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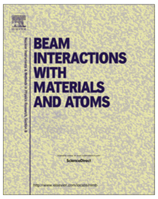

Non-linearity issues and multiple ionization satellites in the PIXE portion of spectra from the Mars alpha particle X-ray spectrometer

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ABSTRACT

Spectra from the laboratory and flight versions of the Curiosity rover's alpha particle X-ray spectrometer were fitted with an in-house version of GUPIX, revealing departures from linear behavior of the energy-channel relationships in the low X-ray energy region where alpha particle PIXE is the dominant excitation mechanism. The apparent energy shifts for the lightest elements present were attributed in part to multiple ionization satellites and in part to issues within the detector and/or the pulse processing chain. No specific issue was identified, but the second of these options was considered to be the more probable. Approximate corrections were derived and then applied within the GUAPX code which is designed specifically for quantitative evaluation of APXS spectra. The quality of fit was significantly improved. The peak areas of the light elements Na, Mg, Al and Si were changed by only a few percent in most spectra. The changes for elements with higher atomic number were generally smaller, with a few exceptions. Overall, the percentage peak area changes are much smaller than the overall uncertainties in derived concentrations, which are largely attributable to the effects of rock heterogeneity. The magnitude of the satellite contributions suggests the need to incorporate these routinely in accelerator-based PIXE using helium beams.

1. Introduction

The Curiosity rover carrying the Mars Science Laboratory (MSL) has been using its ten instruments to study the geology of Gale Crater, Mars since landing in August 2012. This site was chosen in part because of orbital observations which suggested the presence of sedimentary layers in a central mound, potentially recording the evolution of the regional Martian environment from warm and wet to the present cold and dry [1]. Among many achievements since Curiosity's landing are the findings [2] that an ancient lake existed in the crater with a pH that could have supported microbial life. The present paper is concerned with Curiosity's alpha particle X-ray spectrometer (APXS), which employs a combination of particle-induced X-ray emission (PIXE) and X-ray fluorescence (XRF) for elemental analysis of rocks and unconsolidated material. The first encounter of APXS with the Martian regolith [3] revealed the presence of unexpected high-alkali rocks thought to have originated in the Martian mantle in the presence of water. APXS units were also deployed on the Mars Exploration Rovers (MER) Spirit and Opportunity [4].

The APXS employs a ring of six ^{244}Cm radionuclide sources, with the alpha particles providing PIXE and the L X-rays of the daughter plutonium providing XRF. The characteristic X-rays emitted by the sample are recorded by a silicon drift detector (SDD), protected by a collimator, in the center of the ring. For the MSL APXS instruments the SDD was provided by Ketek GmbH, and the subsequent signal processing system, compatible with the Curiosity rover electronics, was built by McDonald-Dettweiler Space Research Inc. with support from the Canadian Space Agency. There are two MSL APXS units: the flight-equivalent module (FEU) in the Guelph laboratory and the proto-flight module (PFM), now on Mars.

One approach to interpreting the combined PIXE + XRF spectra from the APXS is the GUAPX code [5]. This is essentially the widely used PIXE code GUPIX [6–9] with an analogous fundamental parameters treatment of X-ray fluorescence grafted on. Like its GUPIX parent, GUAPX accomplishes non-linear least-squares fitting of the spectra in a conventional manner using the Marquardt algorithm [10]. Conversion of peak areas to element concentrations involves detailed computation of all PIXE and XRF matrix effects. GUAPX was the basis of a calibration of the instrument on Curiosity [11]. This calibration is independent of the main calibration in use

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on the mission, which is a semi-empirical approach first developed for the Mars Exploration Rover Mission [4]. Both calibrations rest on a suite of ~60 geochemical reference materials (GRM) obtained by the APXS team from a wide range of national laboratories and geological surveys.

Fig. 1 shows a spectrum (denoted below as PFM5) recorded on Mars by the proto-flight module. In several regions, notably those of the lightest elements, iron, and the plutonium Lβ and Lγ scatter groups, the residues are not as satisfactory as we would wish. These effects are common across the PFM spectra. Despite this, the program generates acceptable results for element concentrations in the mineralogically homogeneous subset of our GRM suite [11].

Systematic residue excursions were also observed by us in recent PIXE analyses [12] of mineralogically homogeneous geostandards using a 3 MeV proton beam. This work used a Ketek 'AXAS' silicon drift detector unit (integrated sensor, pre-amplifier and amplifier). Its aim was to optimize the accuracy of PIXE analysis of minerals for major and minor elements. This was a preliminary step towards improving the accuracy of the PIXE component of APXS in order that we might subsequently reach a better understanding of the marked influence of sample mineralogy upon element concentrations determined when using GUAPX with igneous GRMs [11,13]. While visually obvious, these residue excursions did not cause significant error in the element concentrations provided by GUPIX. Detailed examination showed that the cause of the excursions was a departure at the lowest X-ray energies from the linear channel-energy relationship used in GUPIX. An empirical correction for this non-linearity was derived, affording major improvement in quality of fit and assisting in achieving accuracy of ~±1% in our analytical results for major and minor elements [12].

The calibration approach currently in use for the MSL APXS [4], and on which all published analyses on Mars are based, differs in a number of ways from the GUAPX approach. One difference is that while GUAPX enforces a linear energy calibration, the Gellert et al. approach [4] allows for a degree of non-linearity by permitting limited variation of peak positions relative to an overall linear relationship. The main objective for the present paper is to elucidate the impact on fitted peak areas of any non-linearity in spectra from the two Curiosity APXS instruments. Because the alpha particle PIXE excitation branch results in multiple ionization satellites, this added a layer of complexity that was essentially absent in our proton PIXE work [12] and which has not been considered in APXS work to date. The outcomes of this APXS-directed study have implications for accelerator-based PIXE using ^{3}He or ^{4}He ions.

2. Data

Six PFM spectra (labeled simply as PFM1.....PFM6, with PFM5 shown in Fig. 1)) recorded on Mars prior to the 938th day of the mission were selected for analysis, based on two criteria. The first of these was to have a wide range of peak energies present. The second criterion was to have sufficient high-intensity peaks beyond those of iron in order to accurately define the energy calibration at the high energy side of the spectra. The six PFM spectra selected had either a high-intensity Kα peak from zinc or germanium (or both) in the sample, together with a well-defined zirconium Kα peak from collimator fluorescence and Rayleigh scatter peaks from plutonium Lα, Lβ1 and Lγ1. All had excellent energy resolution (141–148 eV FWHM at 5.9 keV).

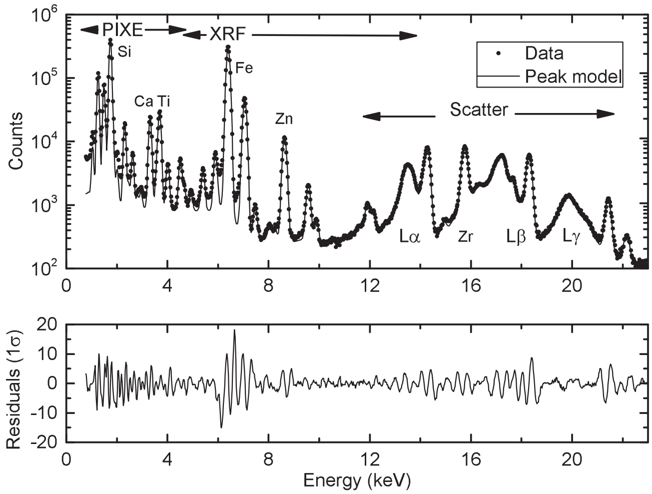

Fig. 1. The spectrum of Martian sample PFM5. The GUAPX fit was done with no energy-shift correction applied. The lower panel shows the residuals indicating the goodness of fit. A digital filter is used to remove the background, which is not shown in the fit, and thus the fit curve shows only the contributing peaks.

A subset of eight GRMs, labeled as FEU1, FEU2,...., FEU8 was selected from the sixty GRMs employed in the calibration of the FEU APXS (11). A minority of these provided zinc and/or copper peaks. All, of course, exhibited the same zirconium peaks and plutonium L X-ray scatter features as the PFM. During the calibration campaign (~2010) the energy resolution was ~180 eV. Given the broader peaks relative to the PFM, the eight spectra were selected to include cases where either the sodium or the magnesium content was close to zero, thereby improving the definition of the Kα peak of the other element of this pair.

3. Methodology

In our recent PIXE work with 3 MeV protons [12], low-energy tail parameters were accurately determined as a function of X-ray energy and could be included in the peak description within GUPIX. Their inclusion did not result in significant improvements in the overall fit residues, leading us to attribute the behavior of the latter in the main to other possible causes. In the present work, tailing parameters were derived (from single-element spectra) for the FEU-2010 exercise; such work was not possible for the PFM due to time constraints imposed by the MSL mission requirements. The FEU tail parameters were incorporated in GUAPX and their effect investigated for both APXS units. Again, while affording a slight improvement of the fit for the lightest elements, inclusion of peak tailing was not a remedy for the overall residue behavior seen in Fig. 1.

Determination of the nature and magnitude of the residue problem was undertaken using an in-house version of GUPIX (referred to below as GUFIT) which affords extended flexibility in spectrum fitting. After conclusion of the standard non-linear least-squares fit procedure, a 'manual mode' becomes available; this enables the user to experiment manually with parameter adjustments and examine ensuing residues, after which automatic mode can be restored to allow the program to make final refinements. The program employs the linear energy calibration

$$C = P_1 + P_2E \tag{1}$$

where C represents channel number and E the corresponding X-ray line energy in keV, with the parameters P_1 and P_2 being determined in the fitting procedure. The peaks are represented by Gaussians whose centroids are determined by this relationship. The APXS energy dispersion is about 25 eV per channel and so the error function is used in the Gaussian peak description to ensure proper integration of intensity over each channel; this is especially important for the narrower low-energy peaks. In the GUPIX database which