Application of the *CHEMIN* XRD/XRF Instrument in Analyzing Diagnostic Mineralogies: Quantitative XRD Analysis of Aragonite and Basalt.

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We are developing a miniaturized X-ray diffraction and X-ray fluorescence (XRD/XRF) instrument for space exploration that will minimize the uncertainties in mineralogical and geochemical evaluation inherent in remote analysis. The instrument has been named CHEMIN, in reference to its role as a simultaneous CHEmical and MINeralogic analyzer. A functioning prototype of this instrument uses a Cu X-ray tube, transmission geometry, and an energy-selective CCD in single-photon counting mode to collect simultaneous XRF (energy-dispersive) and flat-plate XRD data (see [1,2] for instrument descriptions). The ultimate goal of this instrument will be to obtain combined XRD and XRF data from planetary samples. Such an approach will greatly improve the accuracy of remote petrologic analysis by constraining the number of possible mineralogic interpretations. For example, although the Viking landers provided very useful XRF data on martian regolith, the complex chemistry reported (particularly the mixed-anion suite that includes S, and Cl, as well as O) allows a wide range of mineralogic interpretations. Since remote XRF has provided proven results, we focus in this paper on preliminary tests in obtaining quantitative XRD data from the prototype CHEMIN instrument.

X-ray diffraction is the most direct and accurate analytical method for determining the presence of mineral species because the data obtained by this method are fundamentally linked to crystal structure. Other methods, based on chemical or spectral properties, are derivative and subject to much greater uncertainties. Moreover, significant progress has been made in the last decade in the development of *quantitative* XRD of multicomponent mixtures. The Rietveld method, which fits the entire observed diffraction pattern with a pattern calculated using the crystal structures of the constituent phases of the model mineral system, shows great promise for mineral analysis. This method can provide rapid quantitative estimates of mineral abundance as well as compositional, unit-cell parameter, and structural data on individual minerals [3,4]. In addition, recent advances in quadratic goal programming allow solution of simultaneous linear equations using chemical and mineralogic data. Use of these techniques with combined bulk-sample XRD and XRF data makes possible extraction of considerable information on individual mineral compositions [5,6].

To test the capabilities of CHEMIN against realistically complex samples, we have used Rietveld analysis to determine mineral abundances from CHEMIN-derived diffraction patterns of a basalt and of a relatively pure sample of aragonite. These samples were chosen to represent a rock type that is known to be abundant on the martian surface and a mineral that in many terrestrial occurrences is biogenic.

XRD and XRF data for these samples were obtained with the prototype CHEMIN instrument using repetitive 30-s counts. After accumulation of numerous 30-s count data sets, the data were analyzed on a pixel-by-pixel basis. XRF data were obtained from the energy deposited in each pixel, and X-ray powder diffraction rings were generated by plotting the two-dimensional distribution of those pixels containing Cu Kα photons. The powder rings were then integrated to generate conventional 2Θ vs. intensity powder diffraction patterns. The resulting XRD data were used as input to Rietveld refinements. During the refinements, the fit between observed and calculated patterns was optimized through a least-squares process in which parameters related to each phase, including their relative abundances, were varied.

Basalt is a common lithology of all terrestrial planets, fundamentally important in characterizing the nature of a planet's internal processes. Martian basalts have been fortuitously delivered to Earth as SNC meteorites, although these meteorites are very diverse, ranging from fine-grained basalts to a variety of cumulate lithologies. This small suite of samples has generated considerable speculation about martian volcanism. Although basalts *per se* are not sought as lithologies likely to preserve fossil life on Earth, the debate about fossil life in martian meteorites provides impetus to the consideration of basalt in an exobiologic context. Indeed, volcaniclastic facies of some terrestrial basalts in systems cemented by calcite have yielded exceptionally well-preserved fossils of soft body parts [7]. For both planetary understanding and for exobiology goals, the ability to determine a martian basalt’s chemistry and mineralogy is important.

A diffraction pattern of a terrestrial basalt was obtained using the prototype CHEMIN instrument. The quantitative mineral results from

Rietveld analysis of these data are listed in Table 1, and the observed and calculated diffraction patterns are shown in Fig. 1. The X-ray fluorescence pattern is important in analyses of complex mixtures such as basalts because the chemical data provide constraints useful in limiting the mineralogies used in fitting the pattern. Despite the complexity of the basalt sample and the significant limitations in the prototype CHEMIN instrument, the Rietveld analysis is surprisingly good, with a calculated pattern that agrees well with the observed pattern. In addition, the resulting mineral analysis agrees well with optically determined modes for this sample. This level of success has only recently been obtained, and considerable improvement in the CHEMIN results are anticipated in the near future.

Table 1. Rietveld Quantitative Analysis of Basalt Sample

Mineral	**Wt. %**
Forsterite	7.5
Albite	28.9
Anorthite	17.5
Augite	4.7
Magnetite	1.9
Phlogopite	0.1
Fluorapatite	1.6
Sanidine	37.9

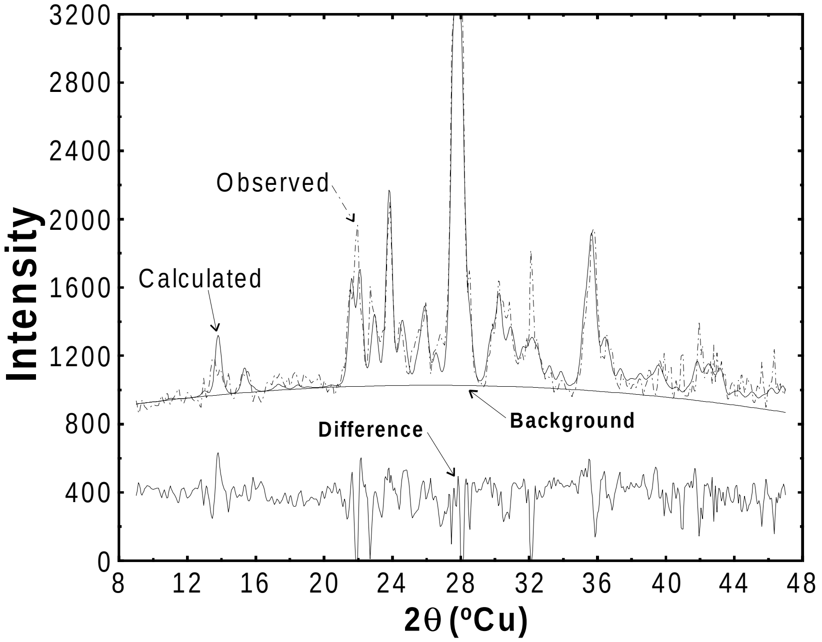

Figure 1. Rietveld refinement results, showing observed CHEMIN data (dashed line), calculated data (solid line), and difference and background curves (solid lines) for a terrestrial basalt sample.

In contrast to the basalt, the aragonite sample was relatively pure and was easily characterized. Nevertheless, the XRD component of the CHEMIN analysis was capable of detecting and, with Rietveld processing, of measuring impurities of 1.6% calcite and 0.2% quartz. These results illustrate the high sensitivity of the prototype CHEMIN instrument in detecting very small quantities of diagnostic minerals. Contaminant detection that can distinguish between clastic, cemented clastic, and chemical sediments will be an important tool in remote petrologic and exobiologic studies. This capability will be very important in selecting appropriate samples with fossil-preservation potential for return to Earth and more detailed analysis.

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