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X-RAY POWDER DIFFRACTION EVIDENCE FOR SHOCKED QUARTZ IN AN UPPER EOCENE SAND DEPOSIT, WARREN COUNTY, GEORGIA, U.S.A.

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ABSTRACT

Shocked quartz grains collected from a transgressive lag at the sequence boundary between the upper Eocene Twiggs Clay and the kaolin-rich middle Eocene Huber Formation in the Georgia Coastal Plain were examined by X-ray powder diffraction (XRD) for evidence of crystal defect line broadening. The deposition of the sand was approximately correlative with the Chesapeake Bay impact (35 Ma), and thus the sand is a logical place to look for impact debris, especially because similar-age tektites occur in south-central Georgia. Sample comparisons were made between three groups of fine to medium sand-size quartz separates: (1) quartz grains that display single or multiple sets of deformation features, which are petrographically similar to planar deformation features (PDFs) induced by shock loading, (2) quartz grains that were randomly selected from the sand unit, and, as a control, (3) quartz grains from the Crow Creek Member of the Pierre Shale (Upper Cretaceous Nebraska) that display obvious sets of PDFs formed in association with the Manson impact. Alluvial quartz grains from crystalline rocks of the Georgia Piedmont were used an instrument standard. Fourier numerical analysis of the quartz (*100*) peaks shows that grains exhibiting PDFs have a higher defect density than grains from the random sampling. The mean coherent scattering domain size of the Eocene sands with PDFs is 960Å, which is about half the size of those in a random sampling. The presence of quartz with PDFs and defect densities higher than the surrounding grains is consistent with the notion that the deposit contains remnants of material ejected by the Chesapeake Bay impact. These XRD findings, taken with the petrographic evidence for PDFs in quartz grains provide the first evidence for in-place preservation of upper Eocene impact deposits in Georgia Coastal Plain strata.

INTRODUCTION

Previous investigations designed to search for an impact horizon in the southeastern US Coastal Plain associated with the Chesapeake Bay impact (Albin, 1997; Albin and others, 2000; Horwath, 1990; Zwart, 1978) have fallen short, in part because they were designed to look for geochemically unstable microtektites. A second factor includes limiting the hunt to units that are isochronous with the impact event. Albin and Wampler (1996) were the first to make inference that evidence for impact ejecta could be found in Eocene Dry Branch Formation (Twiggs Clay member). In this study, we focus on characterization of the more geochemically resilient quartzose material as a recorder of impact events in Eocene age sediments.

In east-central Georgia, the upper Eocene Twiggs Clay overlies the middle Eocene kaolin-rich Huber Formation. The contact between the two units is a sequence boundary and transgressive surface overlain by a patchy coarse-grained sand layer as thick as 10 cm. Harris and others, (2002) determined that approximately 3-5% of fine- to medium-grained quartz examined from the layer contain optical planar elements (spacing and orientation) similar to planar deformation features (PDFs). Most of the quartz grains display one set of planar features, but some exhibit two or three intersecting sets (Harris 2003). We interpret these linear optical features are PDFs and propose that the quartz was shocked by bolide impact. We hypothesize that quartz grains exhibiting PDFs have a higher crystal defect density than quartz grains that do not display PDFs. The coherent X–ray scattering dimension (CSD_{hkl}) is defined as the *d*–spacing for an *hkl* plane multiplied by the number of defect-free translations perpendicular to the plane. A single coherent scattering domain is easily understood as a set of perfectly aligned cards bounded by faults. Larger mineral grains can be visualized as a mosaic of domains that are characterized the mean of all the CSD_{hkl} lengths. Shocked-quartz grains should therefore have measurably smaller mean CSD_{hkl} lengths than optically clear quartz grains.

Two major concerns arise when X-ray powder diffraction (XRD) is used to analyze ejecta for identification of shocked quartz. The first concerns the frequency of shocked quartz in sediments that preserve a record of distal ejecta. Shocked grains are often rare in siliciclastic sediments, because allochthonous non-shocked quartz grains may dilute the system (e.g., Exmore Breccia, Poag and Poppe, 1998). The presence of only a few non-shocked grains in an XRD experiment overwhelms the XRD pattern because of contributions from their large CSDs. XRD peak intensities (I) (*i.e.*, shapes) are proportional to the square of the number (N) of defect-free scattering domains. This is illustrated in the theoretical intensity function, which is the basis for the calculation of continuous XRD patterns (Moore and Reynolds 1997):

$$I(\theta) = LpG^2\Phi \quad (1)$$

where

$$\Phi(\theta) = \frac{\sin^2(2\pi ND \sin\theta/\lambda)}{\sin^2(2\pi D \sin\theta/\lambda)} \quad (2)$$

and Lp = Lorentz-polarization factor for random powders, G = layer scattering factor, Φ = the interference function, D = interplanar d-spacing, Θ = the Bragg angle, and λ = wavelength of X–ray radiation.

A solution to this problem is to handpick shocked grains and conduct XRD analysis on minimal quantities (8 to 11 grains ~ 2 mg) of powdered specimen. One potentially detrimental effect of having small sample quantity is a lack of statistical representation of coherently diffracting crystal domains. This is partially compensated by using long counting times for data collection and by repeated data collection after remounting of the sample. Additional consequences of a thin sample are that transparency effects become minimized and that higher order reflections are diminished (Hurst and others, 1997).

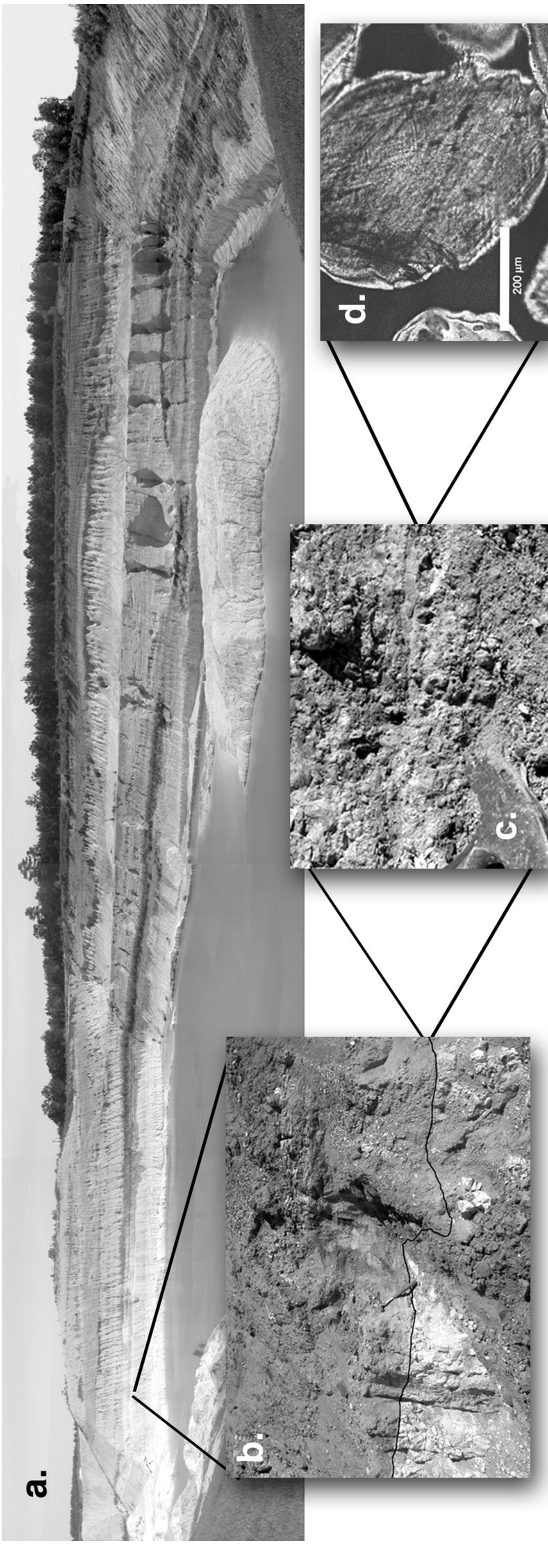
The second concern arises because XRD instrument optics significantly distort peaks and a mere comparison of observed profiles is not enough to know the line broadening contribution due to the distribution of CSDs. CSDs are therefore evaluated by correcting for instrumental line broadening and assuming that grains without linear features are defect free (*i.e.,* the size of CSDs = ∞). The correction of widths and shapes of X-ray powder diffraction lines is accomplished by the numerical Fourier-analysis of Stokes (1948). It is assumed that the observed intensity function $h(x)$, is related to the instrument broadening function $g(x)$ and the CSD broadening function $f(x)$,

$$h(x) = \Sigma f(y) g(x-y) \delta y \quad (3)$$

where x and y are auxiliary variables that are typically measured in units of °2Θ. Eq 3 constitutes the set (a) of linear simultaneous equations in which the intensity values for each °2Θ of $h(x)$ and $g(x)$ are known, and the values of $f(x)$ are unknown. By considering the values of °2Θ in the range of $-a/2$ to $+a/2$, where $h(x)$ and $g(x)$ fall to zero, it is possible to obtain the Fourier series of all the functions. In practice this results in a range that includes 60 equations or ±0.3 °2Θ in increments of 0.01°.

METHODS

Samples from the Twiggs Clay, sand layer, and Huber Formation were collected in the J.M. Huber Corp. Purvis Mine located near the Pur-



vis School on the west side of Georgia highway 17, approximately 8 km north of Wrens, Georgia (Fig. 1a,b). The underlying Huber Formation is ~ 97 percent kaolinite, with trace amounts of silt-sized quartz. The quartz in the overlying Twiggs Clay is very-fine sand and silt-sized and is a minor component. Consequently, optical selection of quartz with and without PDFs from the Twiggs and Huber deposits was not possible. Only the sand layer yielded sufficient quantities of fine to medium sand-sized quartz, for which grains with and without PDF could be clearly selected. We note here that the overlying sand units of the Irwinton Sand and Tobacco Road Sand (Elzea-Kogel and others, 2000) were specifically examined and did not yield grains with planar fabrics.

Control quartz grains used in this study included (1) alluvial grains collected from Beech Creek, located in the metamorphic Appalachian Piedmont near Athens, Georgia, and (2) grains collected from the known Manson impact ejecta in the Crow Creek Member of the Cretaceous Pierre Shale, Nebraska (provided by Sarah Chadima, South Dakota Geological Survey); (Witzke and others, 1996).

Figure1. Site of sampling near Wrens, Georgia. (a) Panoramic north-east-south view of the Purvis mine, operated by the J.M. Huber Corp. Visible are the middle Eocene Huber Formation, overlain by the marine upper Eocene Twiggs Clay, which in turn is overlain by migrating channel-fill sands, of the Irwinton and Tobacco Road Sands. (b) Sequence boundary (high lighted by line) showing the position of the thin (0-10 cm) sand lag deposit. (c) Close-up view of lag deposit (hammer for scale). (d) Cross-polarized photomicrograph of quartz grain from the lag layer, exhibiting PDFs.

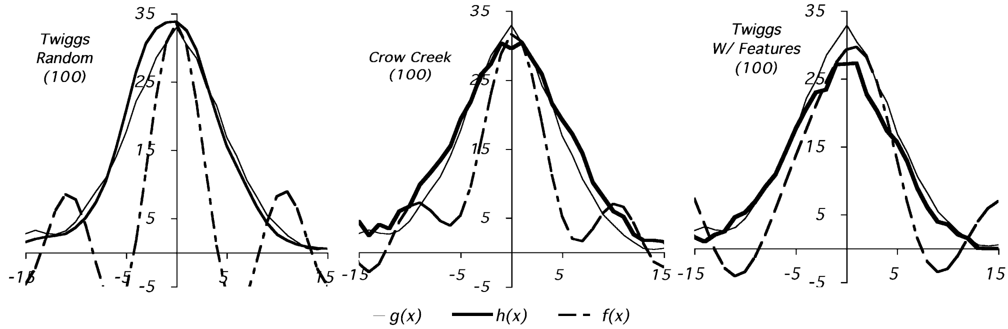


Figure 2. X-ray diffraction line profiles of the (*100*) quartz peak for Twiggs Clay randomly selected grains, Crow Creek Member with PDFs, and Twiggs Clay with PDFs. The thin line, *f(x)*, in all three comparisons is the Beech Creek, Georgia, instrument standard. The bold line is the observed profile, *h(x)*, and the dashed line is the true peak profile, *g(x)*, unfolded using the numerical Fourier analysis of Stokes (1948). CSD_{100} lengths were determined by a least-squares fit of *g(x)* to equation 2 and then multiplying the resultant optimized *N* value by 4.2725 Å (the d–spacing for the (*100*) reflection).

Samples were hand ground using a zirconium mortar and pestle with alcohol. The powdered material was transferred to a zero-background plate; a large (30 x 30 mm) single quartz crystal cut and polished 6° off the *c*-axis, which has the effect of minimizing substrate scattering effects. XRD analyses were conducted using a Scintag diffractometer, with Co Kα radiation, a 250 mm goniometer circle, 2°/4° primary and scattering slits, 0.5°/0.3° scattering and receiving slits, 40 kV and 40 mA, a step size of 0.01°, and a count time of 10 s per step. The quartz (100) and (101) reflections (indexed in the $P3_221$ space group) were used in this study because they provide sufficient signal to noise to give reliable counting statistics. The use of thin sample thicknesses precludes the use of the higher order reflections (peaks at higher angles) because of inadequate signal to noise response. For each sample, three to four pattern replicates (after remounting) were corrected for displacement and averaged to minimize orientation. Averaging also reduced noise generated from the instrument and Compton scattering. All Fourier transform calculations were performed using the equations of Stokes (1948) and Klug and Alexander, (1974) facilitated in an Excel spreadsheet.

RESULTS AND DISCUSSION

As discussed above, coherent scattering domains are most easily visualized as mosaics of crystallites that are bounded by faults (Schnieder and others, 1984). The disorientation between adjacent domains need be only a matter of fractions of a degree in order for one to be considered separate from another (Moore and Reynolds 1997). The Fourier analysis method allows for the study of true peak shapes (*i.e.*, unfolded functions), whose breadths can be attributed to the average length of the CSD_{hkl}. Microstrain (*i.e.*, variation of the interplanar d–spacings for each *hkl* set) also contributes to peak broadening. However, as noted by Schneider and others, (1984), strain values tend to be constant when CSDs are beyond 220Å. Given the large size of the CSD in our samples (discussed below), the strain effect was considered to be constant among the samples analyzed and differences in broadening are attributed to differences in mean CSD sizes.

Figure 2 illustrates the observed, instrument, and unfolded functions, *h(x)*, *g(x)*, and *f(x)* respectively, for the quartz (100) reflection. Shown are the peaks for quartz grains randomly selected from the Twiggs Clay sand lag (fig 2a), the peaks for quartz grains with PDFs from the Crow Creek Member (fig. 2b), and the peaks for quartz grains with possible PDFs from the

Twiggs Clay sand lag (fig. 2c). Peaks shapes are, in theory, influenced by *Lp* and *G* (Eq.1), however, over this small region of 2Θ space these functions are nearly constant and do not affect peak shape (Klug and Alexander 1974). *Lp* and *G* corrections were therefore not applied.

The average number of (*100*) domains in the random Twiggs Clay, Crow Creek Member, and Twiggs Clay with possible PDFs are $N = 460$, $N = 330$, and $N = 225$, respectively. This corresponds to CSD_{100} lengths of 1970Å, 1410Å, and 960 Å, respectively. *N* values were derived by a least-squares curve fit of the data sets $f(x)$ to the interference function, Eq 2 (Raner 1998). All fits have an R^2 of 0.99.

Relative comparison of quartz grains in the Twiggs Clay lag deposit reveals that grains with PDFs have twice the defect density in the (*100*) planes compared to grains that do not exhibit PDFs. The CSD_{100} length of shocked Twiggs Clay quartz is seven times smaller than the mean CSD lengths of laboratory annealed quartz (Schneider and others, 1984). It is six times larger than quartz experimentally shocked at 15 GPa and about the same as quartz experimentally shocked at 1.5 GPa (Schneider and others, 1984). At first this seems contradictory to experimental work, which suggests that at least 10 GPa is needed to create PDFs (Grieve and others, 1996). However, making such direct comparisons between laboratory and natural shock events is difficult, because natural shock events can be marine (wet) impacts or terrestrial (dry) impacts, and the target can be either porous (sedimentary) or non-porous (metamorphic and igneous). Moreover, the shocked quartz domains can anneal over long periods of geologic time at earth surface temperatures (Sokur, 1999).

The (*101*) reflections were also examined for X-ray line broadening and in all cases a constant CSD_{101} of about ~1500Å ($N = 450$) was determined. We have no clear explanation as to why the (*100*) and (*101*) shapes do not co-vary. The reason may be that preferential directions of planar dislocations are present in the PDF grains.

A recognized difficulty in the Fourier analysis is choice of background correction (Young and others, 1967). The tails of the diffraction peaks determine the Fourier coefficients. Our study suffers from less than ideal signal-to-noise ratio because the data comes from the analysis of only eight to eleven grains. Obtaining larger sample mass would allow for both better counting statistics and for analysis of higher order reflections. However, as noted in our introduction and by Schneider and others, (1984), XRD of thousands of grains is a method biased by grains with large mean CSD sizes.

The second factor of directional defects may be possible. Goltrant and others, (1992) discussed the fact that shock deformation in quartz is a strongly heterogeneous process. Critical sets of PDFs identified optically commonly include the (*001*), (*102*), and (*103*) planes and less commonly (*101*) and (*104*) planes. Is it important to note that CSDs for only the (*100*) and (*101*) can be studied by XRD. XRD intensities for planes seen optically, with exception to the (*101*), are too low to determine a mean CSD_{hkl} value. The distinction amongst these various factors may only be resolved by high-resolution methods of electron diffraction and transmission electron imaging.

Our results show that XRD analysis of selected grains serves as a screening tool to support the recognition of shocked quartz. XRD units are common to most geology departments and the sample preparation and data collection do not require any special tools (except a zero-background substrate). The correlation of mean CSD lengths to actual shock deformation processes is possible with careful XRD analysis.

CONCLUSIONS

Bulk XRD methods that analyze large populations of quartz grains with variable CSD lengths are not capable of distinguishing the presence of shocked quartz. However, the XRD technique of analyzing selected grains on a zero-background plate provides an easy way to screen quartz grains suspected to have been shocked by hypervelocity impacts. Analysis of quartz grains exhibiting PDFs from a basal lag in the upper Eocene Twiggs Clay near Wrens, Georgia is consistent with the notion that the deposit contains ejecta from the Chesapeake Bay impact.

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