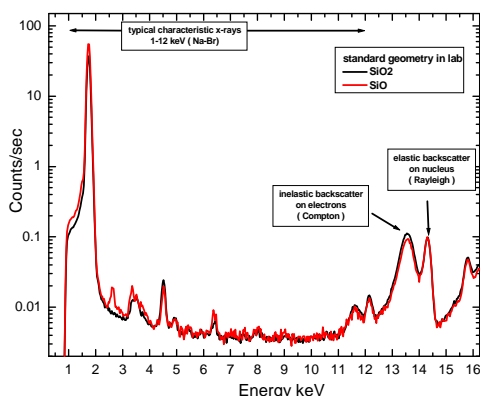


Quantitative determination of water content of in situ samples at Gusev Crater using a new x-ray scatter peak investigation of APXS spectra

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Introduction: The Alpha-Particle-X-ray Spectrometer (APXS) [1] is part of the in-situ payload of the Mars Exploration Rovers. It determined so far the elemental composition of ~ 300 samples on both landing sites along the traverse. The composition is determined by x-ray spectroscopy which limits the detectable elements to higher Z than Na. For lighter elements like Oxygen and Carbon the APXS is also equipped with an RBS mode detecting the backscattered alpha particles. However, RBS is rendered quite useless by 10 mBar CO₂ atmosphere and low counting statistics. We report here a new, innovative method to analyze the so called scatter peaks within the x-ray spectra for x-ray invisible light elements, like excess oxygen. We find evidence of significant amounts of bound water (up to 18 % H₂O) in several subsurface soils in Gusev Crater, which are highly enriched in ferric sulfates. This exceeds by far the few percents of water implied by the unambiguous detection of Jarosite and Goethite.

Method and Calibration: The APXS Cm244



sources emit x-rays (14.3 and 17.6 keV) and high energy alpha particles (>5MeV) to excite characteristic x-rays in the sample. The detected energy range in the x-ray spectrum is wide enough to capture the elemental x-rays as well as the backscattered spectrum of the excitation x-rays. These x-rays can be backscattered in two distinct ways: either by interaction with the nuclei of sample atoms (Rayleigh) or by scattering on the electrons of the sample atoms (Compton). Rayleigh scattering is an elastic process and results in a narrow peak at 14.3 keV. By Compton scattering the primary x-ray loses a variable amount of energy, resulting in a much broader peak at ~ 13.6 keV, see fig.1.

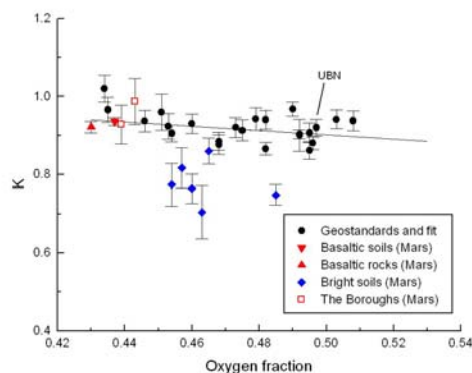
Both effects have different Z-dependencies. The method can be visualized with laboratory calibration

spectra of SiO and SiO₂ shown in fig. 1. In the laboratory at standard measuring distance it is possible to extract the absolute abundance and check for normalization. On Mars with unknown distances as well as irregular shapes of the sample this capability is lost. We normalize the abundances of the detected elements (assumed as their typical oxides) to 100 percent and would not be able to distinguish between SiO and SiO₂. However, in fig.1 the scatter peaks of SiO and SiO₂ differ in the intensity ratio of Compton to Rayleigh. Lighter elements have a preference for increasing the Compton peak and allow us to extract a value for the Oxygen in the sample.

Detecting x-ray invisible elements is straightforward. We use the standard APXS oxide composition to simulate the expected Compton to Rayleigh ratio. Depending on the agreement with the actual measured ratio one adds or lowers the Oxygen until agreement is reached within the statistical uncertainties.

However, there are several caveats of this method:

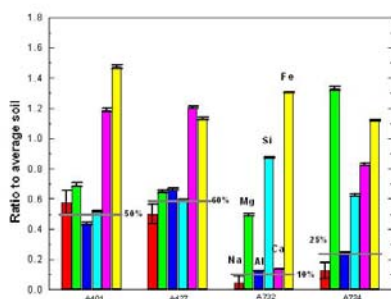
- We can not distinguish between Carbon, Oxygen or other lighter elements. We therefore assess the elemental composition and mineralogy to find the most probable appearance of the light element excess.
- The high energy scatter peaks stem from larger depth (up to 300 um) than elemental signals (5-50 um). Therefore layering might influence the results. On the other hand layering might be assessed by this method.
- The MER calibration spectra were not intended for water detection. The actual water content was not determined properly. However, the calibration spectra show a good agreement with our method, including three water-bearing standards.



Our strongest argument for the suitability of this method is the wealth of basaltic samples we acquired

on Mars. We applied our method to all Spirit soil samples and to basaltic rocks and got the mean ratios of simulated to experimental ratios (K) shown in Fig.2. The terrestrial calibration samples (with their certified composition including water) and the basaltic soils (assumed to be essentially dry, <1% H₂O) on Mars are in excellent agreement with the simulations. We find a slight dependency on the oxygen fraction in our simulation which might point to some imperfections in the used theoretical cross sections models.

Results: The important finding of fig. 2 is that all the high ferric sulfate salts (Paso Robles and DeadSea) found by Spirit show a large negative deviation from the simulations. This can be explained by the presence of x-ray invisible elements. The Paso Robles type of soils were discovered by chance when the rover wheels excavated these bright subsurface soils. Their composition is extremely rich in sulfur (35% SO₃ by weight) accompanied by various enrichments of Fe, Si, Mg, Ca and P and a varying admixture of typical soil.



From APXS mass balance once can extract that ferric sulfates and silica are the major components of the purest PR type soil, named Samra, fig. 3. The ferric character of these sulfates is confirmed by the MB spectrometer which detects a dominating Fe(3+) phase in these soils. This MB phase cannot be specified further. Several hydrated sulfates are candidates [3][4].

The APXS composition plus the extracted water content can be used to constrain the ferric sulfate phase. Under the assumption that all water is bound to a ferric sulfate phase (Fe₂³⁺(SO₄)₃ · nH₂O), we can determine the expected nH₂O of this phase. Our results in tab. 1 are well within the upper range of existing ferric sulfate minerals and exclude any lower hydrated minerals as dominating components.

This new method adds several new capabilities to the APXS and complements well its elemental results.

The depth distribution – especially after expiration of the Spirit RAT – can be checked. The discovered nearly pure Silica deposits [5] show perfect agreement with scatter peaks of Quartz, indicating that the Si enrichment is not just a ~ 10um thin surface layer.

For the PasoRobles type soils it shows that S is indeed present as sulfate. Large portions of elemental S as speculated occasionally would increase the extracted water content even more.

The new method is a valuable consistency check of the APXS results. We conclude that we have a detection limit of ~ 6% H₂O so far for typical single samples, mainly due to limited statistics in the peaks. By grouping samples by their composition this DL can be lowered significantly to extract even lower H₂O.

This determination of up to 18 % H₂O in Martian subsurface soils is the first qualitative in-situ measurement of a significant total amount of bound water. It might be one of the existing reservoirs of water and can help to reconcile in-situ results with the detected several % H₂O by orbital instruments.

We will proceed next to apply the scatter peak method for the samples from the high sulfate outcrops at Meridiani to extract their water content. The new version of the APXS in built for MSL will undergo a dedicated H₂O calibration. It will have enhanced sensitivity and will have an extended energy range to use also the 17.6 keV scatter peak.

Table 1 APXS composition, extracted H₂O content. Hypothetical extracted nH₂O for ferric sulfate. K-ratio of simulation to experiment. Samples are: PR: PasoRobles, PRL:PasoRoblesLight, BR: The Boroughs, trench, HK: Hell'sKittchen.

Sample	Mg	Fe	S	K	H ₂ O	n.H2O
PR	3.3	16.2	12.6	0.77(5)	16±8	10 ± 5
PRL	3.1	12.4	12.5	0.76(4)	15±6	13 ± 5
Samra	2.4	14.8	14	0.75(3)	18±5	9 ± 3
Hula	6.9	13.4	13.1	0.86(3)	6 ⁺⁸ ₋₅	4 ⁺⁶ ₋₃
BR Mills	5.9	13.6	4.5	0.93(5)	0±8	N/A
BR HK	6.3	12.8	5.6	0.99(7)	-5±8	N/A
Ave soil	5.3	12.2	2.3	0.94(1)	< 1	N/A

References: [1] Rieder et al (2003), *JGR* 108, JE002150. [2] Campbell et al, *JGR*, in press, [3] Yen et al, *JGR*, in press [4] Morris et al, *JGR*, in pres., [5] Squyres, S.W. (2007), AGU, Fall meeting.