DEFINITIVE MINERALOGICAL ANALYSIS OF MARTIAN ROCKS AND SOIL USING THE CHEMIN XRD/XRF INSTRUMENT AND THE USDC SAMPLER.

D.F. Blake[1], P. Sarrazin[1], S. J. Chipera[2], D. L. Bish[2], D. T. Vaniman[2], Y. Bar-Cohen[3], S. Sherrit[3], S. Collins[4], B. Boyer[5], C. Bryson[6] and J. King[7]. [1]NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035 (dblake@mail.arc.nasa.gov), [2]Hydrology, Geochemistry, and Geology, Los Alamos National Laboratory, MS D469, Los Alamos, NM 87545, [3]Science and Technology Development Section, Jet Propulsion Laboratory, MS 82-105, Pasadena, CA 91109, [4]CCD Imaging Group, Jet Propulsion Laboratory, MS 300-315L, Pasadena, CA 91109, [5]Oxford Instruments, Scotts Valley, CA 95066, [6]Bryson Consulting, Morgan Hill, CA 95037, [7]Engineering Clinic, Harvey Mudd College, 260 East Foothill Blvd. Claremont, CA.

Mars Astrobiology Goals & Definitive Mineralogy: The search for evidence of life, prebiotic chemistry or volatiles on Mars will require the identification of rock types that could have preserved these. Anything older than a few tens of thousands of years will either *be* a rock, or will only be interpretable in the context of the rocks that contain it. In the case of Mars soil, identifying the nature and quantity of both crystalline and amorphous components will be essential to understanding sources and processes involved in its generation.

The key role that definitive mineralogy plays is a consequence of the fact that minerals are thermodynamic phases, having known and specific ranges of temperature, pressure and composition within which they are stable. More than simple compositional analysis, definitive mineralogical analysis can provide information about pressure/temperature conditions of formation, past climate, water activity, the fugacity (activity) of biologically significant gases and the like.

Definitive mineralogical analyses are necessary to establish the origin or provenance of a sample: The search for evidence of extant or extinct life on Mars will initially be a search for evidence of present or past conditions supportive of life (e.g., evidence of water), not for life itself. Definitive evidence of past or present water activity lies in the discovery of:

* *Hydrated minerals*: The "rock type" hosting the hydrated minerals could be igneous, metamorphic, or sedimentary, with only a minor hydrated mineral phase. Therefore, the identification of minor phases is important.

* *Clastic sediments:* Clastic sediments are commonly identified by the fact that they contain minerals of disparate origin that could only have come together as a mechanical mixture. Therefore, the identification of all minerals present in a mixture to ascertain mineralogical source regions is important.

* *Hydrothermal precipitates and chemical sediments*: Some chemical precipitates are uniquely identified only by their structure. For example, Opal A, Opal CT, tridymite, crystobalite, high and low Quartz all have the same composition (SiO_2) but different crystal structures indicative of different environments - from hydrother-

mal formation to low temperature precipitation. Other silica types such as stishovite can provide evidence of shock metamorphism. Therefore, identification of crystal structures and structural polymorphs is important.

The elucidation of the nature of the Mars soil will require the identification of mineral components that can unravel its history and the history of the Mars atmosphere. Examples include:

* *Cement components of the soil*: magnetic experiments conducted on Mars pathfinder suggest that composite grains exist with mixed mineralogies, possibly cemented by a sulfur-containing component (Gypsum, anhydrite, Mg-sulfates, other complex sulfates).

* *The iron-magnetic component:* (ferrihydrite, hematite, etc.). The hydration state, oxidation state and degree of crystallinity of these components provide information on water activity and oxygen fugacity.

* *The oxidative component*: Is this a UV photolyzed surface layer or a phase ubiquitous in the soil?

* *The global/local dust and soil units:* Much of the Mars surface will have been mapped multispectrally at high resolution by the time data are returned from the Mars Science Laboratory. Ground truth mineralogical data will serve to validate much of this information.

Crystal Structure Information is Required for Definitive Mineralogical Analysis: Mineralogical identification - the determination of *crystal structure* - is a critical component of Mars Astrobiological missions. Chemical data alone are not definitive because a single chemical composition or even a single bonding type can represent a range of substances or mineral assemblages. Definitive mineralogical instruments have never been deployed on Mars, and as a result, not a single rock type or mineral has been identified with certainty.

Minerals are defined as unique structural and compositional phases that occur naturally. There are about 15,000 minerals that have been described on Earth. There are likely many minerals yet undiscovered on Earth, and likewise on Mars. If an unknown phase is identified on Mars, it can be fully characterized by structural (X-ray diffraction; XRD) and elemental (X-ray fluorescence; XRF) analysis without recourse to other data because XRD relies on the first principles of atomic arrangement for its determinations. An un-

known mineral discovered on Mars could be fully de-scribed (structure and composition), named and likened to terrestrial counterparts without recourse to other data. X-ray diffraction is the principal means of identification and characterization of minerals on Earth.

Modern X-ray diffraction methods are able to iden-tify all minerals in a complex mixture using full-pattern fitting methods such as Rietveld refinement [1]. When X-ray amorphous material is present, Rietveld refine-ment can determine the relative amount of amorphous material, and a radial distribution function can be cal-culated which will help identify the principal atom-atom distances present in the material.

The CheMin XRD/XRF Instrument: The CheMin XRD/XRF instrument [2-6] is capable of de-finitive mineralogical analysis. The original prototype has been modified (and made portable) by replacing the original laboratory source with an Oxford Instruments Apogee[TM] small-focus X-ray source (figure 1). In the current version, the small-focus source (70 µm diame-ter) and a 30 µm final aperture yield a beam diameter at the sample of ~100µm.

A wide variety of minerals and rocks has been analyzed utilizing 40 KV accelerating voltage and 0.25 µamps beam current (10 watts). Interpretable patterns of single minerals can be obtained in less than an hour and quantifiable patterns of complex rocks can be ob-tained in a few hours.
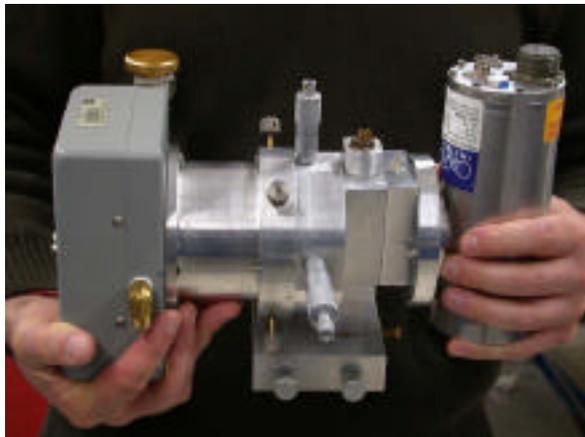

Figure 1: CheMin II instrument

Quantitative mineralogical analyses have been ob-tained for a variety of minerals using the CheMin II prototype. Rietveld refinements have been made using data for apophylite (a zeolite), limestone, limestone-evaporite, San Carlos olivine, the basaltic Mars meteor-ite Zagami and many others. Refined unit-cell parame-ters for the San Carlos olivine from CheMin data are 4.757(4), 10.235(5), and 5.995(3) Å, yielding a compo-sition of Fo90 - Fo95 (figures 2-3).

Sample preparation for X-ray Diffraction: Powdered samples are required for XRD because a near-infinite number of orientations of crystallites to the beam is needed in order to produce an interpretable pattern [7]. Chipera et al [8] report on the use of a flight prototype Ultrasonic Drill (USD) to produce powders suitable for XRD. Although a two-dimensional detector as used in the CheMin instrument will produce good results with poorly prepared powders [9], the quality of the data will improve if the sample is fine grained and randomly oriented.
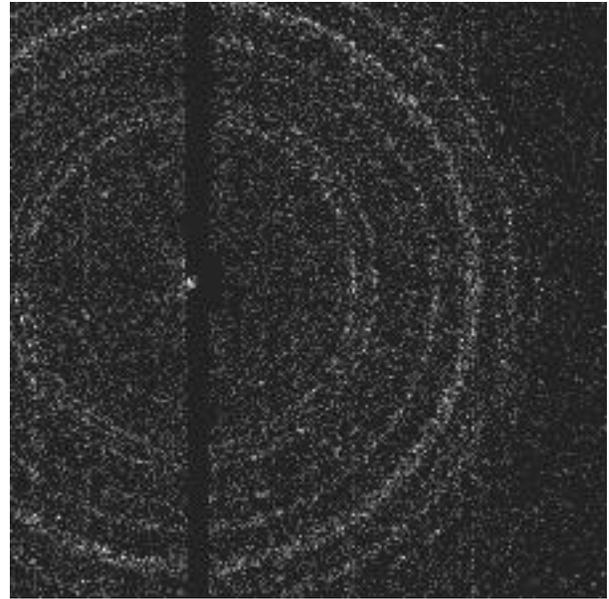

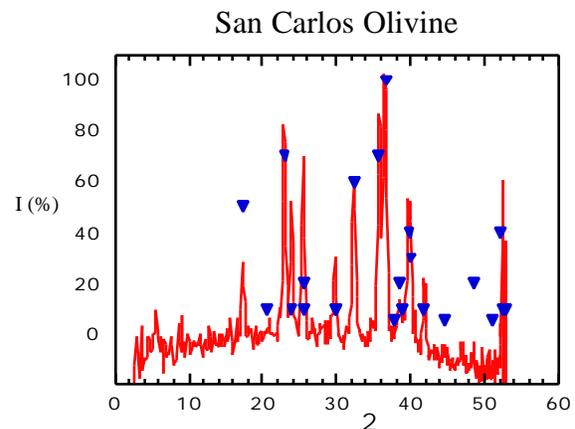**Figure 2**: 2-D diffraction pattern of Olivine

Figure 3: Diffractogram of CheMin olivine data (red) vs. positions & intensities of forsterite standard (blue triangles)

An Ultrasonic/Sonic Driller/Corer (USDC) cur-rently being developed at JPL (Figure 4) is an effective mechanism of sampling rock to produce cores and

powdered cuttings. It performs best with low axial load (< 5N) and thus offers significant advantages for operation from lightweight platforms and in low gravity environments. The USDC is lightweight (<0.5kg), and can be driven at low power (<5W) using duty cycling.

To assess whether the powder from an ultrasonic drill would be adequate for analyses by an XRD/XRF spectrometer such as CheMin, powders obtained from the JPL ultrasonic drill were analyzed and the results were compared to carefully prepared powders obtained using a laboratory bench scale Retsch mill.

Eight samples representing potential target rocks for a Mars lander were prepared for study. The samples include igneous volcanic rocks (basalt and andesite), sandstone, and evaporite/spring deposit rocks (tufa, calcite veins, and calcite-gypsum evaporites). To characterize the particle size distribution for samples obtained from the USDC, each sample was wet sieved through 100, 200, and 325 mesh sieves (150, 75, 45 µm respectively) and sample weights were recorded. Further analyses were conducted on the <325 mesh fraction using a Horiba CAPA-500 particle size distribution analyzer set up to bin from 0-50 µm using 5 µm bins.
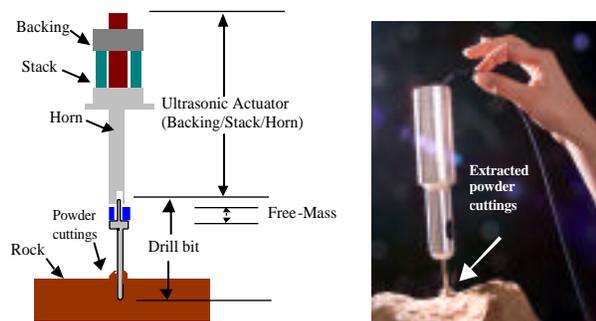

Figure 4: A schematic view of the USDC components. The USDC is shown to require relatively small preload to core a rock.

Two types of rock powder were generated from the drill. Fine powder was generated from the cutting tip itself; the second product consisted of spallation detritus generated during the drilling operation. It was found that the softer materials tended to produce far more spallation detritus than the harder, more competent materials and that the orientation of the drill to the rock also affected spallation. Figure 5 shows results from a sample acquired from the basal limestone of the Todilto Formation (Profile cliffs, Canjilon Creek, New Mexico). This sample is composed mainly of calcite with minor quartz and gypsum. The top histogram shows that the bulk of the ultrasonic drill powder gen-

erated for this sample was composed of spallation detritus. However, the <325 mesh fraction (middle histogram), which is representative of the material generated at the cutting tip of the ultrasonic drill, shows that the drill does an excellent job of generating a fine powder for XRD analysis with much of the powder less than 10 µm in size. The bottom histogram shows the particle size distribution obtained on this sample from a laboratory Retsch mill for comparison.
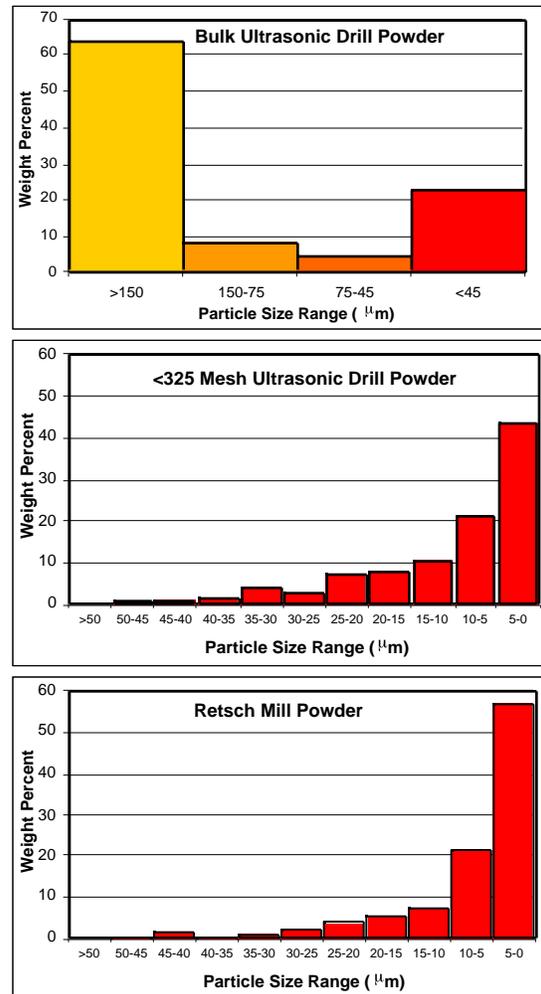
The ultrasonic drill did an outstanding job of gen-

Figure 5: Basal Limestone, Todilto Formation

erating quality XRD powders from all of the materials tested. XRD patterns obtained from the mechanically screened ultrasonic drill powders with CheMin II, as well as with a laboratory Siemens D500 XRD unit, are essentially indistinguishable from powders obtained from a laboratory Retsch mill. The particle size distributions are also quite comparable between the two methods, demonstrating that the ultrasonic drill is more

than adequate to generate powders for a landed XRD/XRF spectrometer. Equally important, the phase composition of powders prepared using the USDC drill is identical to powders prepared from bulk material using the laboratory Retsch mill. In practice, introduction of the powder into an XRD instrument may require passing the sample through a sieve to separate the drill bit powder from spallation detritus.

Future CheMin XRD/XRF Instruments: Two CheMin III laboratory instruments are being built. The first is a deep-depleted CCD version suitable for both XRD and XRF. The second is a phosphor-coated CCD version suitable for XRD only. The XRD/XRF instrument, fitted with a Co X-ray source and a deep-depleted CCD, will record both the positions and energies of individual X-ray photons. Deep-depletion will increase the quantum efficiency (QE) for diffracted X-ray detection from 0.05 to at least 0.50, yielding a 10-fold increase in count rate. XRD data will be utilized along with XRF results to create a fully quantitative system for both data sets. This is a particularly powerful combination since refined lattice parameters from XRD can in many cases be used to calculate composition (e.g., the San Carlos olivine shown in figure 3), enabling a partition of elements into specific oxidation states. In combination with XRF, this will allow the quantification of complex mineralogies in which solid solution series are present (olivines, pyroxenes, amphiboles, carbonates, etc.).

The second instrument, intended for XRD only, will be fitted with a phosphor-coated CCD and a Mo X-ray source. This instrument will be used to evaluate a more conservative fall-back strategy which would not require cooling, single-photon counting or thin X-ray windows. In addition, the phosphor will result in a QE of 1.0 for the device. A pin diode will be evaluated to collect qualitative XRF data for use with the XRD results.

A fourth prototype (CheMin IV) which is being designed for the Mars '09 MSL opportunity, will utilize a CCD camera based on the MER '03 camera and a carbon nanotube field emission (CNTFE) X-ray tube developed by Oxford Instruments in collaboration with the Center for Nanotechnology at NASA/ARC (figure 7). The integration of a USD and powder delivery mechanism with CheMin IV will yield a robotic, deployable and flight-worthy XRD/XRF instrument.

CheMin IV will weigh less than a kilogram and will operate with as little as five watts of power (although increased power will result in shorter data acquisition times). Individual XRD patterns and XRF spectra will comprise a data volume of 2X1024X16 bits.

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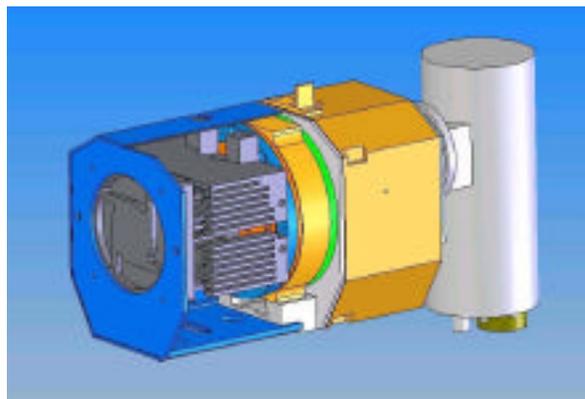

Figure 6: CheMin III prototype. The camera is built by Andor, Inc. The camera is fitted with an e2v Technologies 55-30 front-illuminated, deep depletion sensor 1242 X 1152 pixels in size with 22.5 µm square pixels. The Sample Loading and Manipulation System (SLIMS) unit is designed and built by students from the Engineering Clinic of Harvey Mudd College, and the X-ray tube is a commercially available Apogee[TM] Co tube from Oxford Instruments.

Figure 7: CNTFE X-ray tube manufactured commercially by Oxford Instruments, Inc.