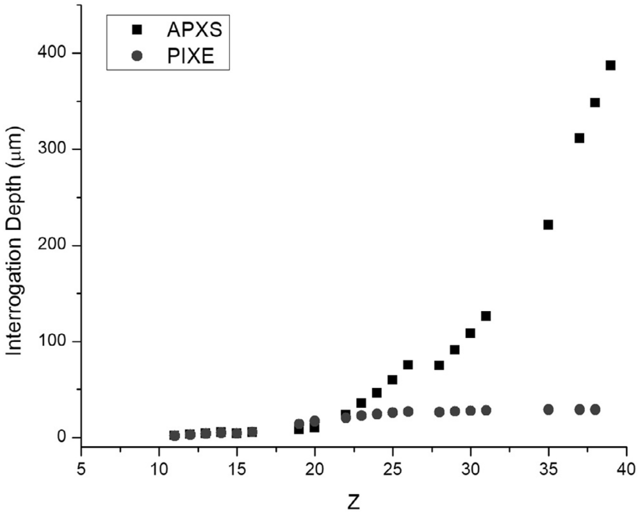

Fig. 2. Dependence on atomic number of interrogation depth (depth from which 90% of the excited X-rays emerge) for a Martian mudstone. The increased difference between the APXS and PIXE interrogation depths starting around Z = 25 is due to the XRF contribution of the APXS.

We report here our PIXE study of a subset of the GRM suite and we compare PIXE *R*-values with those determined earlier [7] for the MSL APXS. Additionally, we have expanded the suite of reference materials to include several previously excluded terrestrial rock types which are analogues for rocks [8] found unexpectedly in Gale Crater by Curiosity.

2. Reprise of APXS results

Fig. 3 is an example of the trends revealed in the FPS calibration exercise [7] for the laboratory APXS unit. The *R*-value for aluminum increases, albeit with significant scatter, as the iron content increases, i.e. as the rock type changes from felsic to mafic. New data from five Icelandic basalts provided by the Royal Ontario Museum (ROM) were recorded just after publication of Ref. [7], and are added in this figure. Analogous results for sodium show a clear correlation with the aluminum *R*-values. The magnesium results are similar but in the opposite direction. Within error limits the silicon results show no dependence on rock type or iron content.

These effects reach a maximum in basalts. In basalts the iron is housed in mafic minerals (pyroxenes, olivines…) while the aluminum and sodium are located mostly in feldspars, which have negligible iron content. It follows that in the near-surface interactions of the alpha particles the escaping sodium and aluminum X-rays are not subject to attenuation by iron. But the presently unavoidable assumption of atomic homogeneity that is common to both spectrum treatment approaches [1,7] does not recognize these differentiated locations of the elements; as a consequence the computation of matrix effects imposes