Notes on Alpha-Particle X-ray Spectrometer (APXS) Data Reduction

R. Gellert, J. Brückner, G. Dreibus, G. W. Lugmair, R. Rieder, H. Wänke and J. Zipfel,
Max-Planck-Institut für Chemie, Department of Cosmochemistry, Becher-Weg 27, D-55128 Mainz, Germany
J.L. Campbell, J. Maxwell and M. Omand
Department of Physics, University of Guelph, Guelph, Ontario, Canada N1G 2W1

Introduction

The Alpha-Particle X-ray Spectrometers (APXS) [1] on board of NASA's MER-rovers *Spirit* and *Opportunity* are small instruments, with which the chemical composition of rocks and soil can be measured by simply holding them against a sample for some time (from 10 minutes to several hours - the longer, the more accurate). The instruments have high sensitivity and selectivity for all essential rock-forming elements, because they employ radioactive sources of ^{244}Cm for excitation, and novel x-ray detectors for registration of the characteristic x-rays, emitted by the atoms in the sample: the sources emit alpha particles and x-rays, thereby effectively exciting light atoms, like Na, Mg, Al, or Si, as well as heavier atoms like Fe, Ni, Zn or Br. These sources have been especially developed for use in the APXS by the Russian Central Research Institute for Atomic Reactors in Dimitrovgrad [2]. They consist of a thin layer of curium-silicide on highly polished semiconductor-grade silicon wafers. The detectors are *silicon drift-chamber* designs, manufactured from high-purity, high-resistivity silicon by modified integrated circuit manufacturing techniques (processing of both sides of a silicon wafer is required), and containing matched first stage preamplifier transistors on the detector chips. This design results in an extremely small effective detector/amplifier-input capacitance. Due to this fact and to very small leakage currents (both bulk and JFET gate) these detectors exhibit excellent low-noise performance at temperatures close to ambient. They are a German development and are commercially available from Ketek GmbH, Munich [3]. It is most unfortunate that this feature could not be fully exploited with the flight instruments in their flight configuration: good resolution could only be obtained at temperatures below -30 °C. To explain the reasons is beyond the scope of this note: suffice it to say that we have only become aware of the circumstances at the time of integration, and that nothing could be done to resolve the problem at this late moment. In the test configuration the flight instruments did indeed deliver spectra with good resolution at temperatures as high as -10 °C and would have been perfectly suitable for *touch-and go* campaigns.

To illustrate the advantages of the *alpha plus x-ray excitation* approach, Fig.1 shows a comparison of spectra, obtained with the same sample (SSK 1.1, an andesite from a South Pacific island, which is similar in composition to the rocks at the Mars-Pathfinder landing site), using (a) combined excitation by alpha particles and x-rays (Pu L-series) from a ^{244}Cm source, (b) excitation by x-rays from a ^{244}Cm source only (alpha particles are blocked by a thin aluminium foil), and (c) excitation by a 20 keV electron-beam in a Scanning Electron Microscope.

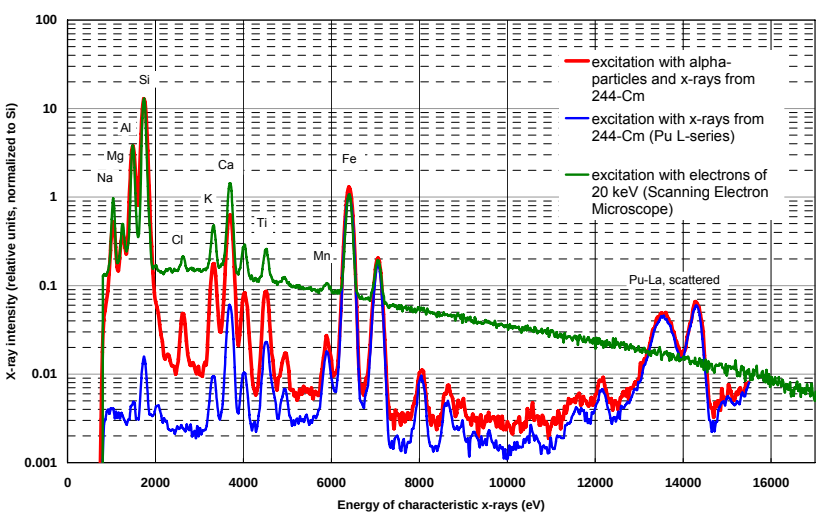

Fig 1: Comparison of x-ray spectra obtained with different excitation sources. Sample: SSK 1.1 (Andesite)

Fig. 2 shows a photograph of the flight sensor, and Fig. 3 shows the location of the APXS on the rover's Instrument Deployment Device.

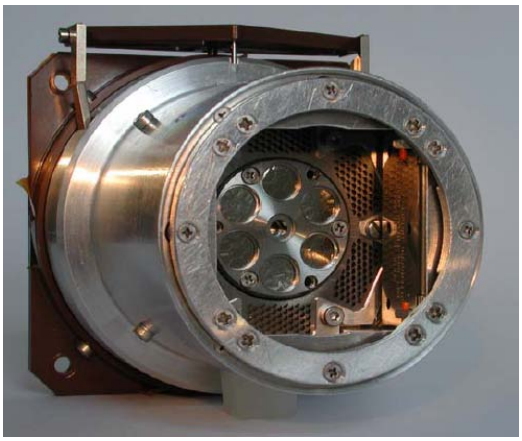

Fig.2: APXS flight sensor head with open doors

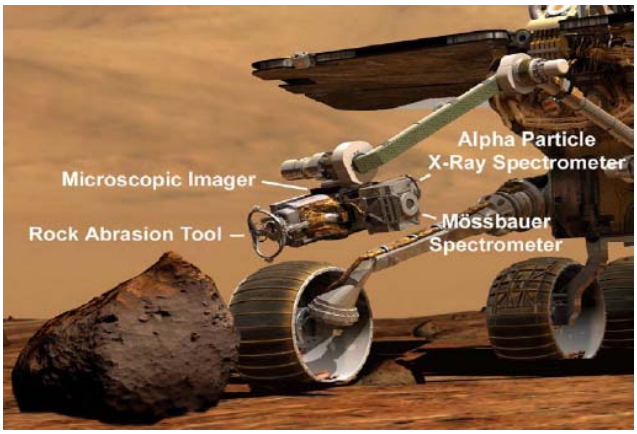

Fig.3: Mounting position of the APXS on the rover's IDD

Calibration Samples and Procedures

All instruments built for NASA-MER (two flight units, two flight-spares, and one identical *lab-reference* model, besides a fully functional engineering model) have been calibrated, using 11 complex rock samples, high purity metal oxides (sputter targets), metals and a special *calibration-standard* for cross-calibration. Most rock samples are either certified *geo-standards*, or samples with an independent analysis of their composition, obtained in our own laboratory and/or other laboratories with qualified records. An additional number of about 20 rock samples (equally qualified) and about 40 analytical grade chemical compounds have been used in an extended calibration campaign with the *lab-reference* model only. On the basis of a careful cross-calibration, results can be applied to the flight instruments, as well. The various instruments can be easily cross calibrated by comparing the response, which in this case mainly means elemental peak areas, of each instrument when identical samples are measured under identical conditions. To this end individual cross-calibration factors have been established on an element by element basis, which take care of subtle differences between the instruments in terms of thickness of detector entrance windows and source exit windows, as well as different source strength of the excitation sources.

All samples are in the form of ground powder with grain-sizes of usually less than 100 µm. Some rock samples were also available in the form of cut plates. Agreement of data measured with powders and cut plates is generally good, although there are deviations that require further study (grain-size effects, etc.). Measurements of these samples were performed both under vacuum (at a pressure of less than 10^{-2} mbar) and in a simulated Martian atmosphere (CO_2 at a pressure of 10 mbar). Special care was taken with respect to a reproducible sample-instrument geometry (flat sample surface; distance error of less than 0.05 mm), and samples were dried in vacuum at 120°C for several hours prior to exposure to the instrument.

Spectrum Deconvolution (Peak Fitting)

To extract element-specific information (peak intensities), the measured complex spectra must be *deconvoluted*. This is done by performing non-linear least squares fits, using the well-known code MINUIT [4]. The mathematical model, describing the spectral contributions, consists of functions describing the individual peaks of each element (up to 5 lines per element), exponential tailing at the low energy side of the peaks, a background component due to Compton scattering, a general

background component due to Bremsstrahlung, and functions describing the distributions resulting from elastic (Rayleigh -Thomson) and inelastic (Compton) scattering of the exciting x-radiation in the sample. Instead of using the more common Gauss-function to describe the individual peaks, this model uses error functions (integrals of Gauss-functions). This approach has yielded significant improvements, when peaks extend over only a few channels in the spectrum. Parameters of the model functions have been derived in individual fitting procedures with simpler single-element spectra, and are kept fixed relative to one another, when fitting more complex spectra. Inspection of the residua reveals that the agreement between the model and the measured data is usually well within the limits defined by counting statistics.

Matrix Correction and Derivation of Concentrations

Theoretical x-ray yields have been calculated for all calibration samples, using the computer codes YLD (for alpha-excitation) and XRFY (for x-ray excitation), provided by Campbell et al. [5]. These codes model the physical processes for alpha- and x-ray-excitation (PIXE and XRF), assuming a homogeneous matrix, a smooth surface, and well defined entrance- and exit-angles. From these yields we determined *matrix-factors* that describe the x-ray intensities (per unit concentration) of each element in the matrices of the individual calibration samples, relative to an average intensity (per unit concentration) of the whole set of samples. One of the results of these model calculations was that yields closely correlate with a function of the form $1/(\mu_{in} + \mu_{out})$, where μ_{in} stands for the mean x-ray absorption coefficient of the matrix for the *incoming* (exciting) radiation (Pu-L lines), and μ_{out} stands for the mean x-ray absorption coefficient of the matrix for the *outgoing* radiation (Fig. 4).

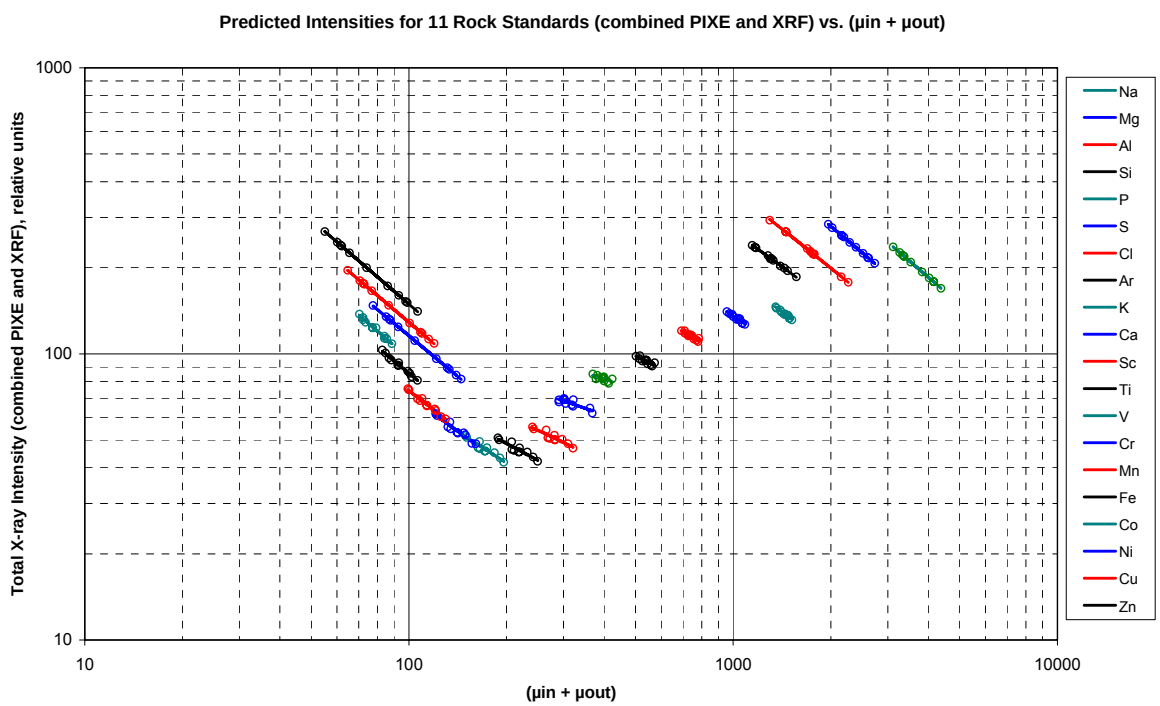

Fig. 4: Predicted x-ray yields for combined excitation by alpha-particles and x-rays from ^{244}Cm sources in the 11 rock standards used for cross calibrations between the flight instruments and the lab-reference instrument.

This was to be expected for all cases, where x-ray excitation predominates (e.g. Fe). Here, $\exp -(\mu_{in}*d)$ describes the production of x-rays in depth d in the sample by the *incoming* radiation, and $\exp -(\mu_{out}*d)$ the attenuation of the *outgoing* radiation from depth d in the sample. Integration for an infinitely thick sample (from $d = 0$ to $d = \infty$) then yields the above form. It was, however, at first a surprise that this form is also applicable to cases, where alpha excitation predominates. The

explanation is that in these cases (Na through ~ Ca) μ_{out} is much larger than μ_{in}, which means that only x-rays generated in a very shallow layer (1 to 5 µm) can penetrate to the surface. As this layer is also much thinner than the range of alpha particles (~ 30 µm), the decrease of production with depth is small and the dominant factor is μ_{out}. When applying these *matrix-factors* to the measured intensities (peak area intensities obtained from the deconvolution of the spectra), we expected to find a linear relationship between corrected intensities and concentrations. For most samples this is indeed the case. There are, however, *outliers* that we have not yet fully understood. The most obvious reason is that the above assumptions – homogeneous matrix, smooth surface, and well defined entrance- and exit-angles – are certainly not true. In particular, the assumption of homogeneity may be grossly misleading, when certain elements only occur in certain mineral phases, and we have evidence that this is indeed the case for, e.g. phosphorus, which is known to predominantly reside in apatite, and for which matrix-corrected intensities show poorer correlations with *true* concentrations than uncorrected intensities. After the behaviour of phosphorus had become apparent, a pragmatic approach was taken to include such effects: all standards have been subject to a least squares analysis, by which a linear relationship between *true* concentrations and a combination of matrix-corrected and uncorrected intensities of the form {x * corrected + (1-x) * uncorrected} was investigated, which yielded specific values of ($0 < x < 1$) for each element that appear plausible in the light of their mineralogical occurrences. For samples measured to date this pragmatic approach of *matrix correction* has been applied.

Ultimately, the composition of a sample is derived by converting results for individual elements into stoechiometric oxides (in this case Fe is converted to FeO; if Mößbauer data on the ratio of Fe^{2+}/Fe^{3+} are available, this can be refined to properly partition Fe between FeO and Fe_2O_3) and calculating closure to 100 %, neglecting possibly present *invisible*s, like H_2O and CO_2. This is done iteratively until convergence is obtained, and also yields information about the geometry (distance), in which the sample was measured.

Work in Progress

In the meantime, work continues at the University of Guelph on a more sophisticated model calculation, and first results look very promising: most importantly (and encouragingly), the differences in reduced data obtained by the more sophisticated models and the pragmatic model described above, turn out to be quite small. The more sophisticated model may, however, lend itself to the inclusion of more elaborate algorithms that could eventually include a breakdown of samples into normative minerals and a detailed computation of matrix effects in a mix of different matrices. Another issue to be handled by this model concerns the estimation of *invisibles*, in particular water, from the evaluation of the elastic and inelastic scatter peaks of the exciting x-ray lines. It is anticipated that this model will be completed and tested by the end of 2005, at which time all data (both from calibration standards and from samples on Mars) will be reprocessed and published as – hopefully – final results.

One last Comment

Readers, familiar with the problems encountered in XRF analysis of powder samples, may be surprised by the performance of the APXS – in particular with respect to light elements, like Na, Mg, Al and Si. It appears that when using alpha-particles for excitation, paired with a careful calibration, the APXS can render results of a quality far superior to the commonly adopted notion of a *qualitative*, at best *semi-quantitative* nature of such analyses.

References

[1] R. Rieder, R. Gellert, J. Brückner, G. Klingelhöfer, G. Dreibus, A. Yen, and S. W. Squyres, JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 108, NO. E12, 8066, 2003

[2] Research Institute of Atomic Reactors of the Russian Federation (RIAR) in Dimitrovgrad, Russia; http://www.niiar.ru/

[3] Ketek GmbH, Munich; http://www.ketek.net/

[4] F. James, M. Roos: MINUIT Handbook, CERN, Version 89.12 j; http://wwwasdoc.web.cern.ch/wwwasdoc/minuit/minmain.html

[5] YLD is a modified version of the PIXE-yield program GUYLS, which is part of the program package for PIXE analysis – GUPIX – available from the University of Guelph; http://pixe.physics.uoguelph.ca/gupix/main/

XRFY is a program especially written for APXS analysis by John Maxwell to predict x-ray yields from excitation by discrete x-ray lines from radioisotopes.

Both codes will become available from the University of Guelph as part of a comprehensive package (GUPIX-APXS), especially developed for the analysis of APXS data. This will also include a program for spectrum deconvolution. Anticipated time of completion is end of 2005.