An Analysis of the Effects of Sample Processing on X-ray Powder Diffraction Peaks and the Implications for Studies of Shock Metamorphosed Carbonates. E.S. Simpson[1] and K.A. Milam[1], [1]Ohio University, Department of Geological Sciences, 316 Clippinger Laboratories, Athens, OH 45701-2979 (es940714@ohio.edu).

Introduction: Studies of shock metamorphosed minerals have heretofore focused chiefly on silicates because of their dominance in the Earth's crust and the wide variety of shock metamorphic textures (PFs, PDFs, and high pressure polymorphs) that they display [1]. Carbonate minerals have been the subject of lesser attention due to their comparatively higher solubility and lower abundance in terrestrial target rocks. Carbonates respond to shock metamorphism by twinning, cleaving, and fracturing as they do when subjected to endogenic deformation mechanisms [2]. Shock metamorphism can also produce disorder within carbonate crystalline lattices that can be measured by X-ray diffraction (XRD) [3, 4, 5, and 6]. Diffraction peaks of shocked minerals have been shown to display reduced peak heights and broadened peak widths [4]. It has been suggested that peak broadening may be a good indicator of what shock pressures were experienced by target rocks in different parts of an impact structure [6] and may also aid in documenting shock wave dissipation [3]. Understanding how minerals are deformed by shock pressure is vital in order to understand what has occurred in the target rocks of a terrestrial impact. Earlier XRD studies however, paid relatively minimal attention to the potential that post-impact alteration and sample processing may have in masking shock metamorphic signatures. When rock samples are processed for XRD analyses they are commonly ground into fine powders to minimize crystallographic orientation effects in diffraction data. Grinding may introduce disorder into the crystal lattice and increase peak broadening [4].

Hypotheses: This study assessed the following hypotheses using both shocked and unshocked dolomite specimens: 1) longer duration grind times increase the magnitude of peak broadening in X-ray diffraction patterns, 2) mechanical pulverization of the same sample using variable grind times leads to differences in peak broadening that are more consistent and predictable than comminution by hand, and 3) samples from an impact structure will show lower intensities and more peak broadening in the central uplift than in the crater rim when processed using mechanical pulverization. Assessment of the later hypothesis would be a means of determining if the effects of sample processing overprint the effects of shock metamorphism.

Sample Collection: Samples of the unshocked Neoproterozoic Beck Springs Dolomite (lower laminated member) [7] were collected from Inyo County, CA from a natural exposure without the use of a hammer (in order to eliminate any artificially induced lattice deformation).

Samples of the shocked Peebles Dolomite from the Serpent Mound impact structure were collected at the sites shown in Figure 1 in a similar fashion. The Serpent Mound impact structure represents the remnants of an 11-14 km diameter complex impact crater located in southwestern Ohio (Fig. 1) at the corner of Pike, Highland, and Adams counties. Shatter cones[8, 9], shocked quartz [10, 11], and coesite have been detected in the central uplift [9, 12] confirming the impact origin of this structure.

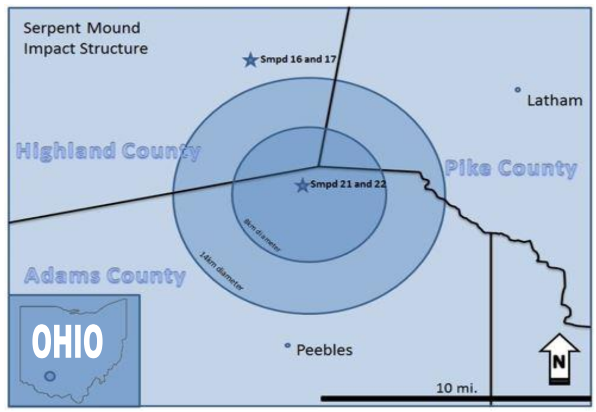


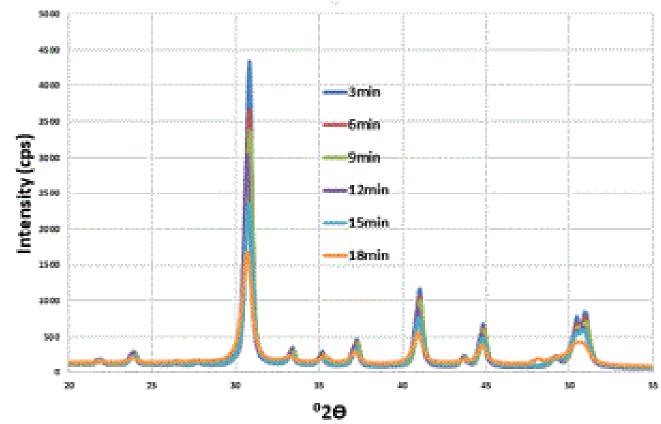
Figure 1: Map of Serpent Mound Impact Structure showing the sample collection locations

Samples were collected from both the northern rim (samples 16 and 17) and the central uplift (samples 21 and 22) (Figure 1) and processed in a similar fashion to determine if sample grinding might overprint possible shock metamorphic signatures in diffraction data.

Methods: One sample of the Beck Springs Dolomite was cut into 6 thin slabs using a trim saw. Slabs were then cut into <cm-sized pieces to eliminate the need to further crush the sample using a hammer. Each aliquot was then divided into 3 portions, one ground by mechanical ring pulverizer, one ground dry in a mortar and pestle, and the third ground in solution with alcohol in a mortar and pestle (as is the usual method for XRD work on impact structures) [13]. Using these 3 methods of grinding, the samples were ground into powders and sieved to a particle size of $<25\mu m$. This size fraction was used to minimize bias in X-ray diffraction data that has been shown to occur due to crystal lattice orientation [14]. After all of the aliquots were ground by all 3 methods, 20 diffraction patterns were obtained for each aliquot in the Rigaku MiniFlex benchtop X-ray diffractometer (sampling parameters: 2θ of 20º to 120º, 15kV, 30mA, scan speed of 2º/min, and a sampling interval of 0.02º) and averaged to produce a mean diffraction pattern. Once analyses were completed, Reitveld peak refinements were performed on each diffraction pattern in order to compare the amount of peak broadening.

Results: Diffraction peaks of unshocked samples (Fig.2) processed by mechanical pulverization display an overall trend of decreasing intensity and increasing peak width with increased grind time (~62% decrease in intensity from 3 to 18 minutes). Peak intensities from aliquots dry ground by mortar and pestle are generally higher than samples ground by pulverizer, but peak broadening doesn't correlate in a linear fashion with grind time when ground by hand. Diffraction patterns for the wet hand ground aliquots also have variable peak broadening and intensities, but overall peak intensities are lower than those ground in the pulverizer.

Results indicate that mechanical pulverization produces the most predictable and consistent amounts of peak intensity and broadening with increased grind times and therefore was the method used to analyze the shocked Serpent Mound samples. XRD patterns for these samples ground for 3 minutes in the mechanical pulverizer are shown in Fig. 3.



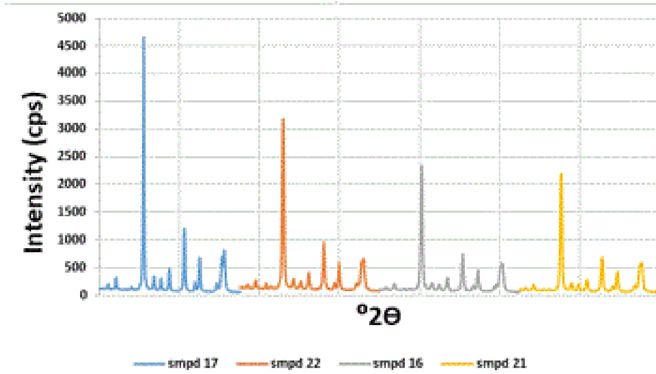


Figure 2 (top): Diffraction patterns for unshocked dolostone samples ground in the mechanical pulverizer

Figure 3 (bottom): Diffraction patterns for all four Serpent Mound samples (X-axis separated for clarity)

Discussion: Hypotheses 1 and 2 are consistent with results reported in this study. As observed in Figure 2, longer duration grind times do result in decreased peak intensity and increased peak broadening in similar amounts for aliquots ground in the mechanical pulverizer.

For hypothesis 3, 1 of the 2 samples from the crater rim has higher intensity XRD peaks than the 2 samples from the central uplift when processed for 3 minutes (Fig. 3). This is the expected outcome as the rocks in the central uplift typically experience higher shock pressures than those on the crater rim. While smpd 16 has higher average peak intensities than one of the central uplift samples, it has a lower intensity than the second. This hypothesis needs to be studied further in order to have definitive results. Ongoing work looking at the full width half maximum plots and statistical analyses will provide additional insight. Thus far it appears that samples processed for longer times (6-18 min.) produce highly variable results indicating the peak intensities and peak broadening may not entirely be a result of shock metamorphism, rather inconsistent lattice deformation caused by grinding. Preliminary results indicate that the best method of processing carbonates may be to grind samples for 3 minutes or less in a mechanic pulverizer to minimize peak broadening created by sample processing in shock metamorphic studies.

References: [1] Melosh H.J. (1989) *New York, Oxford University Press* [2] Langenhorst F (2002) *Bulletin of the Czech Geological Survey, 77, 265-282.* [3] Bell M.S et al. (1998) *LPS XXIX* [4] Hanss R.E. et al. (1978) *LPS IX, 2773-2787* [5] Huson et al. (2009) *Meteoritics and Planet. Sci. 44, 1695-1706*. [6] Skala R. et al. (1999) *LPS XXX* [7] Gutstadt A.M (1968) *Journal of Sedimentary Research, 38, 1280-1289.* [8] Dietz R.S. (1960) *Science, 131, 1781-1784.* [9] Cohen A.J. et al. (1961) *Science, 134, 1624-1625.* [10] Carlton R.W et al. (1998) *Earth and Planet. Sci. Letters, 162, 177-185.* [11] Koeberl C. et al. (1998) *LPS.* [12] Gaddis S.J. et al. (2001) *11th Annual V.M. Goldschmidt Conference.* [13] Foit F.F. (1992) *Powder Diffraction, 7, 236.* [14] Warren, B.E. (1969) *Addison-Wesley Publishing Company 101-108.*