Determining Mineralogy on Mars with the CheMin X-Ray Diffractometer

The CheMin team logo illustrating the diffraction of minerals on Mars.

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The rover Curiosity is conducting X-ray diffraction experiments on the surface of Mars using the CheMin instrument. The analyses enable identification of the major and minor minerals, providing insight into the conditions under which the samples were formed or altered and, in turn, into past habitable environments on Mars. The CheMin instrument was developed over a twenty-year period, mainly through the efforts of scientists and engineers from NASA and DOE. Results from the first four experiments, at the Rocknest, John Klein, Cumberland, and Windjana sites, have been received and interpreted. The observed mineral assemblages are consistent with an environment hospitable to Earth-like life, if it existed on Mars.

Keywords: X-ray diffraction, Mars, Gale Crater, habitable environment, CheMin, Curiosity rover

INTRODUCTION

The Mars rover Curiosity landed in Gale Crater on August 6, 2012, and is making its way up the flanks of Mt. Sharp. One of the principal goals of the mission is to identify and characterize past habitable environments on Mars (Grotzinger et al. 2012; Meyer 2012). Determining the mineralogy and chemical compositions of Martian rocks and soils provides constraints on formation and alteration pathways, and consequently provides information on climate and habitability through time. Sample compositions are measured with the Mars Science Laboratory (MSL) in three ways: (1) ChemCam, which uses laser-induced breakdown spectroscopy to measure the composition of a spot smaller than ~550 µm from a distance of 7 m (Maurice et al. 2012); (2) Sample Analysis at Mars (SAM), which digests sieved or drilled powders in a furnace and measures their compositions by mass spectrometry (Mahaffy et al. 2012); and (3) the alpha particle X-ray spectrometer (APXS), which uses a combination of X-ray fluorescence and alpha particle induced X-ray emission (Gellert et al. 2015 this issue). X-ray diffraction on MSL is conducted with the chemistry and mineralogy instrument CheMin (Blake et al. 2012), which provides diffraction patterns of particles smaller than 150 µm and results in accurate and time-tested mineralogical identification and quantitative phase abundances. Minerals are natural crystalline materials with limited ranges of chemical composition. The century-old technique of X-ray diffraction is exquisitely sensitive to the crystal structure and secondarily sensitive to the chemical composition of minerals; as such, the CheMin instrument is used to identify the minerals and, through crystal-chemical calculations, to determine constraints on their empirical compositions.

The mineralogy of the Martian surface is dominated by the phases found in basalt and its ubiquitous weathering products. To date, the major basaltic minerals identified by CheMin include Mg–Fe-olivines, Mg–Fe–Ca-pyroxenes, and Na–Ca–K-feldspars, while minor primary minerals include magnetite and ilmenite. CheMin also identified secondary minerals formed during alteration of the basalts, such as calcium sulfates (anhydrite and bassanite), iron oxides (hematite and akaganeite), pyrrhotite, clays, and quartz. These secondary minerals form and persist only in limited ranges of temperature, pressure, and ambient chemical conditions (i.e. humidity, water activity, Eh, pH, etc.), and provide clues about the habitability of Mars. A source rock, such as basalt, may be transformed into a range of different mineral assemblages depending on the physical and chemical conditions that it experiences. Thus, knowledge of the minerals in Martian environments provides insight about the conditions under which the samples were formed or altered and, in turn, about past, potentially habitable environments on Mars.

In addition to crystalline minerals, significant amounts of amorphous and poorly crystalline compounds occur on the Martian surface (Blake et al. 2013; Bish et al. 2013; Vaniman et al. 2014). These amorphous / poorly crystalline materials are not well understood, but they likely occur both as primary phases, such as volcanic and impact glasses, and as secondary phases, through the alteration of primary minerals. Their identification and characterization can lead to an understanding of how they formed. For instance, the presence of volcanic glass indicates that the glass has not undergone aqueous alteration since its formation because such glass weathers readily in the presence of water. In addition, the presence of poorly crystalline phases such as allophane and hisingerite indicates low-temperature alteration of volcanic glass and olivine, respectively. Orbital and in situ measurements of the amorphous / poorly crystalline material found globally in Martian soils suggest that it consists of at least three phases: nanophase iron oxide (Morris et al. 2008), an amorphous silicate consistent with altered volcanic glass, and amorphous sulfate (Vaniman et al. 2004; Chipera and Vaniman 2007). Along with these globally distributed amorphous components, there are local hydrated silica deposits in various places on Mars, such as Valles Marineris, western Hellas Basin, and the Nili Fossae region; their geologic settings suggest that they formed by aqueous alteration of preexisting crystalline or amorphous phases (Ehlmann et al. 2009).

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THE DIFFRACTOMETER

X-ray diffraction techniques are the "gold standard" for identifying minerals, but the use of diffractometers on planetary missions has been problematic mainly because they are bulky and massive. They range from lab diffractometers that are generally the size of a double-wide refrigerator to the huge and powerful synchrotrons located in national laboratories that are from several hundred meters to several kilometers in circumference. In addition to their large size, the power requirements of X-ray sources are severe. The diffraction instruments in my lab operate at about 50,000 volts, and, before MSL, it seems that NASA had never sent a high-voltage power supply into space. Around 1990, in spite of these significant obstacles, Dave Blake, from NASA–Ames, and Dave Bish, Steve Chipera, and Dave Vaniman, from DOE–Los Alamos, independently came up with ideas on how to put a diffractometer into space. They met at a Lunar and Planetary Science Conference, where their posters were located next to each other, and decided to pool their respective talents to solve the problem. Materials scientist and engineer Philippe Sarrazin joined the team as a postdoc in 1994 to solve difficult practical problems and condense the instrument to the size of a breadbox (Fig. 1).

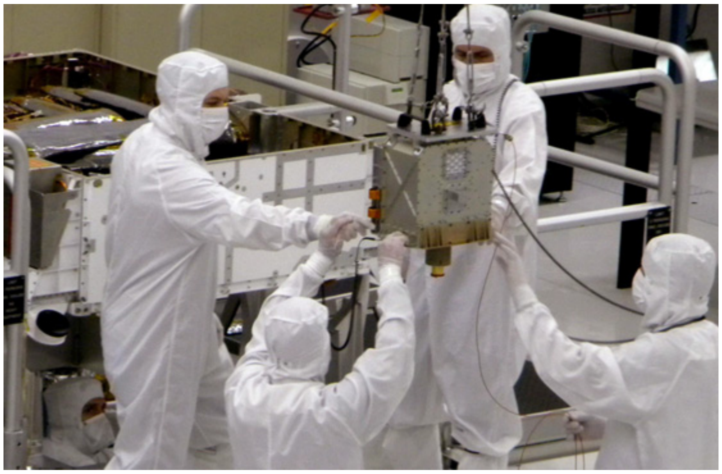

Figure 1 The CheMin instrument being loaded into the rover body during rover assembly. Note that for extraterrestrial use the powder diffractometer has been reduced from the size of a refrigerator to the size of a breadbox. Photo courtesy of NASA/JPL-Caltech

The instrument, described in detail by Blake et al. (2012), has a cobalt X-ray source that operates at a nominal voltage of 28 keV and a current of 100 µA. During an analysis, a collimated X-ray beam is directed through powdered or crushed sample material. An X-ray-sensitive CCD (charge-coupled device) detector is positioned on the opposite side of the sample from the source and directly detects X-rays diffracted or fluoresced by the sample (Fig. 2). The CCD detector is operated in single-photon counting mode (the detector is read out sufficiently often that most pixels contain either no charge or charge derived from a single photon). When operated in this manner, the CCD can be used to measure the amount of charge generated by each photon (and hence its energy). Diffracted characteristic X-rays strike the detector and are identified by their energy (with CheMin, CoKα X-rays with an energy of 6.929 keV are selected). Energy discrimination is important not only to reduce the sample-generated X-ray fluorescence background from a diffraction pattern but also to remove the signals from cosmic rays and high-energy protons and neutrons from Curiosity's Radioisotope Thermal Generator power source (illustrated in Fig. 12 of Blake et al. 2012). CheMin's angular range of 5° to 50° 2θ with <0.35° 2θ resolution is sufficient to identify and quantify virtually all minerals.

This setup is not too different from the original diffraction geometry of Bragg and von Laue, except that they used photographic film instead of a CCD detector. What truly differs, however, is the way the sample is processed. Powder diffraction studies on Earth typically utilize samples that are ground into a fine powder ideally consisting of ~5 µm diameter grains, and the grains are carefully placed into the diffraction position on the instrument. On Mars, we do not have the luxury of grinding samples into fine powders. Instead, we sieve the unconsolidated dust, sand, or drill tailings with Curiosity's CHIMRA processing system to <150 µm (Anderson et al. 2012) and drop the sieved sample into an automated shaker, which consists of a small sample chamber with transparent, plastic windows attached to piezoelectric actuators that vibrate the sample like a tuning fork at ~2000 Hz. This shaker sends the grains into convective motions (as shown in Figs. 3 and 6-8 of Blake et al. 2012). The constant movement of grains allows the X-ray beam to sample crystals in an endless stream of random orientations that, over time, provide a two-dimensional powder diffraction pattern collected as bitmaps from the CCD (Fig. 3). The bitmaps are downloaded from Mars when transmission time and bandwidth are available, and, after 20–25 hours of collecting data, the diffraction pattern is ready to be analyzed. It is first converted into the typical one-dimensional pattern familiar to most scientists, as shown in Figure 3. In the event that the instrument gets clogged, there is a "chaos" mode of larger-amplitude vibrations. We actually found that our nominal vibration during data collection was too strong, and we were losing sample from the top of the cell. To decrease the vibration, we invented the "kumbayatic" mode, where a neighboring cell vibrates strongly enough to induce grain circulation but the sample cell itself is not being vibrated. For most samples, however, we now vibrate the cell directly, but at the lowest-possible energy.

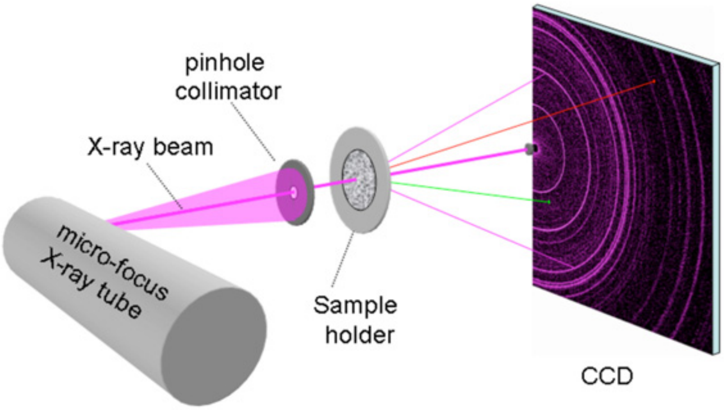

Figure 2 Geometry of the CheMin X-ray diffractometer. In transmission geometry, the X-rays travel from the tube, through a pinhole collimator, and into the sample holder, where they diffract off the random array of grains onto a CCD (charge-coupled device) detector, as illustrated by the purple color. X-rays are also produced from fluorescence effects, shown in red and green, and are discriminated by energy. Figure from Blake et al. (2012)

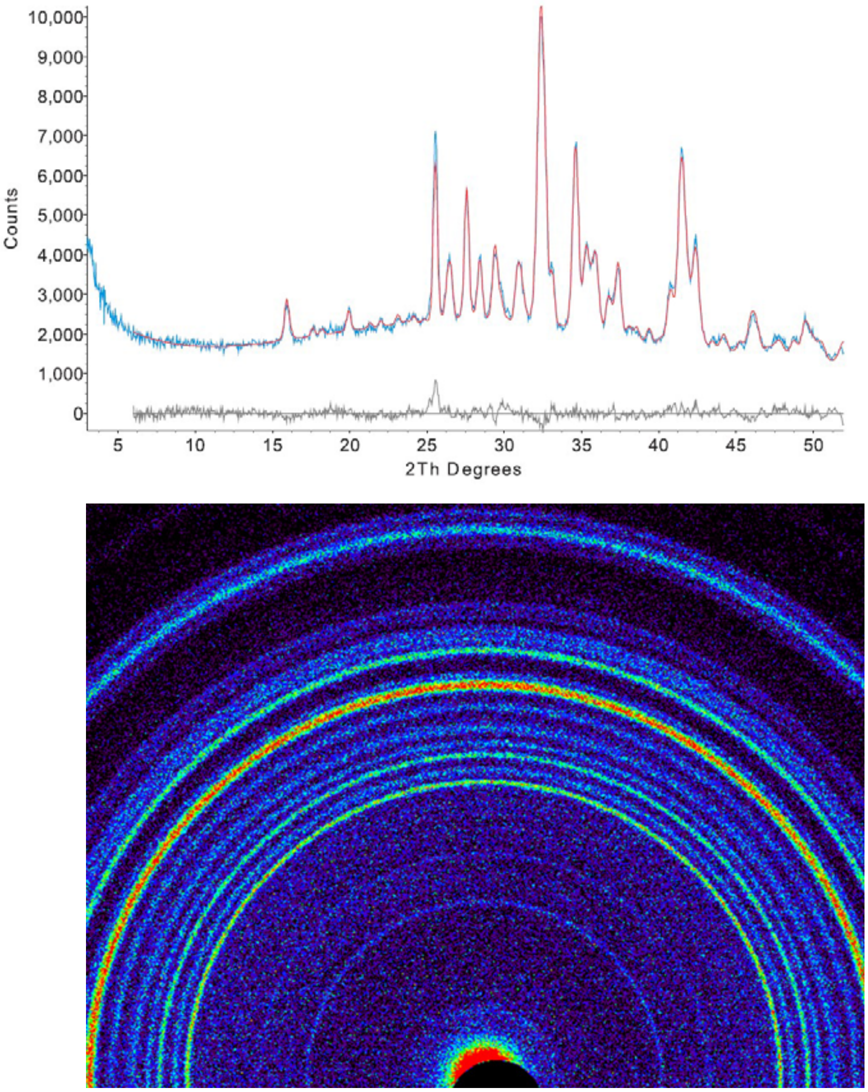

Figure 3 A two-dimensional diffraction pattern collected on the CCD from the eolian soil at Rocknest is shown in the lower panel, and the fitted one-dimensional diffraction pattern is shown in the top panel. Two-dimensional data from the CCD are converted into a one-dimensional pattern that is processed using Rietveld and FULLPAT fitting routines to determine mineral phases and their cell parameters. In the one-dimensional pattern, plotted as intensity (counts) versus detection angle of the diffractometer (degrees 2-theta), the blue line is measured, the red line is fitted, and the grey line is the difference between the two.

The design and successful operation of the CheMin instrument are remarkable engineering feats! An operating diffractometer was reduced to the size of a breadbox, furthering the tradition of NASA and JPL engineering to miniaturize its instruments, making them increasingly portable. Someday we will probably use NASA-engineered devices built into our cell phones for identifying and characterizing many materials, like the fictional tricorder device used on the television show *Star Trek*. The development and deployment of CheMin are good examples of the process necessary to put an instrument into space. It took 22 years of work on the project to get the instrument ready to fly. I saw an eight-page list of proposal titles related to the development of CheMin, and most proposals were closed and labeled as “Failed” or “Denied.” To get an instrument into space requires not only a good idea, but more importantly, bullheaded perseverance. In recognition of the breakthroughs in technologies, the CheMin instrument and design have won several prestigious awards, including the 1999 *R&D Magazine* R&D 100 Award for outstanding technology developments with commercial potential; the 2009 Pittcon Gold Medal for “Best New Product” for CheMin commercial derivatives; the 2010 NASA Commercial Invention of the Year, focused on the sample-handling techniques; the 2011 FLC Far West Regional Award for outstanding commercialization success; and the 2013 Government Invention of the Year. There is a strong culture at NASA to turn its research into benefits for society, and CheMin has demonstrated success here too. The larger agencies of the federal government are required to put monies from their research budget into the Small Business Innovation Research program, which fosters technological innovation in the small business sector and the creation of commercially successful products. The CheMin instrument was commercialized by the company inXitu as a portable bench-top instrument; it is now available through Olympus Instruments and can be operated in the field without significant training (Fig. 4).

ANALYSES AT ROCKNEST

At the time of this writing, the CheMin team has analyzed the data from four samples that represent the lithologies and soils present in the Aeolis Palus region where Curiosity landed (Grotzinger et al. 2015 this issue). The first sample, unconsolidated sand from a small eolian dune called Rocknest, was fed into the instrument on sol 94 (Blake et al. 2013; Bish et al. 2013). The second and third samples were drill tailings from the Sheepbed mudstone at Yellowknife Bay (Vaniman et al. 2014) and were collected on sol 195 (John Klein sample) and sol 282 (Cumberland sample). The fourth sample was drilled on sol 621 (Windjana sample) from fine-grained sandstone at the Kimberley outcrop, as Curiosity made its final approach to Mt. Sharp. At the time of writing, a fifth sample is being processed from a location called Pahrump; this is probably Curiosity’s first opportunity to sample the Murray formation, which comprises the basal stratigraphic unit at Mt. Sharp. See Mahaffy et al. (2015 this issue) for a map of sample locations.

Mars is dusty, although not as dusty as the Moon, and there is plenty of unconsolidated “dirt” lying about (Yen et al. 2005). A fine dust layer coats every available surface. Dust devils have been recorded racing around on the surface of Mars, and dust storms encompassing the entire planet are occasionally observed. In some places the dust collects in eolian deposits of fine to coarse sands. Because these eolian deposits, dust aggregates, and dusty soils are found all over the planet, every mission has had an opportunity to sample them. They display a remarkably homogeneous chemical composition, no matter where the dust is sampled, confirming that the material is circulated and mixed through these planet-wide dust storms. The APXS chemical analyses conducted at Rocknest corroborate the earlier compositional measurements of fine-grained, wind-transported materials (Blake et al. 2013). The eolian

Figure 4 The commercial spinoff version of CheMin, known as Terra, developed by inXitu and now available through Olympus Instruments, is shown in the orange case next to Dr. Pablo Sabron of the Spanish Astrobiology Institute in Spitsbergen, Norway.

material at Rocknest was chosen as the first target to be investigated by CheMin, with the objective of identifying the minerals related to this homogeneous composition.

After about 20 hours of exposure of the eolian material to the X-ray beam, the image in Figure 3 was produced by CheMin. It was an exciting day when the first diffraction pattern arrived from Mars. Our office was a nonstop visitor's center of scientists, politicians, administrators, and colleagues, all wanting to see for themselves the first X-ray diffraction data collected and analyzed from another planet! Remarkably, the event happened more or less on the centennial of the discovery of X-ray diffraction. One hundred years earlier, Laue changed how we interrogate the crystalline solids of the world by conducting the first X-ray diffraction experiments.

The two-dimensional bitmap was converted into the conventional diffraction pattern shown in Figure 3. Using a combination of two rather recent analytical techniques known as Rietveld refinement (Bruker AXS 2000) and FULLPAT matching (Chipera and Bish 2002), the pattern was modeled as a mixture of crystalline and amorphous components. The crystalline components include feldspar (41% by weight of crystalline component), pyroxene (28%), olivine (22%), and some minor phases (as summarized in Table 1 of Bish et al. 2013). The diffraction patterns of the major phases were intense and sharp enough to allow determination of their cell parameters. In addition, the diffraction pattern appears to ride on a major hump, in the 15–40° 2θ region, which is due to the amorphous components (Fig. 3, top panel). We model its abundance as 13–40% of the total sample weight.

The cell parameters of the major phases were optimized during the Rietveld fit and were precise enough to provide meaningful constraints on the compositions of the minerals. For instance, the cell parameters of Mg–Fe-olivine form a well-defined linear trend that increases with iron concentration. Morrison et al. (2013) estimated the chemical compositions of the olivine, pyroxenes, and feldspar at Rocknest. In particular, they reported that the iron content of olivine was 0.88 atoms per formula unit (apfu), which can also be expressed as $(Mg_{1.12}Fe_{0.88})SiO_4$ or $Fo_{56}Fa_{44}$. On Earth, typical mantle olivine, say the well-studied material from San Carlos, Arizona, has an iron content of about 0.18 apfu, or $Fo_{91}Fa_9$. If the Rocknest dune represents a global average, then the average olivine on Mars is $Fo_{56}Fa_{44}$ (Morrison et al. 2013). Indeed, there is more iron on the surface of Mars than there is on the surface of Earth! The composition of pyroxene has been estimated in a similar way and shown to include a Ca component along with Mg and Fe.

Feldspar is not as simple to model as pyroxene and olivine because the crystal-chemical trends are not linear. Not only do Na, K, and Ca variations affect feldspar's cell parameters but so does the ordering of Al and Si in feldspar's tetrahedral sites. In spite of these variables and the large uncertainties in composition, the feldspar data yielded the formula $(Ca_{0.52(12)}Na_{0.48})(Al_{1.52}Si_{2.48})O_8$, which corresponds approximately to labradorite or andesine composition. Pieces of what appears to be plagioclase have also been seen in some of the photos (Edgett et al. 2013). In Figure 5, gemmy fragments of plagioclase can be seen lying in the sands of Mars. Coincidentally, a basaltic lava flow in the Pinacate mountains of northwestern Sonora, Mexico, also yields large gemmy fragments of labradorite, which are used to produce cut gemstones (Fig. 5). These fragments may prove to be good analogues for what is observed on Mars. After an extensive analysis of the mineralogy and composition of the Rocknest sample, the science team concluded that the sands of Mars are similar to the weathered basaltic soils of Mauna Kea, Hawaii (Bish et al. 2013).

Another important result came from the Rocknest site. The ability to estimate the chemical compositions of the crystalline components of the Rocknest eolian deposit permits us to determine the bulk composition of the crystalline materials (Morrison et al. 2013). By coupling this bulk composition with the APXS-derived composition of the entire rock (Gellert et al. 2015), we can constrain the composition of the amorphous component. While previous Martian missions measured the composition of the sand, there was no way to partition this into individual mineral phases. The best that could be done was to apply sensible mineralogical models that were consistent with the composition. With this strategy in mind, Table 4 of Blake

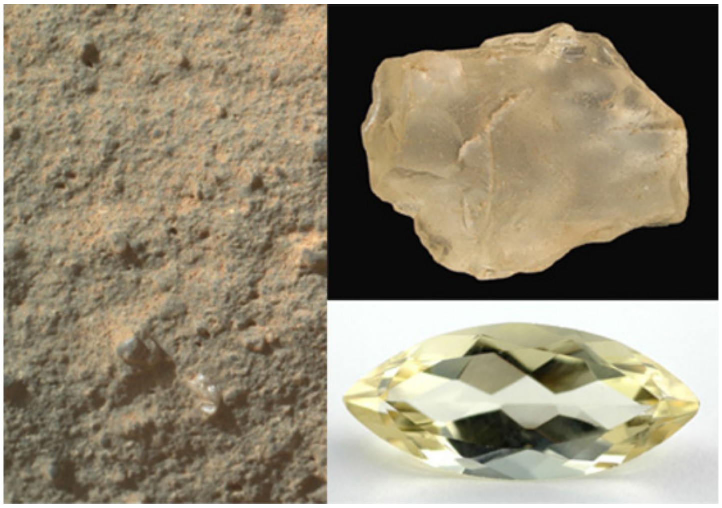

Figure 5 Feldspar fragments on Mars, including several gemmy fragments, are visible in the left panel. In particular, what appears to be a couple of 2 mm feldspar crystals can be seen in the lower center. Figure modified from Edgett et al. (2013). The top-right panel shows a labradorite fragment that weathered out of basalt in the Pinacate mountains of northwestern Sonora, Mexico; it is remarkably like the fragments of feldspar found on Mars, with similar chemistry and cell parameters. Figure from the RRUFF project, R060082. The lower-right panel shows a facetted labradorite gemstone from the Pinacate mountains. These stones may be an analogue material for the Martian feldspar. Photo by Ellen Walmer, sample from the University of Arizona Mineral Museum

et al. (2013) provides an estimate of the compositions of both the crystalline component deduced from the CheMin diffraction profile and the amorphous component derived from the assumption that the overall composition from APXS is amorphous + crystalline. A limiting constraint on the amorphous composition is the assumption that it does not contain Mg. This seems reasonable because if all the Mg is present in the crystalline component, there is still an excess of every other oxide component. This constraint puts a lower limit on the amorphous component of the sand at 37 wt%, with a major-oxide composition of $SO_3 + 3FeO + 4SiO_2$.

ANALYSIS AT YELLOWKNIFE BAY

Based on regional mapping of the landing site, coupled with knowledge of thermal inertia mapped from orbit, the science team decided to investigate a 5 m thick sequence of sedimentary rocks exposed about 450 m east of the landing site (Grotzinger et al. 2014). Called the Yellowknife Bay formation, these rocks comprise an upper assemblage of largely fluvial sandstones and conglomerates, which overlie a basal lacustrine mudstone known as the Sheepbed member. Collectively, these rocks could represent an ancient habitable environment that lasted at least hundreds to thousands of years, and perhaps as much as millions of years. In this environment, water would have been flowing in streams, collecting in a lake, and penetrating into the subsurface via pores and fractures (Grotzinger 2014). Investigating the mineralogy of the mudstone could provide clues about the ancient environment. Accordingly, two samples from two drill sites about 3 m apart, named John Klein and Cumberland, were sent to CheMin for analysis. The analysis proceeded much as it did for the sand at Rocknest. A two-dimensional X-ray diffraction pattern, similar in appearance to that shown in Figure 3, was collected using the CCD detector. This pattern was sent to Earth, where it was processed and turned into a one-dimensional pattern similar to that also shown in Figure 3 and analyzed using the Rietveld and FULLPAT methods. Whereas the Rocknest sand analysis indicated Hawaiian-like basaltic soil, the mudstone revealed the smoking gun for demonstrating habitability (Grotzinger et al. 2014; McLennan et al. 2014; Ming et al. 2014; Vaniman et al. 2014). As a result of chemical weathering of the olivine grains in the detrital basaltic mix, the mudstones contain significant amounts of trioctahedral saponitic smectite clay along with magnetite. The pyroxene, feldspar, and olivine peak positions are the same as those measured at Rocknest, demonstrating that the compositions of the respective mineral species at the two sites are similar. Diffraction signals for minor Ca sulfate in the forms of bassanite and anhydrite were observed, along with pyrrhotite (an iron sulfide). The presence of smectite and the absence of sulfate minerals that form in acidic environments are evidence of near-neutral pH in a freshwater lake with low salinity. The mixed valence states of iron in the magnetite and sulfur in sulfide and sulfate indicate that the environment had a variable redox potential. The mineralogy of the mudstone is consistent with an environment that would have been hospitable to life as we know it. A detailed analysis of the clay and a discussion of olivine reaction pathways that could have provided energy for chemolithotrophic life (life forms, such as bacteria, that derive their energy from the oxidation of inorganic compounds of iron, nitrogen, sulfur or hydrogen) are given in Bristow et al. (in press).

ANALYSIS AT WINDJANA

Initial results from the Windjana sandstone demonstrate the presence of the following major components: augite (21%), monoclinic sanidine or orthoclase (15%), pigeonite (12%), magnetite (10%), clay (8%), and amorphous / poorly crystalline phases (20%). Abundant magnetite and potassium feldspar is a surprise, and more work is needed before firm conclusions are drawn. However, this sample may provide evidence that the sedimentary material came from a differentiated source area—perhaps an alkaline igneous province, first hinted at by the compositional analysis of float rocks early in this mission (Stolper et al. 2013). The presence of substantial quantities of fine-grained clay minerals in the coarser-grained sedimentary rock indicates that the sandstone may have experienced aqueous alteration.

EARTH ANALOGUES FOR MARTIAN SAMPLES

Until we are able to return samples from Mars for further analyses, a fruitful way to investigate Martian mineralogy and geologic processes is to work on analogue materials. What samples on Earth are similar to samples from Mars? It is well known that NASA will go to great lengths and will travel to extremely remote locations to get samples for study. So, anticipating such a field trip, it was a surprise for the CheMin team members to find out that the analogue material most similar to the clay minerals in the Sheepbed mudstone are the clays associated with the basalts at Griffith Park, Los Angeles, a 20-minute drive from the Jet Propulsion Laboratory. The Griffith Park clays are so unusual that they were originally given their own mineral name, griffithite (Larsen and Steiger 1917); however, they have since been found to be an iron-rich variety of saponite. The team conducted several field trips to collect samples of the material at Griffith Park in order to study it and understand the reaction pathways that led to its formation (Treiman et al. 2014). Figure 5 illustrates the incongruousness of studying minerals on Earth that are analogues of minerals on Mars; the sample site is located

Figure 6 A part of the CheMin team, during a collecting trip for the Martian analogue iron-rich saponite clays found in Griffith Park, Los Angeles. From the left: Alan Treiman, Dick Morris, Liz Rampe, and Dave Vaniman, with Dave Blake in the back. Note the Hollywood sign in the background. The famous bat cave from the *Batman* TV series is just to the left of the team. This location has hosted a hundred B-grade science fiction movies about alien invaders, and it now appears to host clays that are most like those from the Sheepbed mudstone on Mars.

near the famous Hollywood sign and next to the Bronson bat cave from the *Batman* TV series of the 1960s, and is home to a hundred B-grade science fiction movies about alien invasions. Considering all the places on Earth that could be similar to a habitable zone on Mars, the presence of analogue clays in Hollywood is amazing! Fortunately, the easy access to Griffith Park has helped us procure materials containing valuable information on the interactions among clays, magnetite, and olivine that may hold important clues about the habitability of the environment on Mars at the time the mudstones were being deposited and during subsequent geochemical changes.

CONCLUSIONS

The minerals and assemblages identified by the CheMin and MSL teams demonstrate that the ancient surface of Mars in Gale Crater was habitable for chemolithotrophic microbes, if such organisms ever evolved on Mars. Water pH was near neutral, freshwater ran in streams, and life, if it existed, would have found the locations sampled by Curiosity to be hospitable. All the identified minerals are common on Earth. The amorphous material is not understood well enough yet, but the planet-wide Martian sand is made of the same minerals as the fertile soils of Hawaii. According to Hazen et al. (2008), the minerals of a planet should coevolve with biological activity, but none of the observations made so far in Gale Crater point to minerals whose origin and distribution require the presence of life. On Earth we have deposits of banded iron formation that some think record the global oxidation event associated with the advent of photosynthesis (Knoll et al. 2012). However, this is a far more advanced metabolic pathway than the chemolithotrophic metabolism suggested by CheMin and other MSL observations (Grotzinger et al. 2014).

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REFERENCES

Anderson RC and 12 coauthors (2012) Collecting samples in Gale Crater, Mars; an overview of the Mars Science Laboratory sample acquisition, sample processing and handling system. Space Science Reviews 170: 57-75

Bish DL and 18 coauthors (2013) X-ray diffraction results from Mars Science Laboratory: mineralogy of Rocknest at Gale Crater. Science 341, doi: 10.1126/science.1238932

Blake DF and 21 coauthors (2012) Characterization and calibration of the CheMin mineralogical instrument on Mars Science Laboratory. Space Science Reviews 170: 341-399

Blake DF and 44 coauthors (2013) Curiosity at Gale Crater, Mars: characterization and analysis of the Rocknest sand shadow. Science 341, doi: 10.1126/science.1239505

Bristow TF and 24 coauthors (in press) The origin and implications of clay minerals from Yellowknife Bay, Gale Crater, Mars. American Mineralogist, doi: 10.2138/am-2015-5077

Chipera SJ, Bish DL (2002) FULLPAT: a full-pattern quantitative analysis program for X-ray powder diffraction using measured and calculated patterns. Journal of Applied Crystallography 35: 744-749

Chipera SJ, Vaniman DT (2007) Experimental stability of magnesium sulfate hydrates that may be present on Mars. Geochimica et Cosmochimica Acta 71: 241-250

Edgett KS, Yingst RA, (2013) Curiosity's Mars Hand Lens Imager (MAHLI): Sol 0–179 activities, observations, range and scale characterization. European Planetary Science Congress 8: EPSC2013-246

Ehlmann BL and 11 coauthors (2009) Identification of hydrated silicate minerals on Mars using MRO-CRISM: Geologic context near Nili Fossae and implications for aqueous alteration. Journal of Geophysical Research 114: E00D08-33, doi: 10.1029/2009JE003339

Gellert R, Clark BC III, MSL and MER Science Teams (2015) Compositional measurements of rocks and soils on NASA's Mars rovers with the alpha-particle X-ray spectrometer (APXS). Elements 11: 39-44

Grotzinger JP (2014) Habitability, taphonomy, and the search for organic carbon on Mars. Science 343: 386-387

Grotzinger JP and 25 coauthors (2012) Mars Science Laboratory mission and science investigation. Space Science Reviews 170: 5-56

Grotzinger JP and 71 coauthors (2014) A habitable fluvio-lacustrine environment at Yellowknife Bay, Gale Crater, Mars. Science 343, doi: 10.1126/science.1242777

Grotzinger JP, Crisp J, Vasavada A, MSL and MER Science Teams (2015) Curiosity's mission of exploration at Gale Crater, Mars. Elements 11: 19-26

Hazen RM and 7 coauthors (2008) Mineral evolution. American Mineralogist 93: 1693-1720

Knoll AH, Canfield DE, Konhauser KO (2012) Fundamentals of Geobiology. Wiley-Blackwell, Chichester, UK

Larsen ES, Steiger G (1917) Mineralogic notes. Griffithite, a new member of the chlorite group. Journal of the Washington Academy of Sciences 7: 6-12

Mahaffy PR and 84 coauthors (2012) The sample analysis at Mars investigation and instrument suite. Space Science Reviews 170: 401-478

Mahaffy PR, Conrad PG, MSL Science Team (2015) Volatile and isotopic imprints of ancient Mars. Elements 11: 51-56

Maurice S and 69 coauthors (2012) The ChemCam instrument suite on the Mars Science Laboratory (MSL) rover: science objectives and mast unit description. Space Science Reviews 170: 95-166

McLennan SM and 50 coauthors (2014) Elemental geochemistry of sedimentary rocks at Yellowknife Bay, Gale Crater, Mars. Science 343, doi: 10.1126/science.1244734

Meyer M (2012) Foreword: Mars Science Laboratory, the first astrobiology mission to Mars since Viking. Space Science Reviews 170: 3-4

Ming DW and 56 coauthors (2014) Volatile and organic compositions of sedimentary rocks in Yellowknife Bay, Gale Crater, Mars. Science 343, doi: 10.1126/science.1245267

Morris RV and 16 coauthors (2008) Iron mineralogy and aqueous alteration from Husband Hill through Home Plate at Gusev Crater, Mars: Results from the Mössbauer instrument on the Spirit Mars Exploration Rover. Journal of Geophysical Research Planets 113: E12S42, doi: 10.1029/2008JE003201

Morrison SM and 22 coauthors (2013) Crystal-chemical analysis of soil at Rocknest, Gale Crater. 44th Lunar and Planetary Science Conference, Abstract #1831

Stolper EM and 18 coauthors (2013) The petrochemistry of Jake_M: a Martian mugearite. Science 341, doi: 10.1126/science.1239463

Treiman AH and 13 coauthors (2014) Ferrian saponite from the Santa Monica Mountains (California, USA, Earth): Characterization as an analog for clay minerals on Mars with application to Yellowknife Bay in Gale Crater. American Mineralogist 99: 2234-2250

Vaniman DT, Bish DL, Chipera SJ, Fialips CI, Carey JW, Feldman WC (2004) Magnesium sulphate salts and the history of water on Mars. Nature 431: 663-665

Vaniman DT and 35 coauthors (2014) Mineralogy of a mudstone at Yellowknife Bay, Gale Crater, Mars. Science 343, doi: 10.1126/science.1243480

Yen A and 35 coauthors (2005) An integrated view of the chemistry and mineralogy of Martian soils. Nature 436: 49-54