GRAIN SIZE, 'SPOTTY' XRD RINGS, AND CHEMIN: TWO-DIMENSIONAL X-RAY DIFFRACTION AS A PROXY FOR GRAIN SIZE MEASUREMENT IN PLANETARY MATERIALS. M. S. Bramble[1], R. L. Flemming[2], P. J. A. McCausland[2], [1]Dept. of Physics and Astronomy, and the [2]Dept. of Earth Sciences, The University of Western Ontario, London, ON, N6A 5B7, Canada (michaelbramble@gmail.com).

Grain Size from 2D XRD: Two-dimensional (2D) X-ray diffraction (XRD) data can provide textural information about the mineral assemblage of a sample in addition to mineral identification by structure [1-4]. In film and for more modern 2D XRD detectors, diffracted X-rays are recorded as Debye rings, with the radius of the ring representing the 2-theta angle of a particular diffraction condition for an irradiated crystal structure. Debye rings contain textural information about the sample, such as its degree of crystallinity and potentially structural distortion effects such as the degree of strain experienced by individual mineral grains [1,4]. In particular, a 'spotty' ring can be inversely correlated with the grain size of a material (e.g. [1,2]); with increasing grain size a progression is observed from classically smooth Debye diffraction rings (for <5 μm powders), to rings with many discrete spots, to fewer spots, and finally to diffraction spots representing a single crystal (Fig. 1). The observed 'spottiness' of the diffraction rings thus allows for inferences to be made about the mean grain size of the sample between ~ μm crystals up to about the size of the incident X-ray beam. Here, we perform an experimental study of 2D XRD grain size estimation on mineral powders with known sieve fraction grain sizes, and then apply this empirical method to the interpretation of 2D XRD data from the Mars Science Laboratory.

Theory and Method: We have used the method of He [3] to estimate grain size by relating an integrated window on a 2D XRD detector to the volume of an irradiated material. The number of grains contributing to a particular diffraction ring is measured by integrating in the χ direction and then fitting a polynomial or average intensity trendline. Half the number of times this χ-profile crosses a trendline represents the number of irradiated grains contributing to the ring. The grain size is then measured by ratioing the beam divergence, multiplicity, and instrument angular window to the number of grains in the profile and cube-rooting the result. The X-ray source beam diameter and linear absorption coefficient for the target mineral are also taken into account, along with changed constants, for reflection-mode as opposed to transmission-mode XRD.

Application to well-characterized pyroxene: Using the Bruker D8 Discover micro-X-ray diffractometer (μXRD) at the University of Western Ontario [4], the grain size measurement method [3] was applied to a set of well-characterized ferroan enstatite pyroxene samples [5]. The μXRD operated with θ-θ geometry, stationary optics, and no sample motion using a CoKα source (λ = 1.7902 Å) at 35 kV and 45 mA to produce incident X-rays in a 300 μm diameter beam. 2D data were collected on a HI-STAR area detector located 12 cm away from the sample and analyzed using General Area Detector Diffraction System (GADDS) software.

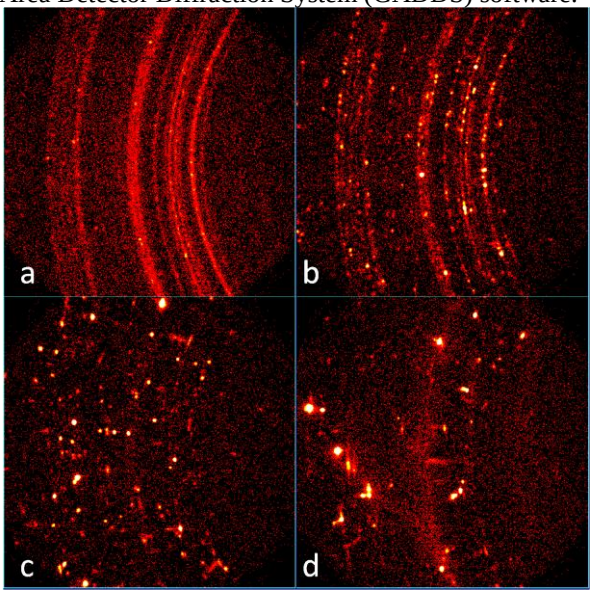

Figure 1. 2D XRD images of pyroxene samples of increasing grain size; (a) relatively continuous rings of a sample ground to <5 μm with a mortar and pestle; (b), (c), and (d), show the progression of 'spotty', closely spaced rings to more discontinuous rings as the grain size increases in sieve size from 10–15, 25–38, to 90–125 μm, respectively. The very fine grained polycrystalline material visible in (d) is mineral dust, as the specimen was not washed after crushing.

The calculated grain sizes by χ-profile analysis of diffraction rings (Fig. 2a-b) correlate well with the sieve size bins of the pyroxene samples. The measured grain sizes either fell within the sieve size bins, or just outside the bin by ± ~5 μm. Discrepancies may result from equation parameters (such as using a given beam divergence [3]), or from the pyroxene physical properties and their effects on sieving. An independent assessment of the sieved samples by electron microscopy will help to quantify their mean grain size, allowing for firmer conclusions about the 2D XRD method. For grain sizes >100 μm the effectiveness of the method breaks down [3]. With the geometry used in this study, the close detector distance causes the equation to begin to significantly underestimate grain size (≥14 μm) as the sieve sizes increase above ~50 μm. This is likely the result of fewer diffraction spots reaching the detector area for a given Debye ring.

Effect of oscillation / granular convection: This method of grain size measurement relates the detector image with the irradiated sample volume, and therefore it is necessary for the sample to remain stationary during data collection. Samples analyzed by CheMin are vibrated [6] to increase the number of grains achieving diffraction condition, so the application of the above method may subsequently underestimate grain size. We therefore collected some oscillated sample data for three of the sieved pyroxene bins (ranging from 10 to 38 μm) with an oscillation in Y of 3.5 mm, to investigate the effects of sample motion on the diffraction rings. The 'spotty' rings became more uniform. The calculated grain size fell into the correct sieve bin for one sample and the other two samples underestimated the grain size by ~5 μm, suggesting that a similar calculation applied to CheMin data would similarly underestimate grain size.

Calculated MSL Rocknest grain size: The grain size measurement calculation was applied to CheMin 2D XRD images collected from the fifth scooped sample at the Rocknest site at Gale Crater [7]. The 2D XRD images were analyzed with a ten-step integration per degree χ. The transmission-mode calculation is independent of sample chemistry, but for multi-phase materials a volume fraction of the analyzed material must be known. We used the refined modal mineralogy from [7]. Transmission-mode does not require assumptions about the effective sampling volume and therefore should generate a more direct grain size calculation.

The first image analyzed was one generated from the 55 images uploaded from sol 94 to sol 119. The χ-profile analysis (Fig. 2c-d) calculated grain sizes for plagioclase, enstatite, and forsterite with resultant values of 4.8, 6.7, and 5.1 μm, respectively. With the above arguments, these values are likely underestimates of the actual mean grain size. *Curiosity*'s hardware provides an upper grain size limit of 150 μm and these XRD calculations provide the lower limit.

According to the PDS labels for CheMin data products, it appears that a brief, yet unsuccessful, experiment was conducted in the aim of collecting a pattern without grain motion. The resultant 2D image displayed no diffraction spots, but the image (generated from frames uploaded on sol 148) was analyzed using the χ-profile method. If the degree of granular convection was reduced, there should be fewer diffraction spots contributing to the Debye ring and the grain size should be less underestimated and closer to the actual value. The calculation resulted in an increase of <1 μm for the plagioclase and forsterite and a decrease in <1 μm for the enstatite. The absence of a significant increase in calculated grain size suggests that granular convection still occurred, but it should also be noted that due to the collection time and data resolution this calculation was possibly compromised by signal to noise factors.

If future 2D XRD data are successfully collected from *Curiosity* without any granular convection, then a more confident grain size calculation can be made. XRD is essential for mineral identification, and if future planetary spacecraft are equipped with an *in situ* μXRD as proposed in [8], precise grain size measurements could be calculated on a regular basis. This method, when paired with a stationary sample, should provide a quantitative, non-optical method for grain size measurement by planetary spacecraft.

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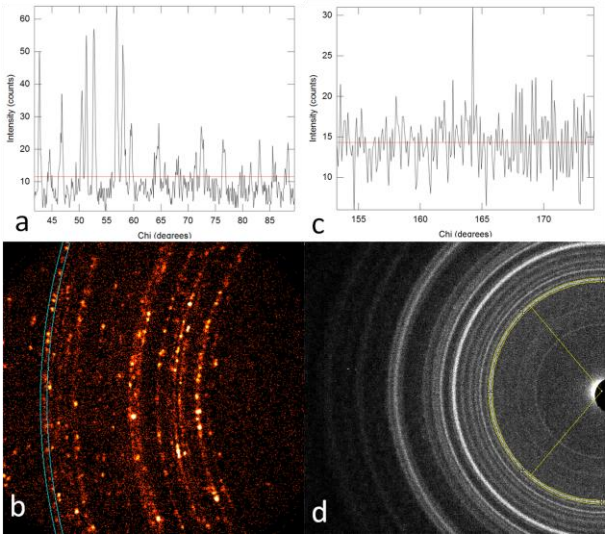

Figure 2. Pyroxene χ-profile (a), and corresponding 2D image showing the window of integration (in blue) (b). Pyroxene sieve size: 10–15 μm, wet sieved [5]. CheMin 2D XRD image generated from frames uploaded from sol 94 to sol 119. A χ-profile (c) segment is depicted along with the 2D image window of integration (d).