SOME ASPECTS OF THE CALIBRATION OF THE MARS PATHFINDER ALPHA PROTON X-RAY SPECTROMETER. T.E. Economou¹, C.N. Foley^{1, 2}, W. Dietrich¹, and C. Hernas¹, ¹Laboratory for Astrophysics and Space Research, University of Chicago, 933 East 56th Street, Chicago, IL 60637, ² Department of Geophysical Sciences, University of Chicago, e-mail: tecon@tecon.uchicago.edu.

Introduction: The previously published APXS results [1] indicated that all the Martian soil samples analyzed at the Pathfinder site showed remarkable resemblance to those analyzed by the Viking at two different sites several thousand kilometers apart [2]. It is not unreasonable therefore to assume that, due to the mixing mostly by eolian processes, all of the soils of martian surface are of the same composition. There are, however, some differences between the Pathfinder and Viking soil samples, mostly in the amount of sulfur content, and some differences even among the Pathfinder soils that probably reflect, to some degree, the local rock contribution. The martian rocks that were analyzed by the APXS on the Pathfinder site, however, reveal a different story. All analyzed rocks are high in silica and iron and low in Mg, similar to those of terrestrial basaltic andesites or andesites, but completely different from those of SNC meteorites. These findings have significant implication about the origin and history of the planet Mars.

APXS Accuracy in the X-ray mode: During the past year, we have extensively reanalyzed and scrutinized all the data, looking for any possible source of errors that could change the conclusions drawn from the APXS analyses. One of the discovered sources of error in analyses originated in the difference between the flight instrument and the instrument used for calibration in the laboratory. For safety reasons, the flight instrument was flown without the protective thin film on the metallic supportive grid that is used in the laboratory work to avoid contamination by the intensive radioactive alpha source. That resulted in about a 14% greater alpha intensity in the flight instrument on Mars as compared to the laboratory calibrations, while the X-ray intensity is the same in both instruments. Since the excitation of the characteristic X-ray lines for each element is caused by both alpha particles and X-rays from the ²⁴⁴Cm in different ratios, our preliminary results overestimated the light elements and underestimated the heavy elements up to six relative percent.

We have analyzed the X-ray data using several methods: the abundance vs. peak area calibration curves, the fundamental parameter analysis software, and relative comparison methods. All of these analysis methods give similar results. Our confidence has increased after the comparison of the results of many geological standards analyzed by the APXS with those of conventional analyses. These comparisons, both in vacuum and in CO_2 atmosphere (see Table1), show now excellent agreement. Furthermore, we have analyzed many other powder samples and rocks where the conventional analyses were poorly or completely unknown. As shown in Fig.1, all the powders as well as the rocks are clearly separated into their expected composition zones.



Fig.1 Classification of rocks measured by APXS

Table 1: Comparison of the APXS results in the CO₂ atmosphere with those of conventional analyses (in atom %).

	A	ndesite	;]	Basalt		Granite			
	AGV1*				BCR1		G-2			
El	APXS	Conv	Δ	APXS	Conv	Δ	APXS	Conv	Δ	
0**	62.31	62.07		62.24	62.18		62.65	62.73		
Na	2.57	2.98	-0.41	2.35	2.31	+0.04	2.86	2.76	+0.09	
Mg	0.88	0.82	+0.06	1.39	1.89	-0.50	0.50	0.39	+0.11	
Al	6.69	7.30	-0.61	6.63	5.86	+0.77	6.36	6.34	+0.03	
Si	21.84	21.25	+0.59	20.19	19.71	+0.48	23.85	24.16	-0.30	
Р	0.33	0.15	+0.17	0.10	0.11	-0.01	0.00	0.04	-0.04	
S	0.03	0.00	+0.03	0.05	0.10	-0.05	0.03	0.01	+0.02	
Cl	0.02	0.01	+0.01	0.01	0.00	+0.01	0.00	0.00	0.00	
K	1.46	1.35	+0.11	0.70	0.79	-0.09	2.08	2.00	+0.08	
Ca	2.02	1.91	+0.11	2.56	2.71	-0.16	0.75	0.73	+0.01	
Ti	0.20	0.29	-0.08	0.53	0.61	-0.08	0.16	0.13	+0.04	
Mn	0.025	0.03	0.00	0.05	0.06	-0.01	0.00	0.01	-0.01	
Fe	1.62	1.84	-0.22	3.22	3.67	-0.45	0.78	0.70	+0.08	

Key: *= APXS analysis before bias correction applied **= APXS oxygen from stoichiometry.

From these analyses we have established the average bias for each element (see Table 2) and then applied it in the analyses of the martian data. The results will be verified and reported after completion of the alpha analysis. The next step in the analysis of the APXS data will be to introduce a feedback from the alpha mode into the X-ray mode and vice versa that would improve the accuracies for some elements.

Table 2: APXS average bias for each element

El	Na	Mg	Al	Si	S*	K	Ca	Ti	Mn*	Fe
Bias	-0.32	+0.07	-0.55	+0.50	+0.01	+0.24	+0.09	-0.04	-0.01	-0.19
Key:	* = mi	inimun	ı value	e due t	o low	abunda	ance of	eleme	ent in s	amples
tested										

Although several other minor errors (e.g. inconsistencies in the reference library, mixed reference library with polished and rough surfaces, etc.) were identified and their effect on the analysis evaluated, none were significant to change the general conclusions reached from the original APXS results.

Alpha and Proton modes: So far, all the results reported by the APXS were derived from its X-ray mode. The alpha and proton modes, as implemented on the Pathfinder APXS instrument, were handicapped by several design and implementation problems. The rather poor geometry of backscattering (large variation in the backscattering angle) from the sample and especially the forward scattering from the thin martian CO_2 atmosphere in the detector vicinity degraded the performance of the alpha mode. Also, the necessity to substitute for the Mars missions the 244 Cm (E α =5.8 MeV) for the originally used 242 Cm $(E\alpha=6.1 \text{ MeV})$ in other missions, resulted in operating at a region of one of the largest resonances in the scattering cross section of alpha particles from carbon in the CO₂ atmosphere. Another problem in the analysis of the alpha data is the rather large variability of the peak area of carbon and oxygen in the martian atmosphere due to the change of the gas column in the source-sample-detector geometry either by variation of the distance to the sample, or more importantly by wide diurnal changes of martian temperature and pressure. However, in spite of these problems, the alpha and proton modes are very useful in providing total concentration of C and O for absolute normalization purposes. Also, they will give redundant information on many other elements that can be compared with the results from the X-ray mode.

One of the easiest elements to determine from the alpha data is Fe. Iron on Mars, as determined from the X-ray data, is consistently lower in rocks than in the soil samples. However, iron determined from the alpha data showed practically no such difference. When the Fe alpha raw intensities were plotted against the X-ray intensities from the same sample, all the rocks lay on a different line than the line for soil samples and all the terrestrial rocks we have analyzed (Fig.2).



Fig.2 Fe intensities from alpha and X-ray modes

We think that this is connected with the amount of dust that covers the Martian rocks: the alpha mode determines the Fe of the top few microns covered mostly by dust and therefore it sees mostly the dust, while the X-rays samples the rock down to tens of microns. From this finding we hope to establish the fraction of the rock area covered by the martian dust.

Another element that can be determined only by the alpha mode is carbon. Carbon on Mars, although strongly affected by the CO_2 atmosphere, can still be detected in the alpha mode if present above about 0.5% by atom.

Oxidation State: The direct determination of oxygen by the alpha mode can help to determine the oxidation state of Fe and S. Even with the preliminary determination of oxygen, Fig. 3 shows that most of the residual oxygen that is still available after accounting for the stoichiometry with any metal can be explained if we assume sulfur to be in - SO_4 form rather than in pure elemental form.



Fig.3 Residual oxygen in martian samples

References: [1] Rieder, R., T. Economou, H. Wänke, A. Turkevich, J. Crisp, J. Brückner, G. Dreibus, H.Y. McSween, Jr (1997) Science, Vol.278, pp. 1771-1774. [2] B.Clark et al., (1982), J. Geophys. Res. 87, 10059.