NOVEL SAMPLE-HANDLING APPROACH FOR XRD ANALYSIS WITH MINIMAL SAMPLE PREPARATION. P. Sarrazin[1], S. Chipera[2], D. Bish[3], D. Blake[4], S. Feldman[4], D. Vaniman[2] and C. Bryson[1], [1]Apparati Inc., 110 Pioneer Way, Suite I, Mountain View, CA94041, (psarrazin@apparati.com), [2]Los Alamos National Laboratory, MS D469, Los Alamos, NM 87545, [3]Indiana University, 1001 E 10th St., Bloomington IN 47405, [4]NASA Ames Research Center, MS 239-4, Moffett Field, CA 94035.

Introduction: Sample preparation and sample handling are among the most critical operations associated with X-ray diffraction (XRD) analysis. These operations require attention in a laboratory environment, but they become a major constraint in the deployment of XRD instruments for robotic planetary exploration. We are developing a novel sample handling system that dramatically relaxes the constraints on sample preparation by allowing characterization of coarse-grained material that would normally be impossible to analyze with conventional powder-XRD techniques.

Requirements for Sample Preparation: Performing an XRD analysis consists of measuring the direction and intensities at which crystalline matter diffracts X-rays. Placing an individual crystal in a fixed orientation in a monochromatic X-ray beam can at the best lead to a single diffracted beam, which does not allow identification of the crystal structure. In order to identify the structure, one must present the crystal to the X-ray beam under all orientations to record all possible diffracted beams within the angular range covered. With a single crystal, this can be accomplished by rotating the sample about several axes. The most common technique for XRD is called powder-diffraction because it uses powdered materials - or solid polycrystalline materials - to create a sample that offers all possible crystalline orientations for each mineral. In laboratory powder-XRD instruments, the very high number of crystallites in the analytical volume is obtained by grinding the sample to a very fine-grained size of less than 10 μm [1], or using fine-grained polycrystalline solids. With miniature XRD instruments such as would be deployed for planetary exploration, the grain-size constraint is much more stringent because the analytical volume must be dramatically reduced to preserve an acceptable resolution. In such case, an ideal sample would have a submicron grain size practically impossible to achieve.

Interest has been shown in planetary XRD instruments that would directly characterize geological samples (soil, rock) with no sample preparation. Although this approach is appealing for its apparent mechanical simplicity, it is fundamentally limited to the characterization of very fine-grained materials such as fine soils and aphanitic rocks. Phaneritic rocks such as gabbro and granite have grain sizes on the order of 100's of μm to centimeters, much larger than the analytical volume of the instrument. Attempts to directly characterize such materials would fail unless complex single-crystal diffraction techniques are applied. Any technical solution for achieving this would be far more complicated than a sample preparation and handling system for quality powder-XRD.

Sample handling principle: When non-ideal fine-grained powders are being characterized in a powder-XRD instrument, one must find a means of increasing the number of crystallite orientations explored during analysis. One approach is to translate the sample in the beam to analyze a larger amount of material. Another solution, commonly used in laboratories, is to rotate or rock the sample to present each crystallite in a range of orientations in the beam. Both solutions require complex mechanisms.

The approach we are developing is to generate random motions within powdered samples to increase the *effective* number of grains being analyzed as well as randomly rotate the grains to expose them to the X-ray beam in many different orientations. Random motions are induced by sonic or ultrasonic vibrations applied to the sample holder to fluidize the powder. Depending on the design of the sample-holder, one can obtain an overall flow of material through the system or generate internal motions by granular convection. This provides greatly improved orientation statistics when samples are too coarse to be analyzed in a conventional manner. Additionally, the technique allows easy insertion and removal of the sample into the instrument and offers possibilities of thickness adjustment for optimizing the output of diffracted X-rays in transmission geometry instruments.

Experimental: Vibrating sample-holders were built and tested with a laboratory instrument and a breadboard prototype of the CheMin XRD/XRF instrument. These sample-holders were composed of a vessel with two parallel X-ray-transparent windows having an adjustable gap (100-400 μm) and a mechanically amplified piezoelectric actuator with a power supply that allows control of the amplitude and frequency of vibration. The sample holders were loaded by simply pouring a small amount of powder into a funnel machined on the top of the assembly and applying sonic vibrations. The vessels contained about 10mg of powder. During XRD analysis, sonic vibrations were ap-

plied to generate granular convection (Figure 1). Unloading the samples was easily done by flipping the assembly upside-down and applying vibrations. Cleaning procedures involving ultrasonic vibrations generated by the same actuator were shown to be effective in preventing cross-contamination.

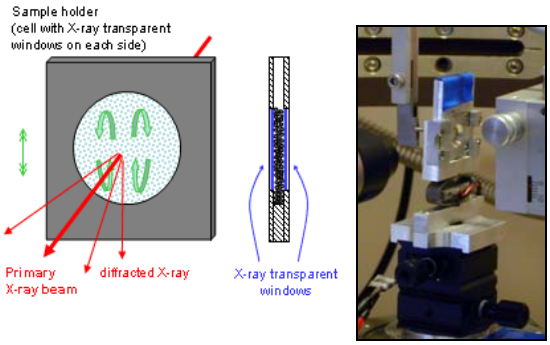

Figure 1: Sample holder allowing granular convection; Left: schematic diagrams; Right: prototype with piezo-actuator installed in an INEL XRD instrument.

Laboratory instrument: An INEL CPS120 (Curved Position Sensitive detector, 120°) diffractometer at Los Alamos National Laboratory was configured in transmission geometry and fitted with a vibrating sample holder. A range of minerals was prepared by crushing and wet sieving to obtain different size fractions: <45 µm, 45-75 µm, and 75-150 µm. XRD measurements were made with and without granular convection. Figure 2 shows the results obtained with a coarse-grained fraction of a crushed quartz crystal loaded in a sample holder with a 175 µm gap between windows.

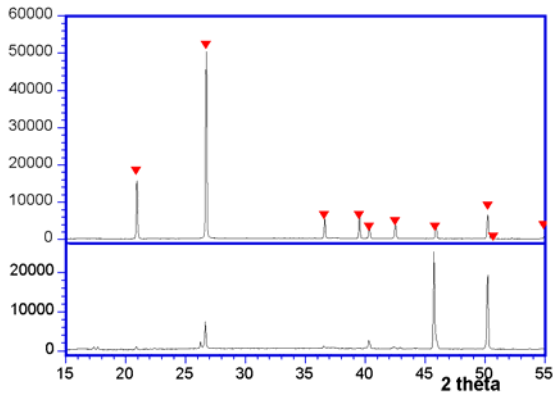

Figure 2: Diffraction pattern of the 75-150 µm fraction of a crushed quartz crystal; Upper: with vibrations (PDF reference in red); Lower: without vibrations; Cu Kα radiation; analytical volume 3x0.3x0.175 mm.

Although the pattern collected with a fixed sample is not interpretable, that collected when vibrating shows all peaks with relative intensities matching reference data from the Powder Diffraction File. Similar results were obtained with other minerals.

Miniature XRD: A 3rd generation CheMin instrument as described in Blake et al. [2] was fitted with a vibrating sample holder. The analytical volume dimensions were approximately 50 x 50 x 200 µm. Figure 3 shows a 2-D diffraction pattern recorded with a sandstone crushed and sieved to <150 µm. It displays perfectly smooth rings that could normally only be obtained with extremely fine powders (<1 µm). Integration of the intensity of the rings allows construction of a 1-D diffraction pattern that can be analyzed with conventional powder-XRD analysis methods. This sample handling technique was used for characterizing a range of minerals as reported in Bish et al. [3] and was successfully tested with a sample prepared with the miniature rock crusher developed at JPL.

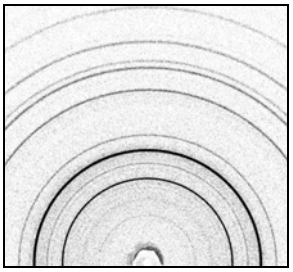

Figure 3: diffraction pattern of a <150 µm size fraction of a crushed sandstone recorded with CheMin III using a vibrating sample-holder. (Co Kα)

Conclusion: This new approach for handling powder during XRD analysis shows a dramatic improvement in data quality for coarse-grained samples. Powders with grain sizes as large as 150 µm can be accurately analyzed in either laboratory or miniature instruments. This grain size range can be directly obtained from crushing systems with no need for further grinding. Insertion and removal of the sample is very simple and does not require movement other than vibrations and valve actuation. Future versions under development will provide automatic sample delivery, sample removal and cleaning of the sample holder, and will allow characterization of a stream of powder when large quantities of material are available. The resulting assembly will be very compact and robust. Fitted to the CheMin XRD/XRF instrument, it would enable characterization of powders produced by the rock crusher planned for the Mars Science Laboratory. A NASA patent application has been filed for this technique.

References: [1] Bish D. L. and Post J. E., *Modern Powder Diffraction*, Reviews in Mineralogy, 20, publisher: Mineralogical Society of America.[2] Blake D. et al., (2004) LPSC XXXV [3] Bish D. L. et al. (2004) LPSC XXXV.