

IN-SITU PLANETARY SURFACE ANALYSES: THE POTENTIAL OF X-RAY DIFFRACTION WITH SIMULTANEOUS X-RAY FLUORESCENCE; D. T. Vaniman, D. L. Bish, and S. J. Chipera, Geology and Geochemistry Group, Los Alamos National Laboratory, Los Alamos, NM 87545

Powder X-ray diffraction (XRD) analysis of geological samples is a venerable field that is currently undergoing a rapid expansion in capabilities. The availability of more powerful computers has led to significant advances in quantitative XRD and in Rietveld refinement of crystal structures [1]. Rietveld refinement can not only determine crystal structures and lattice parameters from powder XRD data, but can also be used to obtain very good determinations of mineral abundances in complex mixtures [2]. These new capabilities are important, but the conventional application of XRD to mineral identification remains a most powerful tool. No other technique can provide as definitive an identification of crystalline materials, and no other technique has the potential of XRD for recognizing unique crystalline structures and thereby discovering previously unknown minerals on other planets. We are well attuned to the similarities in mineralogy between Earth and Moon but should be wary of the much greater complexity in mineralogy that may occur on volatile-rich planetary surfaces under unearthy atmospheres. Mars provides a good example of a planet where the capabilities of XRD will be critical for adequate *in-situ* surface exploration.

The Martian Paradigm. Mars is a planet for which some reflectance spectra and a few X-ray fluorescence (XRF) data are available. Most mineralogic models of the martian surface are based on the reflectance spectra, which provide strong evidence for the occurrence of Fe^{3+} -bearing minerals, particularly hematite but probably including some Fe-rich clays [3]. It has recently been argued that the poor crystallinity of many clay minerals formed by alteration of basaltic glass makes near-IR spectral analysis a much better method than XRD for analysis of such materials [4]. For poorly crystalline materials the near-IR reflectance spectra are indeed a powerful indication of mineralogy, but for better-crystallized materials the lack of XRD analysis would lead to a serious knowledge gap. For example, the details of clay mineralogy that have significant importance for determining the environment of formation and response to local atmosphere/hydrosphere (e.g., order-disorder and interlayer spacings) would not be determined. In addition, the martian surface apparently includes many other minerals that are better determined by XRD than by reflectance spectra. The Viking XRF data leave little doubt that there is abundant sulfate and chloride in the martian regolith [5,6] - unfortunately, the XRF data alone are insufficient to determine which sulfate and chloride minerals are present. Present models of mineralogy in the martian regolith are clearly incomplete, and our knowledge of the martian surface would be advanced tremendously if XRD data were available. Figure 1 illustrates the present capabilities in Rietveld determination of mineral abundances in bauxite, a terrestrial regolith with complexities comparable to those that may be expected from Martian regolith. The crosses represent the observed diffraction pattern, a solid line represents the calculated pattern, and the difference between the two is illustrated by the lower line. The mineral abundances listed in Fig. 1 are accurate to better than 5% relative. Comparable analyses may be obtainable with robotic instruments on other planets, using powders that are sufficiently fine.

Advanced Powder XRD Systems: Position-sensitive Detectors. Standard powder XRD systems are bulky, with sensitive gear drives and requirements for sample powdering before analysis. The restriction to analysis of powders is one that can not be circumvented, but this should not detract from the utility of an XRD system mounted on a planetary rover; some powders can be obtained without grinding (e.g., regolith fines or windblown dust) and others will be obtained from the rover's coring or drilling attachments. The other limitations of Earth-based XRD systems, however, are rapidly being overcome by new technical innovations. Position-sensitive detectors (PSD) can now reduce the size and virtually eliminate the moving parts of the XRD system. These detectors form a fixed arc above the sample. Because X-rays of all diffraction angles are measured simultaneously, rather than sequentially by a moving detector, it is possible to collect a diffraction pattern much more rapidly or to acquire many more counts in a

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short timespan for small samples. The fixed geometry and lack of moving parts in PSD systems makes them an ideal application for robotic laboratories, which could be designed to load and analyze samples without mechanical alignment of the source/detector gear train. Should the instrument geometry be perturbed, by thermal or mechanical forces, the exact location of the detector arc can be redetermined by reference to a mineral standard.

Potential Advances: Combined XRD/XRF analysis. Beyond PSD systems, there is the potential to wed XRD and XRF analysis within a single instrument. Both types of analysis can operate from the same source, probably consisting of more than one radioisotope, such as the ^{109}Cd and ^{55}Fe used in the Viking XRF experiment. For the XRD analyses, all but one source would be filtered out or mechanically selected to isolate a specific monochromatic radiation. The availability of short-wavelength and long-wavelength sources may be an advantage for XRD analysis if the samples range from clays collected from regolith to garnet powders drilled from xenoliths in basalt. For the XRF analysis, multiple sources would be used to detect elements from a large portion of the periodic table. Detection limits, precisions, and accuracies using modern energy-dispersive detectors will far exceed those of the Viking instrument. At present, PSD detectors are not energy-dispersive, but it may be possible to fabricate a PSD-like system that will simultaneously collect XRD and XRF data. Tradeoffs between dual-detector and single-detector systems need to be evaluated. Although a combined XRD/XRF instrument would surely save in weight, the greatest advantage of the combined instrumentation would be that both XRD and XRF signals come from a single specimen. With the combined XRD/XRF data, single-mineral samples can be characterized completely in terms of structure and chemistry, and complex mineral mixtures can be deciphered more accurately by solving simultaneous equations to fit the XRD-calculated mineral abundances with the XRF-calculated normative composition. This combined XRD/XRF instrument can not address all sample problems, and the system will be much more powerful if combined with reflectance methods that are sensitive to Fe oxidation states and to water contents. Other instrument synergisms (e.g., Mössbauer analysis) could be grafted to the radioisotope source used in the XRD/XRF instrument. Careful engineering may generate a robotic laboratory capable of definitive analyses, rather than partial data that will lead to decades of speculation and uncertainty.

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