Supplementary Material, Bristow et al: The origin and implications of clay minerals from Yellowknife Bay, Gale crater, Mars

Methods

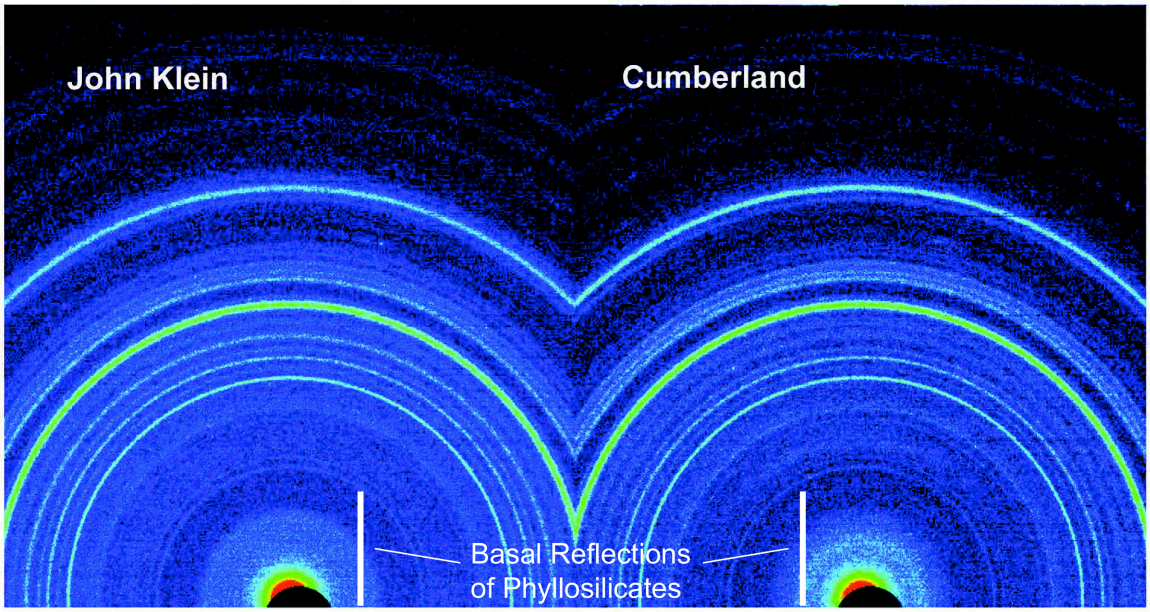
The Sample Analysis at Mars (SAM) instrument performs a range of experiments and measurements (Mahaffey et al., 2012), though evolved gas analysis (EGA) is most helpful in constraining mineralogy. EGA involves heating a powdered sample delivered to the instrument and tracking the evolution of volatiles (e.g., H_2O, CO_2, O_2 and S species) during heating to ~860°C or more. The evolution of HO is particularly interesting for studying clay minerals because the temperature of clay mineral dehydroxylation is influenced by the metal species in octahedral sites (Brigatti, 1983; Brindley and Lemaitre, 1987). The quantity of H_2O evolved also gives estimates of clay mineral abundance (Ming et al., 2014; McAdam et al., 2014; McAdam et al., *in prep*).

CheMin is a miniaturized X-ray diffraction instrument that analyzes powdered samples in transmission geometry using a microfocus Co X-ray source to minimize absorption from iron in samples (Blake et al., 2012). X-ray diffraction data are critical for identifying and characterizing minerals in samples collected by *Curiosity*, and particularly important for clay minerals that are difficult to characterize by other means. Drilled powdered rock is sieved to <150 μm and delivered to the CheMin sample funnel by CHIMRA (Collection and Handling for In-Situ Martian Rock Analysis) – *Curiosity's* sample handling system (Anderson et al., 2012). The CheMin sample funnel delivers powder into one of CheMin's 27 reuseable sample cells. Once in the cell, the loose powder is held between thin (~7 μm) mylar or Kapton™ cell windows and is vibrated at ~2000 Hz to create granular convection which minimizes preferred orientation of the crystallites – a prerequisite for accurate mineral quantification (Blake et al., 2012). Both John Klein and Cumberland were analyzed in mylar cells to minimize potential interferences in clay mineral detection (the diffraction pattern of Kapton™ contains a small maximum which could be mistaken for a 001 phyllosilicate peak; Blake et al., 2012). Analysis of empty cells prior to filling with samples confirmed that there was no significant contamination from previous runs (Vaniman et al., 2014).

The total analysis times for John Klein and Cumberland are 33.9 and 41 hours, respectively. CheMin's CCD detector is operated in energy-discriminating, single photon counting mode so that only CoK〈photons contribute to the accumulated pattern. The 2D diffraction patterns collected by the CCD (Fig. 1) are converted to more familiar one-dimensional (1D) patterns (Fig. 2) of intensity versus 2θ (~3 to 53°). The powder XRD patterns presented and discussed in this paper were converted using a customized computer program written by Przemek Dera (University of Hawaii, Manoa). Conversion requires knowledge of the position of the center of the X-ray beam relative to the CCD, the distance between the sample and the CCD, and any CCD offset from being perpendicular to the beam. These parameters are calculated for CheMin using a measured 2D diffraction pattern and unit-cell parameters of an onboard beryl standard that was analyzed earlier in the mission. The beryl standard has been characterized and its unit-cell parameters determined based on high quality laboratory patterns measured on a Bruker D8 at Indiana University. Instrument geometry parameters determined in this way were

used in subsequent 2D-to-1D conversions of sample patterns. Conversion involves circumferential integration of intensity data after manual removal of 'hot-pixels', which are artifacts of charge defects on the CCD, the result of cosmogenic or Radioisotope Thermal Generator (RTG)-generated radiation and/or the result of individual grains in the sample which on rare occasions become stuck in the beam in diffraction orientation. Detailed characterization of clay minerals is challenging because additional size separation and chemical/physical treatments (e.g., cation exchange, glycolation, heat treatments – see Moore and Reynolds, 1997) of samples that are routine in laboratory clay mineral analysis are not possible onboard *Curiosity*. Also, the angular range of the instrument excludes the 060 region (1.55 to 1.48 Å) typically used in determining the octahedral occupancy of clay minerals (Moore and Reynolds, 1997).

Supporting chemical analysis come from two other instruments. The Alpha Particle X-ray Spectrometer (APXS) provides the bulk chemical composition of ~1.7 cm diameter, circular targets of surface materials (Gellert et al., 2006; Campbell et al., 2012), including the drill tailings (McLennan et al., 2014); however, the mineralogy may only be inferred (e.g., by calculating normative mineralogy). In sufficiently coarse-grained samples (>0.5 mm), individual laser-induced breakdown spectrometer (LIBS) analyses from the ChemCam instrument can determine the chemistry of individual minerals (Wiens et al., 2012).



Appendix Figure 1 – 2D XRD patterns from John Klein and Cumberland. CCD images are summed products of 41 and 33.9 hours of analysis, respectively, with hot pixels caused by aberrations on the CCD manually removed. The dark circle in the lower center of the images is the beam stop, which blocks direct transmission of X-rays onto the CCD. The low-angle region where basal reflections of clay minerals are observed is labeled.

Table 1. Analysis schedule for John Klein and Cumberland samples.

Sample	Mission Sol Analyzed
John Klein	195, 197, 200, 226, 228, 229, 230, 232, 238, 270, 271, 272, 473, 476, 488
Cumberland	282, 283, 287, 289, 293, 300, 310, 418, 421, 425, 432

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