Highlights and Breakthroughs

Crystallography on Mars – Curiosity's Bragging right

(On the article *Crystal chemistry of martian minerals from Bradbury Landing through Naukluft Plateau, Gale crater, Mars* by Shaunna M. Morrison and others.)

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Mineral chemistry and crystallography are both necessary for the full determination and characterization of minerals, which are in turn necessary for thorough understanding of their origin, genesis, and occurrence. Planetary remote sensing and surface-mission instruments routinely return data about the chemical compositions of distant solar system materials, but not crystallographic data. Only recently did the first intentionally crystallographic instrument deployed anywhere in the solar system other than Earth – the CheMin X-ray diffractometer (XRD) on Mars Science Laboratory (MSL) rover Curiosity (Blake et al. 2012) – begin operations on the surface of Mars. Morrison and others (2018a) refine previously acquired CheMin data for rock-forming silicate and oxide minerals, and some alteration products, in unconsolidated wind-blown (dune) sediments and environmentally diverse clastic sedimentary rocks encountered along Curiosity's traverse through Gale Crater, Mars. These refined unit-cell parameters constitute a much-strengthened foundation for the next generation of geologic and petrologic interpretation of Mars' surface minerals.

Minerals are defined by crystalline structure and specifiable composition or compositional range. Structure and composition are related. The smallest structural constituents (for example, cations, silica tetrahedra, or carbonate or sulfate anionic groups), and their linkages with one another, have geometric attributes that are consequences of bonding between specific pairs of atoms. Each member of the bonded pair is commonly visualized as having a size (e.g., an atomic or ionic radius) and a charge (valence). Different combinations of elements commonly results in different bond attributes and different structures. However, pairs of structures with similar symmetry but different unit cell dimensions (isomorphs) are common, as are variations of unit cell dimensions caused by substitutions for one another of ions with similar valence and bond characteristics but slightly different size (solid solution). For many mineral groups, correlations between chemical composition and unit cell parameters permit each to be estimated from the other.

Where samples (including meteorites known to originate from Mars) are available in sufficient abundance for examination in terrestrial laboratories, the full range of crystallographic and compositional methods permits thorough identification and characterization of the minerals in the samples. Many minerals have been well-characterized in meteorites from Mars, but specific source areas on Mars are not known for any individual Mars meteorites, so meteoritic mineral data cannot be linked to specific source regions on Mars.

Mars orbiters acquire images and spectra from large areas, but at spatial resolutions much coarser than individual samples. Robotic surface landers and rovers acquire data at sample (centimeter) scale. However, constrained as they are by cost, payload mass, volume, power, and data transfer rates, the ensembles of instruments on individual landers and rovers include only a subset of the analytical capabilities of terrestrial laboratories. One consequence of the hard choices that must be made in selecting instruments is that crystallographic data are almost entirely lacking. Planetary geology continues to advance with remote mineral characterization data that are the best available, but still incomplete by the standards of terrestrial mineralogy.

As was the case in the progress of terrestrial mineralogy, scientific understanding of Mars' surface materials was supported by morphological crystallography (supported by chemical data) before X-ray crystallography. Eight years before Curiosity landed on Mars (2012), each of the twin Mars Exploration Rovers (MERs) Spirit and Opportunity (landed 2004) carried a variety of tools and instruments relevant to geology, geochemistry, and mineralogy (but not XRD). Each rover's Robotic Arm deployed a brush to remove dust and abraded fines; a Rotary Abrasion Tool

(RAT) for grinding ("RATting") through weathered rock surfaces to expose fresh interior materials; an Alpha Particle X-ray Spectrometer (APXS) for elemental abundances; and a Microscopic Imager (MI; ~30 μm/pixel, yielding images with ~100 μm spatial resolution) (Arvidson et al. 2006). Most MER MI images show rock shapes, vesicles, sedimentary structures, grain sizes and shapes, and compaction features of Mars' granular surface materials. A few show euhedral features.

Mars Exploration Rover Opportunity encountered weathered outcrops of sedimentary rocks (hematite-rich basaltic sandstones) in the Burns Formation at Meridiani Planum (Herkenhoff et al. 2004; Squyres et al. 2004; Grotzinger et al. 2005; Herkenhoff et al. 2008). Some outcrop surfaces displayed randomly oriented euhedral (blade-shaped) or discoid to lozenge shaped cavities (collectively called vugs in the earliest papers) transecting sedimentary laminations (Squyres et al. 2004; Herkenhoff et al. 2004, 2008). The euhedral cavities were interpreted as moldic secondary porosity after euhedral crystals of a water-soluble early diagenetic mineral (Herkenhoff et al. 2004, 2008; McLennen et al. 2005). Their parallelogram outlines are consistent with a tabular (pinacoidal) habit of a mineral that is either monoclinic (Herkenhoff et al. 2004; McLennan et al. 2005) or triclinic (Peterson and Wang 2006; Peterson et al. 2007).

Chemical data from Opportunity's APXS and deconvolution of thermal-emission spectroscopic (TES) data from Opportunity's Mini-TES suggest that magnesium, calcium, or iron sulfate minerals are present in abundances of 15–40 ± 5 modal volume percent (Rieder et al. 2004; Christensen et al. 2004; McLennan et al. 2005). Several sulfate minerals consistent with compositional data for these and related sedimentary rocks at Meridiani Planum are monoclinic (gypsum, kieserite, hexahydrite; Herkenhoff et al. 2004; Squyres et al. 2004; Arvidson et al.

2005; melanterite, McLennan et al. 2005; starkeyite, Peterson et al. 2007) or triclinic (pentahydrite, meridianiite; Peterson and Wang 2006).

Meridianiite ($MgSO_4 \cdot 11H_2O$) was experimentally synthesized, and recognized from natural samples found at terrestrial locales with environmental conditions consistent with the solid's phase diagram (Peterson and Wang 2006; Peterson et al. 2007). The crystallographic parameters of natural terrestrial meridianiite (a = 6.7459 Å, b = 6.8173 Å, c = 17.280 Å, α = 88.137°, β = 89.481°, γ = 62.719°) (Peterson et al. 2007) include $a \approx b$ (within ~1%) and $\alpha \approx \beta$, (both <2° from perpendicular). Thus, the unit cell geometry of meridianiite is very close to monoclinic. If the interpretation that the mineral removed to form the crystal molds observed at Meridiani Planum is meridianiite (Peterson and Wang 2006; Peterson et al. 2007) is correct, then the earlier interpretation that the crystal molds at Meridiani Planum represent a monoclinic mineral can be accounted for. Measurements from the MI images would not have easily distinguished between triclinic morphology with α and β so near 90° and monoclinic crystal morphology.

Images from Mars of crystal morphology have evoked the pioneering role of morphological crystallography in the mineral sciences. Whereas morphological crystallography dominated terrestrial mineralogy for more than a century before the X-ray diffraction revolution, XRD arrived on Mars within a decade after the few tantalizing images of crystal morphology. Although imagery from other rovers will continue to support tentative identifications of minerals based on morphological crystallography, Curiosity's CheMin XRD data enable greatly expanded understanding of mineral structures and chemical compositions on Mars.

MSL rover Curiosity and its CheMin instrument are acquiring XRD data of primary minerals and products of aqueous alteration in unconsolidated wind-blown sediments and fluvial, deltaic,

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lacustrine, and aeolian sandstones, mudstones, and conglomerates at Gale Crater. Among the signature findings uniquely enabled by CheMin, Treiman et al. (2016) used CheMin data to determine compositions of alkali feldspar in sandstones at one sampling site, from their unit cell parameters. Their results yield compositions strongly supporting the hypothesis that potassic alkaline igneous rocks, a rock type for which evidence has "been indirect or speculative until recently" (Treiman et al., 2016, p.98) on Mars, existed in the source area of the sampled sandstones.

Morrison et al. (2018a) refine previously acquired CheMin data for plagioclase, sanidine, clinopyroxenes, orthopyroxene, olivine, spinel, and minerals of the alunite-jarosite group. Using each sample's own plagioclase as an internal standard, Morrison et al. (2018a) correct for each sample cell's offset (<80 μm in all cases), its effect on the sample-cell-to-detector distance and where the diffracted beam intersects the detector, and the consequences for Bragg's Law interpretation of the detected 2θ angles for all of that sample's other minerals. The corrections result in different values of unit cell parameters than previously reported for these samples (e.g., by up to 0.02 Å for olivine), which are in turn extremely important to the subsequent usefulness of the unit cell parameters as indicators of mineral composition.

Morrison et al. (2018a) invoke regression relationships, that they establish in a companion paper (Morrison et al. 2018b), between unit cell parameters and crystal chemical compositions from published data for each relevant mineral group. Combining the improved unit cell parameters and the crystallography-composition regression algorithms, they revise the minerals' inferred chemical compositions. The combined effects of sample-cell offset and the regression algorithms result in compositions that differ subtly for some minerals, and appreciably for others, relative to previously published compositions for the same minerals estimated from the pre-correction CheMin data. For example, olivine compositions from sandstone sample Windjana were first reported to be Fe-forsterite, ~$Fo_{59\pm06}$ (Treiman et al., 2016); correction for sample-cell offset yields improved unit cell parameters corresponding to $Fo_{67.5}$ (Morrison et al., 2018a).

At the present state of NASA's Mars Exploration Program planning, the mineral abundances and compositions determined from MSL Curiosity CheMin data complete the only full mineralogical data set for Mars surface materials until a Mars Sample Return mission (MSR), which is still at least a decade away. The XRD data, acquired with Curiosity's unique CheMin instrument and corrected for small sample-stage offsets by Morrison et al. (2018a), enabled a major expansion from and improvement upon all previous identifications of rock-forming minerals from Mars mission data, all of which were based on observations that did not include crystallography. The refined unit-cell parameters and the updated mineral compositions derived from them by Morrison et al. (2018a) provide a firm new foundation for future interpretations of igneous-mineral and -rock formation conditions, sediment provenance, pre-depositional and diagenetic chemical alteration, and habitability assessment on Mars.

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