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Introduction: Mineralogical analysis is a critical component of planetary surface exploration. Chemical data alone leave serious gaps in our understanding of the surfaces of planets where complex minerals may form in combination with H, S, and halogens. On such planets (e.g., Mars) a single chemical composition may represent a range of mineral assemblages. For example, Viking chemical analyses of excavated duricrust indicate that Mg and S are correlated and ~10% MgSO4 (anhydrous weight) is a likely cementing agent [1]. Pathfinder chemical data support a similar abundance of MgSO4 in the most altered materials [2].

However, there are many possible Mg-sulfates with widely varying hydration states (including dehydrated and 1-, 2-, 3-, 4-, 5-, 6-, and 7-hydrates). In addition, other sulfate minerals such as gypsum (CaSO4·2H2O) and other salts containing Cl may also exist. X-ray diffraction (XRD) has the ability to decipher mixtures of these phases that would be difficult, if not impossible, to unravel using only chemical or spectral data.

The recent Pathfinder APXS data for Mars provided some tantalizing new information indicating more silicic igneous compositions than previously known [3], but the mineralogic underpinning of the new soil and rock data continues to be contentious. Bishop et al. [4], in considering the combined APXS and reflectance spectra data on martian soils from Pathfinder, concluded that “XRD and 4K Mössbauer measurements (in situ or on returned samples) will be necessary for unique mineral identification.” Establishing a rock’s provenance often requires a modal analysis of all minerals present in the rock, i.e., the identity of each mineral present and its concentration. Likewise, specific environments of formation may often be accurately characterized only by identifying accessory mineral phases or the specific solid-solution chemistry of a particular mineral. It is even possible that minerals or natural amorphous materials exist on Mars that have not been identified on the Earth, and XRD is capable of discovering and characterizing such materials. X-ray diffraction is a particularly powerful tool for mineral and rock identification because it is directly linked to the crystal structures of individual phases. Indeed, it is the method of choice for such characterizations in terrestrial laboratories.

A miniaturized XRD/XRF (X-ray fluorescence) instrument, CHEMIN, is being developed for definitive mineralogical analysis of soils and rocks on Mars [5, 6]. The 2-dimensional (2-D) detector used in the CHEMIN instrument produces good results even with poorly prepared powder because it integrates over entire Debye rings. The current third-generation instrument yields greatly improved counting times and resolution compared with earlier versions. With diffraction peak profiles having full-widths at half-maximum (FWHM) <0.3°2θ for Cu Kα radiation, the current instrument version has a greatly improved capability for distinguishing individual minerals in complex samples. In the past, complex mixtures of minerals were difficult to unravel by XRD. However, during the last two decades, search/match methods and Rietveld refinement techniques improved to the point that complex mineral mixtures can be routinely characterized, even when they include amorphous and nanophase materials [7]. We have applied such data analysis methods to recently collected CHEMIN XRD data measured on martian analogue materials.

Methods: A number of samples representing potential target rocks for a Mars lander were prepared for this study. The samples included igneous rocks (andesite, basalt), sandstone, limestone, an evaporite (gypsum/carbonate), calcite, and quartz. Several of these samples are identical to those used in the sample preparation study of Chipera et al. [8]. Samples were purposefully made much coarser than typical laboratory preparations (up to 150 μm), and powders were vibrated during the XRD experiment to improve particle statistics and randomization [9]. Data were collected using CuKα or CoKα radiation at a tube power of 40 kV and 0.25 mA. The 2-D CHEMIN data were linearized and converted to a 1-D set of digital data, interpolated to 0.05° 2θ step sizes. These data were used as input to Rietveld refinements, using the program GSAS. Refinements used an instrument profile determined using the data for pure quartz. Refined parameters included individual scale factors, unit-cell parameters for phases present at >5 wt. %, background coefficients, and profile parameters.

Results: Rietveld refinements using data from the third-generation CHEMIN instrument were considerably improved as a result of the better instrument resolution. Data from the quartz refinement are shown in Figure 1, illustrating the very good FWHM. It is likely
that some of the angle-dependent errors are due to absorption effects, which were not corrected. Data for the evaporate sample are shown in Figure 2. This sample consists of gypsum, calcite, quartz, and alkali feldspar. The refinement provided quantitative information on these four phases and unit-cell parameters for gypsum, quartz, and albite. Calcite, quartz, and albite were present at <1%. Similar results were obtained using the calcite, sandstone, and limestone data. Results using data for the considerably more complex andesite sample are shown in Figure 3. This refinement incorporated eight phases, albite, labradorite, enstatite, augite, cristobalite, dolomite, magnetite, and forsterite, providing unit-cell parameters for all but dolomite, magnetite, and forsterite. Quantitative results on weight fractions agreed well with analyses done using a laboratory Siemens powder diffractometer.

Conclusions: These results from the new CHEMIN instrument demonstrate that relatively high-resolution data can be obtained with a miniaturized XRD/XRF instrument, and the data are suitable as input to advanced methods of data analysis. With use of appropriate standards to calibrate the instrument, accurate peak positions can also be obtained. Rietveld refinement provides precise unit-cell parameters that can be used with published determinative curves to determine compositional and ordering parameters. Several important modifications are still needed to improve the utility of the instrument. First, a modified collimator is currently being designed to facilitate measuring low-angle data to 5° 2θ. In addition, acquisition of higher-angle data would provide improved information on angle-dependent parameters, such as information on crystallite-size and/or strain broadening. Many such parameters are functions of θ, and the present instrument, with a θ range of ~8 to 28°, does not provide the angular spread necessary to refine precise angle-dependent parameters. Future configurations will extend the high-angle limit.