



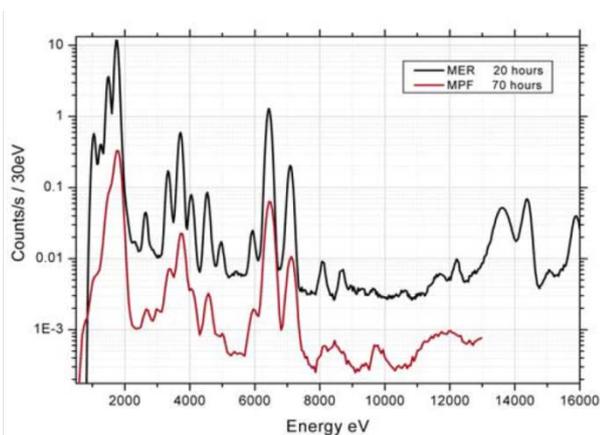
Water on Mars

Extraterrestrial rock chemistry using nuclear methods has been a constant theme ever since Turkevich's report ([Science, 1967](#) [1]) of the *Surveyor V* landing on the Moon. Turkevich used particle elastic backscattering spectrometry (EBS) and nuclear reaction analysis (NRA: from the α, p reactions) using a ^{242}Cm radioactive source to provide 6 MeV alphas.

Particle spectrometry is sensitive to lighter elements, but has little mass discrimination between heavier elements. Thus, the 1976 *Viking I* and *Viking II* missions to Mars used X-ray fluorescence (XRF) instead (see [Clark et al, J.Geophysical Research, 1987](#) [2] for example) even though Martian XRF is blind to light elements.

The *Pathfinder* mission to Mars (landing in 1997) was the next successful attempt to put instruments on Mars. Both of the Soviet *Phobos* probes (launched in 1988), and also the Russian *Small Autonomous Stations* (launched 1996) failed, but they all included a combination of the particle spectrometry of *Surveyor* and the XRF of *Viking*. This combination became known as the "APXS", the alpha-particle X-ray spectrometer, which used a ^{244}Cm source to give 5.8 MeV alphas together with an X-ray detector for the α -PIXE (alpha-particle-induced X-ray emission) yield of the sample and a particle telescope to give separate EBS and NRA (α, p) signals. This is described in eloquent detail (together with the history) by [Rieder et al \(J. Geophys. Res., 1997\)](#) [3].

However, it turned out that because of the ~ 10 mbar atmosphere of CO_2 on Mars, the particle spectrometry had very poor sensitivity to the important elements carbon and oxygen: carbon is central to life and although rock geochemistry assumes all elements are fully oxidised, this only allows the O content to be inferred in the absence of hydration. But in the search for water on Mars the hydration state of the minerals in the rock is of great importance. First reports from *Pathfinder* exclusively used the X-ray spectrometry capability of the APXS (PIXE: see [Rieder et al, Science 1997](#) [4]), and the subsequent Mars missions abandoned the particle detector altogether.



APXS performance comparison between *Pathfinder* (MPF) and *Exploration* (MER). Energy resolution of the MER is twice that of MPF and for MER the Rayleigh and Compton peaks are visible. The count rate is an order of magnitude better, allowing useful 10 minute "test" spectra to be collected. Spectra are normalised to time: ordinate axis is count rate per channel.

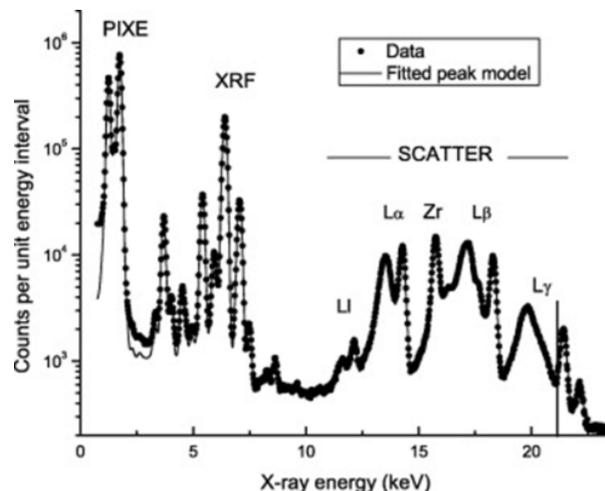
Figure 1 of Rieder et al, *J.Geophysical Res.* 2003

Where has all the water gone? This question is posed by [Rieder et al \(J.Geophysical Res., 2003\)](#) [5], but they do not answer it since they are only introducing the APXS instrumentation subsequently used on the two Mars Exploration Rovers (MER), *Spirit* and *Opportunity*, that landed on Mars in January 2004. The Figure shows the dramatic APXS improvement between the MPF and MER versions: this is largely due to the introduction of high performance SDDs (silicon drift X-ray detector): for Martian results see [McLennan et al, Science 2014](#) [6].



The Figure also shows that higher energy X-rays are accepted: the high energy peaks are due to the fact that the ^{244}Cm source emits not only alpha particles but many Pu L X-rays (14-20 keV) from the excited daughter products of Cm decay. These X-rays fluoresce the rock and soil samples (XRF) and also (as with all XRF spectra) directly suffer elastic and inelastic collisions (known as Rayleigh and Compton scattering).

XRF and PIXE are beautifully complementary techniques: PIXE is more sensitive to the lower Z elements (since the ionisation cross-section depends on the inverse of the ionisation energy) but XRF is more sensitive to the higher Z elements (since the ionisation cross-section depends on the inverse of the energy difference between the excited and the exciting photons).



X-ray spectrum from an APXS instrument equivalent to those on the Curiosity rover.

Figure 2 of Campbell *et al* (NIMB, 2013)

XRF and PIXE together give a high sensitivity to the main elements with $Z > 10$: Campbell and co-workers ([Nucl. Instruments & Methods B, 2016](#)) [7] have recently detailed how the elastic and inelastic scattering of the XRF excitation photons can be interpreted to give an *independent* measure of the O content (see Figure) in a rock. This is because the Compton/Rayleigh (C/R) intensity ratio is determined by the average Z number of the matrix. It turns out that the C/R ratio can be determined at about 1% precision which is sufficient to estimate the hydration of the observed rock.

This is a complex calculation that Hodoroaba & Rackwitz of the BAM (Bundesanstalt für Materialforschung und -prüfung, Berlin: [Analytical Chemistry, 2014](#) [8]) also used to show that the average Z could be obtained with an accuracy of 0.1. Campbell and co-authors ([J. Geophysical Res., 2008](#) [9]) originally used their method with the APXS instrument on the Spirit rover to directly determine the hydration of remarkable highly sulfated soils found in the Gusev Crater (see also [Ming et al, Science 2014](#) [10]).

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