Chemistry of Mars Pathfinder Samples Determined by the APXS. C. N. Foley[1], T. E. Economou[1], R. N. Clayton[2], [1]Laboratory for Astrophysics and Space Research, University of Chicago, 933 East 56th Street, Chicago, IL 60637, USA, e-mail: nfoley@geosci.uchicago.edu, [2]Enrico Fermi Institute, University of Chicago, Chicago IL 60637, USA

Introduction: We have examined numerous samples in the laboratory with a flight duplicate to calibrate all three modes (X-ray, alpha, and proton) of the APXS under Martian conditions. Previously reported preliminary X-ray results [1] were based on calibration data before instrumental biases were determined and before a minor instrumental difference between the laboratory and flight instrument was taken into account. Also, these preliminary results [1] did not include alpha and proton results. The alpha mode in particular reveals the amounts of carbon and oxygen, important for understanding of the volatile contents of the Pathfinder samples. In order to determine the abundances from the alpha/proton modes, a technique for atmosphere subtraction from the spectra was developed [2]. The flight duplicate has been used to determine the accuracy of analysis under Martian conditions with all three modes of the APXS [2,3]. With this laboratory tested analysis technique, we have now re-analyzed the Pathfinder data.

Pathfinder Chemical Results: Pathfinder sample abundances determined by the X-ray mode are listed in table I. The alpha/proton modes yield similar bulk abundances, on a volatile free basis, to the X-ray mode for Pathfinder rocks [3]. However, the alpha/proton mode abundances for soils, on a volatile free basis, are approximately 20 relative % lower than X-ray for iron and approximately 16 and 2 relative % higher for calcium and silicon respectively.

Alpha/Proton Mode Carbon and Oxygen. No carbon is detected in the Pathfinder samples. Therefore, the abundance of sample carbon is below the APXS detection limit of 0.3 wt% [3]. However, the bulk oxygen determination from the alpha mode has yielded some excessive amounts of oxygen possibly indicating the presence of chemically bound water.

The bulk oxygen content of most soils is accounted for assuming stoichiometric oxygen for all elements detected with all iron in the 3+ oxidation state and all sulfur in the 6+ oxidation state. This result agrees with the observations from the imager for Mars Pathfinder (IMP) [4,5,6] that the soils are redder and hence contain more Fe^{3+}. It also agrees with the Viking soil analyses which determined that sulfur is likely to be in the 6+ oxidation state [7]. If some soils, however, contain a mix of FeO and Fe_2O_3 then they contain some excess oxygen unaccounted for by all elements detected. In contrast to the soils, the bulk oxygen content of the rocks cannot be accounted for even by assuming all iron as Fe^{3+} and sulfur as S^{6+}. This excess oxygen is larger for rocks A-7, A-8**, and A-17 and smaller for rocks A-3, A-16, and A-18.

The presence of excess oxygen in some Pathfinder samples is seen in the raw data from the alpha mode. The alpha spectra consist of stacked rectangular-like signals as schematically illustrated in figure 1. Figure 1 also shows the spectral match for A-10 bulk oxygen with the assumptions of Fe_2O_3 and SO_3 indicating no excess oxygen above these assumptions. Figure 2 shows the excess oxygen present in A-17 even after assuming Fe_2O_3 and SO_3. Figure 2 also shows that this excess oxygen is not bound with carbon, which would be detected by a rectangular-like contribution in channels 15-40. The excess oxygen in A-17 as well as other Pathfinder rocks supports the presence of water in these samples, because the H and He are the only two elements that the APXS cannot detect directly. Although hydrogen cannot be directly measured by the APXS, its presence is inferred by excess oxygen above that which can be bound with all other detected elements. Figure 3 shows the validity of this inference from the excess oxygen detected by the alpha mode for Murchison meteorite which contains 8.95 wt% water.

The presence of water in some Pathfinder samples is seen in the raw X-ray mode data also. The X-ray mode cannot directly measure hydrogen or oxygen. But, if water is present, the entire X-ray spectrum will be low due to the undetected presence of water. This effect will be proportional to the amount of undetected water. Figure 4 illustrates that samples A-17 and A-7 contain more water than the other Pathfinder samples. The atmospheric carbon peak area from the alpha mode and the ratio of iron intensity/wt% of iron from the X-ray mode will inversely correlate with distance between a sample and the detectors. However, both A-17 and A-7 have lower iron counts from the X-ray mode than expected at their measurement distance. It is clearly seen that samples A-17 and A-7 which have the highest oxygen excess in the alpha mode (table II), also have the lowest iron X-ray counts which do not follow the suggested correlation function. This supports the presence of more abundant undetected hydroxides in samples A-7 and A-17.

Using the abundances measured from the alpha mode, the amount of excessive oxygen detected can be converted to an amount of water possibly present in the samples with different assumptions of the oxidation state of iron and sulfur as listed in table II. A reasonable range of water content for the soils, based on these analyses and IMP [4,5,6], is between -1.1 ± 1.6 to 1.3 ± 1.6. While a reasonable range of water content for the rocks under the same assumptions, is between 1.5 ± 1.1 to 6.4 ± 1.2.

Conclusions: The newly computed abundances from the X-ray mode listed in table I are slightly different from those initially reported [1]. The most significant differences from the X-ray mode are the lower silicon and higher iron for the new abundances. Moreover, the alpha/proton mode results for the Pathfinder soils are different from the X-ray mode. This discrepancy in composition of soil samples between the X-ray and alpha/proton modes may be explained by assuming a micron-scale coating of the soil grains with a less iron-rich material.

The abundances from the alpha/proton mode, on a volatile free basis, agree with the new X-ray results for the Pathfinder rocks. The alpha mode, however, yields excessive oxygen in the Pathfinder rocks which possibly indicates the presence of some water in them. This brings into question the interpretation of the Pathfinder rocks as igneous. Perhaps the Pathfinder source magma was water rich as suggested by [8] and loss of water during crystallization was minimal. However, the estimated water content listed in table II is high compared with the water content for unaltered terrestrial basalt-andesites. Alternatively, they may be sedimentary or metamorphic rocks.

Table I: Pathfinder X-ray Mode Abundances.

Soils	Na_2O*	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	Cr_2O_3	MnO	Fe_2O_3
A-2	4.1±0.9	9.7±2.1	9.8±0.2	40.0±0.7	0.8±0.2	5.9±1.2	0.7±0.1	0.5±0.03	5.9±0.2	0.8±0.1	0.3±0.1	0.5±0.1	21.0±0.2
A-4	4.2±0.9	9.0±2.0	9.9±0.3	40.1±0.7	1.0±0.3	6.8±1.4	0.8±0.2	0.5±0.06	5.5±0.2	1.2±0.1	0.4±0.1	0.4±0.1	20.2±0.2
A-5	4.4±0.8	8.0±1.8	9.8±0.2	39.8±0.7	0.5±0.1	5.6±1.1	0.8±0.2	0.5±0.04	5.9±0.2	0.7±0.1	0.5±0.1	0.2±0.05	23.4±0.2
A-9	2.2±2.1	7.3±1.6	9.8±0.5	41.4±0.8	0.7±0.2	6.7±1.3	1.2±0.2	0.7±0.08	6.4±0.3	1.0±0.2	0.2±0.1	0.1±0.1	22.3±0.4
A-10	2.5±0.9	8.4±1.9	9.2±0.3	40.6±0.7	0.5±0.2	6.3±1.3	0.8±0.2	0.4±0.04	5.9±0.2	0.9±0.1	0.3±0.1	0.4±0.1	23.8±0.2
A-15	3.8±1.0	7.5±1.7	9.3±0.2	42.2±0.8	0.5±0.1	5.2±1.0	0.7±0.1	0.7±0.06	5.4±0.2	0.9±0.1	0.3±0.1	0.3±0.1	23.0±0.2
Rocks	**Na_2O***	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**Cr_2O_3**	**MnO**	**FeO**
A-3	4.7±0.7	2.4±0.5	12.1±0.2	53.2±1.0	0.6±0.2	2.0±0.4	0.5±0.1	1.1±0.04	5.6±0.2	0.7±0.1	0.1±0.04	0.3±0.1	16.6±0.2
A-7	6.1±1.0	5.9±1.3	10.6±0.2	46.4±0.8	0.5±0.1	4.4±0.9	0.8±0.2	0.7±0.1	6.4±0.3	0.8±0.1	0.1±0.1	0.4±0.1	16.9±0.2
A-8**	4.0±1.0	7.3±1.6	10.1±0.3	45.1±0.8	0.4±0.1	5.5±1.1	0.9±0.2	0.8±0.05	7.0±0.3	0.8±0.1	0.1±0.1	0.4±0.1	17.4±0.2
A-16	6.4±1.2	4.5±1.0	10.8±0.3	47.0±0.9	0.5±0.1	3.0±0.6	0.6±0.1	0.8±0.1	6.8±0.3	0.8±0.1	0	0.3±0.1	18.4±0.2
A-17	4.5±1.0	4.4±1.0	10.1±0.4	53.1±1.0	0.4±0.1	1.7±0.3	0.5±0.1	0.8±0.1	7.6±0.3	0.6±0.1	0.1±0.1	0.4±0.1	15.8±0.2
A-18	5.5±1.0	3.8±0.8	11.6±0.3	49.0±0.9	0.5±0.1	2.9±0.6	0.7±0.1	1.0±0.1	5.9±0.2	0.8±0.1	0.1±0.1	0.4±0.1	17.8±0.2

Key: All Na_2O* values are from the alpha/proton mode except for A-9 which is derived from X-ray. A-8** = Scooby Doo, which may be a soil. Error bars are based on one sigma statistical errors and accuracy determination by analyses of geostandards in the laboratory under Martian conditions.

Figure 1. Pathfinder A-10 Soil Alpha Spectrum.

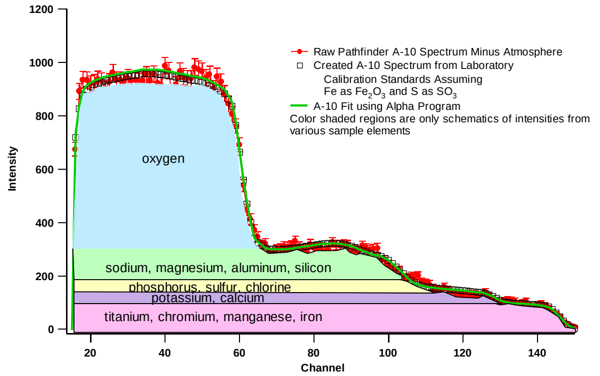

Figure 2. Pathfinder A-17 Rock Alpha Spectrum.

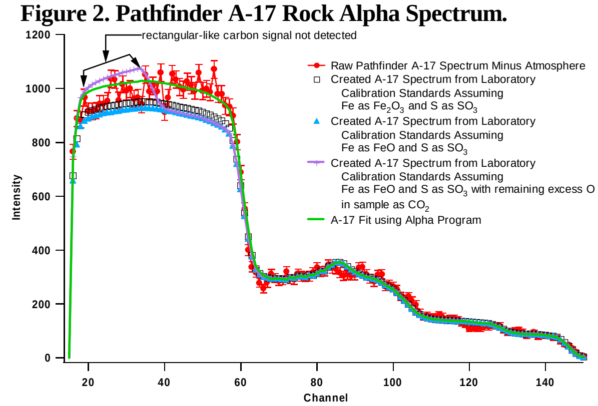

Figure 3. Laboratory Murchison Meteorite Alpha Spectrum.

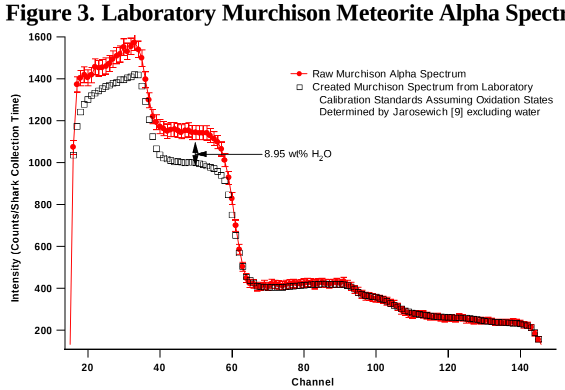

Figure 4. Effect of Excess Oxygen on Raw X-ray Counts.

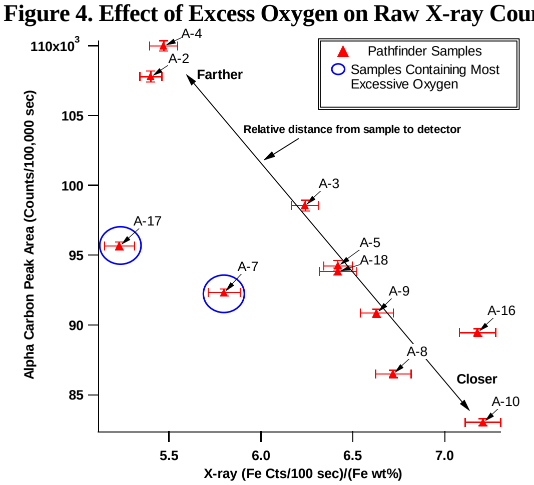

Table II. Potential Water Content of Pathfinder Samples.

Soils	[H_2O wt%][1]	[H_2O wt%][2]	[H_2O wt%][3]
A-2	n.d.	3.5 ± 1.6	**1.3 ± 1.6***
A-4	n.d.	2.7 ± 1.6	**0.6 ± 1.6***
A-5	n.d.	-1.1 ± 1.6*	-3.3* ± 1.6*
A-10	n.d.	1.9 ± 1.7	-0.2 ± 1.7*
A-15	n.d.	1.5 ± 1.5*	-0.7 ± 1.5*
Rocks			
A-3	4.2 ± 1.1	2.5 ± 1.0*	0.5 ± 1.2
A-7	7.7 ± 1.2	**3.9 ± 1.1***	**2.0 ± 1.3***
A-8	8.4 ± 1.3	3.6 ± 1.2	**1.7 ± 1.5***
A-16	4.7 ± 1.3	**2.1 ± 1.2***	-0.1 ± 1.3
A-17	7.9 ± 1.2	**6.4 ± 1.2***	4.6 ± 1.2
A-18	3.9 ± 1.3	1.5 ± 1.1*	-0.6 ± 1.3

[1]maximum water content, sulfur as sulfide and Fe as FeO.
[2]water content, sulfur as SO_3 and Fe as FeO.
[3]minimum water content, sulfur as SO_3 and Fe as Fe_2O_3.
* = probable oxidation state based on IMP data [4].

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