FIELD XRD/XRF MINERAL ANALYSIS BY THE MSL CHEMIN INSTRUMENT. D. L. Bish[1], D. Blake[2], P. Sarrazin[3], A. Treiman[4], T. Hoehler[2], E. M. Hausrath[5], I. Midtkandal[6], A. Steele[7], [1]Dept. of Geological Sciences, Indiana Univ., Bloomington, IN 47405-1405, bish@indiana.edu, [2]NASA Ames Research Center, Moffett Field, CA 94035, [3]inXitu Inc., Mountain View, CA 94043, [4]Lunar & Planetary Inst., Houston, TX 77058, [5]Penn. State Univ., University Park, PA 16802, [6]Univ. of Oslo, Oslo, Norway, [7]Carnegie Inst. of Washington, Washington, DC 20005.

Introduction: The search for evidence of extant or extinct life on Mars (or in any other place) will initially be a search for evidence of present or past conditions supportive of life (*e.g.*, evidence of water), not for life itself. This search will require identification of rock types and mineralogies that could have preserved this evidence. The CheMin XRD/XRF instrument included in the Mars '09 Mars Science Laboratory mission performs definitive mineralogical analysis of crushed or powdered samples through the combined application of X-ray diffraction (XRD, mineral structure analysis) and X-ray fluorescence (XRF, elemental compositional analysis).

The 2006 Arctic Mars Analogue Svalbard Expedition (AMASE) was the latest of a series of expeditions with three main goals: (1) to test portable instruments in the field for life detection; (2) to assess Mars analogue environments for signs of life; and (3) to refine protocols for contamination reduction and to understand the effects of transport on sample integrity by assessing bioloads in the field and then in the laboratory after transportation. AMASE deployed in 2006 at Longyearbyen, Spitsbergen, and traveled by ship to the Billefjord (Ebbadalen) and Bockfjord/Sverrefjell areas where field and laboratory instruments and a rover were deployed for ten days. The CheMin IV instrument was deployed during the 2006 AMASE field campaign to provide a mineralogical context for results obtained from the other AMASE instruments and to provide additional field tests of CheMin.

Methods: CheMin IV includes three main components: a CCD camera, a sample holder, and a Co X-ray source and collimator [1]. The sample cell consists of an 8 mm circular opening fitted with two parallel 7 µm Kapton windows held at a separation of 175 µm. A piezoelectric actuator shakes the sample cell, resulting in granular convection of the powder held within it, exposing all orientations of all grains of the sample to the beam over time. This vibration system allows the analysis of coarse-grained samples that have simply been crushed and passed through a 150 µm mesh screen, eliminating the requirement for fine-grained powder samples. The transmission geometry with a vibrated specimen, yielding partial to full Debye rings, compensates for poor particle statistics and preferred orientation. In the current configuration, the instrument has theoretical X-ray diffraction profiles with a full width at half maximum (FWHM) of ~0.26° 2θ determined principally by the beam diameter at the plane of the sample. Measured resolution was ~0.40° 2θ, due to window movements that caused an effective thickening of the sample volume (subsequently corrected). However, a FWHM of 0.40° 2θ was found to be sufficient to allow field identification of complex mineralogies and for Rietveld refinements.

In operation, a collimated X-ray beam is directed through the sample with the CCD positioned on the opposite side of the sample from the source, directly detecting diffracted or fluoresced X-rays. The CCD is exposed to the X-ray flux for 30 seconds, read out, and erased many times (50-500 exposures) to approach single-photon counting wherein the vast majority of pixels contain charge from either zero or one photon. When operated in this manner, the CCD can be used to measure the charge generated by each photon (and hence its energy). Diffracted X-rays strike the detector and are identified by their energy, producing a two-dimensional image that constitutes the diffraction pattern. This pattern is summed circumferentially about the central beam to yield a one-dimensional 2θ plot comparable to conventional diffractometer data. All X-rays detected by the CCD are summed into a histogram of number of photons vs. photon energy that constitutes an XRF analysis of the sample.

Samples were field prepared by crushing in a percussion mortar, grinding with a mortar and pestle, and sieving to <150 µm. Typically, 5-10 cubic millimeters of material (10-50 mg) was sufficient for an analysis. In most cases, <1 hr of analysis time was necessary to identify an unknown sample's mineralogy. In rare cases in which either the sample did not exhibit sufficient movement in the sample cell (extremely fine-grained material) or a more sensitive analysis was required, greater analysis times were used.

Results: During its deployment, CheMin provided more than 60 quantitative mineralogical analyses of 36 geological samples, many of these co-analyzed by a field version of the SAM instrument (a GC-MS also included in the Mars '09 mission), which consists of a quadrupole mass spectrometer and a gas chromatograph. Samples were of three types: those collected by the scoop of the Cliffbot rover, a variety of samples chosen for analysis by all instruments on the expedition, and other samples chosen by the CheMin team in the field for study. These included variously altered olivine-rich rocks, sulfate and carbonate evaporites, ferric oxides and other Fe-bearing phases, and clay minerals and other weathering products. Most analyses were conducted aboard ship, after a full day in the field in which many samples were collected by the team. In these cases, analyses were conducted within hours of sample collection, providing multi-component analyses of up to seven mineral components with detection to ~3%. On one occasion, CheMin IV analyzed samples halfway up Sverrefjell volcano, the on-board Li hydride batteries providing 6+ hours of continuous operation (Fig. 1). In this case, samples collected by the Cliffbot rover were delivered to the CheMin team, prepared *in situ*, and analyzed on-site. A two-man team hand carried the instrument down the volcano to the zodiac boats after analyses were completed.

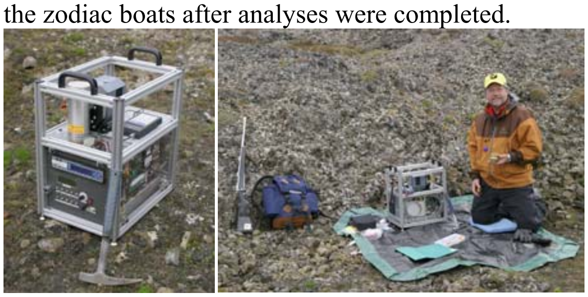

Figure 1. CheMin instrument in the Arctic

Mineralogical analyses of all samples were performed using a combination of qualitative identification (using the program JADE^{TM}) and quantitative Rietveld analysis. Figure 2 shows the 2-D XRD image for the "rover 4" sample provided by the Cliffbot rover, with a 2θ diffractogram derived from the image. The rover 4 sample contained principally quartz with calcite, a mica, a serpentine, and hematite. The broad feature at ~7º 2θ is from the Kapton windows (subsequent versions of CheMin will be fitted with 3.8 µm Mylar windows to eliminate this problem). This is typical of the kind of analysis that CheMin provided to the science team in the field or aboard ship on the day of collection. Figure 3 illustrates the results of a Rietveld refinement using data measured on a sample of gypsum, illustrating the low detection limits achievable with CheMin IV data. Figure 4 shows the results of a refinement on a sample of so-called chicken-wire anhydrite, showing that it is a mixture of both gypsum and anhydrite.

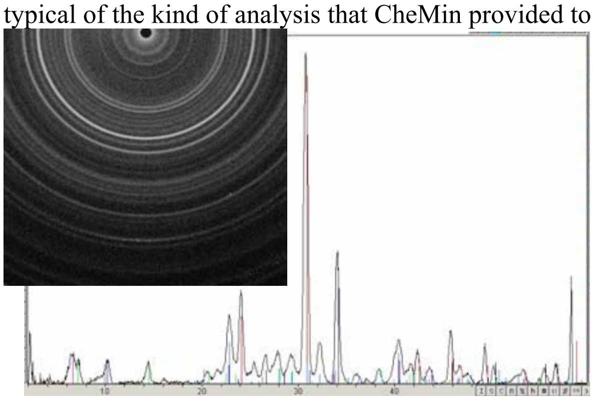

Figure 2. CheMin results for Rover 4 sample.

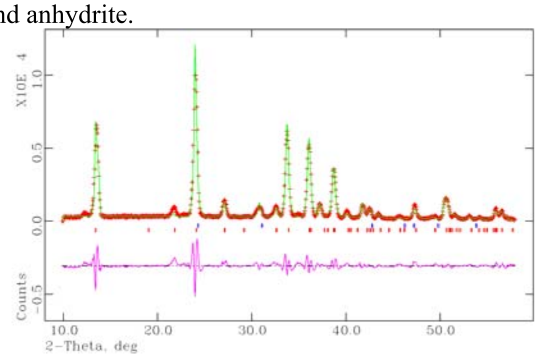

Figure 3. Rietveld refinement results for gypsum sample (97% gypsum-red vertical lines, 3% quartz-blue vertical lines).

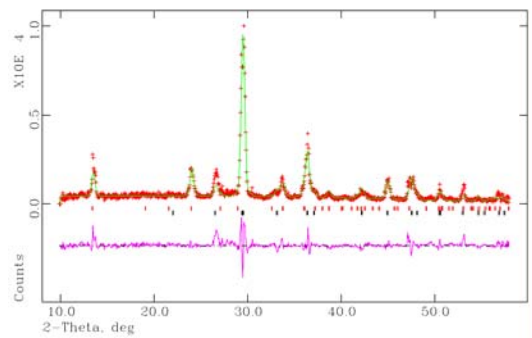

Figure 4. Refinement results for chicken-wire anhydrite sample (74% anhydrite, 26% gypsum).

Conclusions: The 2006 AMASE represents the first time a geological sample was collected, analyzed by XRD, and the results qualitatively and quantitatively interpreted in the field. CheMin provided >60 complete mineralogic analyses, both in the field and onboard ship immediately after sample collection. The speed with which CheMin can definitively identify complex mineralogies in the field (30-60 min) enables knowledge-based collection of field samples, a significant improvement over previous strategies in which samples are exhaustively collected to be analyzed later for significance. This successful field test of the CheMin instrument demonstrates the feasibility of remote XRD/XRF analysis in a compact instrument.

References: [1] Blake, D. F. et al. (2007) *LPSC XXXVIII.*

Acknowledgment: This research was supported by a NASA ASTEP grant to A. Steele.