

RELATIVE SHOCK EFFECTS IN MIXED POWDERS OF CALCITE, GYPSUM, AND QUARTZ: A CALIBRATION SCHEME FROM SHOCK EXPERIMENTS. M.S. Bell, Jacobs Engineering@NASA/ Johnson Space Center, Mail Code KT, Houston, TX 77058, USA, E-mail: mary.s.bell@nasa.gov.

Introduction: The shock behavior of calcite and gypsum is important in understanding the Cretaceous/Tertiary event and other terrestrial impacts that contain evaporite sediments in their targets. Most interest focuses on issues of devolatilization to quantify the production of CO_2 or SO_2 to better understand their role in generating a temporary atmosphere and its effects on climate and biota [e.g., papers in 1,2,3,4]. Devolatilization of carbonate is also important because the dispersion and fragmentation of ejecta is strongly controlled by the expansion of large volumes of gas during the impact process as well [5,6]. Shock recovery experiments for calcite yield seemingly conflicting results: early experimental devolatilization studies [7,8,9] suggested that calcite was substantially outgassed at 30 GPa (> 50%). However, the recent petrographic work of [10,11,12] presented evidence that essentially intact calcite is recovered from 60 GPa experiments. [13] reported results of shock experiments on anhydrite, gypsum, and mixtures of those phases with silica. Their observations indicate little or no devolatilization of anhydrite shocked to 42 GPa and that the fraction of sulfur, by mass, that degassed is $\sim 10^{-2}$ of theoretical prediction. In another (preliminary) report of shock experiments on calcite, anhydrite, and gypsum, [14] observe calcite recrystallization when shock loaded at 61 GPa, only intensive plastic deformation in anhydrite shock loaded at 63 GPa, and gypsum converted to anhydrite when shock loaded at 56 GPa. [15] shock loaded anhydrite and quartz to a peak pressure of 60 GPa. All of the quartz grains were transformed to glass and the platy anhydrite grains were completely pseudomorphed by small crystallized anhydrite grains. However, no evidence of interaction between the two phases could be observed and they suggest that recrystallization of anhydrite grains is the result of a solid state transformation. [16] reanalyzed the calcite and anhydrite shock wave experiments of [17] using improved equations of state of porous materials and vaporized products. They determined the pressures for incipient and complete vaporization to be 32.5 and 122 GPa for anhydrite and 17.8 and 54.1 GPa for calcite, respectively, a factor of 2 to 3 lower than reported earlier by [17].

In contrast to work on shocked carbonates, effects in naturally occurring shock metamorphosed quartz are well documented and they have been generally duplicated in shock recovery experiments [18,19 and references therein]. Because a variety of shock metamorphic effects, occurring over a range of shock pressures, have been well documented in quartz and it occurs ubiquitously in terrestrial rocks, it provides the best shock barometer in terms of utility and occurrence. Shocked quartz has been found in two terrestrial geologic settings: (1) in direct spatial relation to impact structures; and (2) as a constituent of distal or global ejecta deposits [19]. Consequently, quartz has become the most common petrographic criterion for the identification of terrestrial impact structures and lithologies as well.

The Chicxulub Cretaceous/Tertiary boundary impact site contains about 30% anhydrite and gypsum and about

70% calcite in the upper 3 km layer of rock (in the sequence of limestone, anhydrite-dolomite conglomerates, limestone-dolomite, and anhydrite-gypsum layers overlying a Pan African-age crystalline basement [20,21,22]). Comparatively few efforts exist that address solid-state deformation features of calcite and gypsum which may be important for the characterization of ejecta deposits of the Cretaceous/Tertiary event and other impacts into such platform sediments [23,10,24] and no experiments have been reported on relative shock effects in mixed powders of calcite, gypsum and quartz, simulating the crystalline basement of the Chicxulub target. A systematic experimental shock study of these mixed powders was carried out in order to calibrate shock pressures in naturally shocked carbonates and sulfates.

Experimental Methods: The target charge consisted of powders (125-250 μm) of calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and quartz (SiO_2), mixed in 1:1:1 (weight) ratios that were packed into aluminum (9.9 GPa sample only) or stainless steel targets (all other experimental pressures). Porosity in the target material was $\sim 6\%$. Samples were shocked to 47.1 GPa according to the methods of [25].

The recovered materials were impregnated with epoxy prior to thin sectioning for optical description to preserve inter-granular textures. Compositional analysis was obtained via a Cameca SX100 electron microprobe at the Johnson Space Center using an accelerating voltage of 15 kV, a beam current of 4 nA, and a peak count duration of 20 s, using wavelength dispersive spectrometers. Calibration was done using natural mineral and synthetic oxide standards. Back-scattered electron (BSE) images and elemental maps were acquired as well as quantitative analyses (beam current 10 nA) of points in a line crossing individual calcite grains spaced in 5 μm steps. Point count data was collected from digital petrographic images and elemental maps using Image Pro Plus V.6.2 software.

Results and Discussion: The important shock effects for mixed powders of calcite gypsum and quartz documented in this study are as follows: evidence for incipient recrystallization in calcite exists as fine grained aggregates of < 10 micron sized rounded, equant, untwinned calcite grains coexisting with highly twinned and kinked calcite grains in the 24.3 GPa experiment. However, the calcite aggregates lack the 120° triple junctions characteristic of crystallization in equilibrium thus are evidence that a solid-state transformation occurs. This juxtaposition is probably due to localized hot spots resulting from heterogeneous shock effects in the porous medium, coexisting phases of different shock impedance, and the transient nature of temperature excursions in the shock experiment. No evidence that calcite is completely devolatilized and that CaO is formed can be found in experimentally shocked calcite to 47.1 GPa (Figure 1.) and no evidence of carbonate melt or flow textures was found. The progressive nature of calcite twinning in these shock experiments demonstrates the exceptional ability for intracrystalline plastic glide to accommodate strain in calcite.

Evidence for transformation of gypsum to anhydrite is apparent from high relief and high birefringence in the 18.4 GPa shock experiment and the effect is continuous through the 40.7 GPa experiment but whether or not calcium sulfate remains birefringent cannot be resolved in the 47.7 GPa experiment. [14] observe gypsum converted to anhydrite when shock loaded at 56 GPa but have not experimentally shocked gypsum in a step-wise manner to constrain the incipient transformation effects seen in these experiments. The transition of gypsum to anhydrite (a stable polymorph) + H₂O is monotropic (irreversible) in which the temperature required to initiate the transformation is lowered with increasing pressure (200 °C at 1 atm). Another solid state effect manifest in shocked gypsum is its ductile deformation around calcite and quartz grains.

Incipient formation of undecorated planar deformation features and irregular "mottled" extinction patterns (mosaicism) in shocked quartz occur in the 18.4 GPa experiment, multiple sets of undecorated planar deformation features appear and birefringence is visibly lowered in the 24.3 GPa experiment, and quartz is isotropic in the 30.1 GPa and higher shock experiments. At shock pressures higher than 30 GPa quartz deforms in a brittle manner and exhibits no evidence of melt (lechatelierite) or flow textures. The occurrence of undecorated planar deformation features is another indication that temperatures resulting from shock compression were not sufficient to anneal quartz and cause the formation of decorated planar deformation features (~1200 °C). High pressure polymorphs of silica were not identified in these samples within the resolution of the petrographic microscope and EMP techniques used. These results for experimentally shocked quartz agree well with other experimental observations in which quartz starts to melt under shock compression at > 50 GPa [18,19].

No geochemical evidence for even incipient assimilation of shock products from calcite or gypsum to form calcium or sulfur-rich silicates as was reported from the Ries [25], Haughton, [24] and Chicxulub impacts [26,27] was observed in this study of shock experiments to 47 GPa.

The present study also documents the progressive comminution of all mixed powder phases with increasing shock pressure consistent with [10] who found that in their shock recovery experiments on calcite and dolomite the only surviving shock-induced phenomenon to peak shock pressure of 60 GPa is pulverization.

Conclusions: A shock barometry scheme for carbonates and sulfates relative to quartz based on primary effects in the minerals has been developed and allows for the correlation of shock effects in unaltered carbonates and sulfates with those well documented in quartz. Calcite is incipiently recrystallized at 24.3 GPa but shows no evidence of devolatilization and remains birefringent to 47 GPa. Gypsum is transformed to anhydrite at 18.4 GPa. Quartz develops single sets of planar deformation features at 18.4 GPa, multiple sets of planar deformation features at 24.3 GPa, becomes isotropic at 30.1 GPa but shows no evidence of melting to 47 GPa.

Deformation effects observed in these shock experiments on calcite and gypsum are solid-state reactions and by comparison to solid-state shock effects in quartz from the same experiments, can provide a calibration scheme for shock effects in naturally shocked rocks under certain condi-

tions - if those effects have not been overprinted by subsequent processes such as thermal annealing or alteration. If primary shock features in individual mineral grains have been altered, then rock textures on a larger scale may be evidence of shock history (e.g. the frothy, vesiculated texture of some impactites from Haughton [10]). However, impact ejecta formed in a high enough pressure regime will devolatilize and no longer contain carbonates and sulfates but will retain evidence of degassing with respect to the original composition of the target in the form of igneous textured minerals which incorporate the residual oxide component [28].

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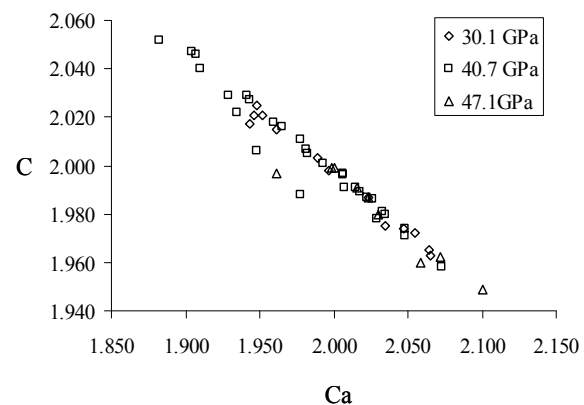


Figure 1. Plot of C (carbon) vs. Ca (calcium) from 42 quantitative EMP analyses of calcite in the 30.1, 40.7, and 47.1 GPa shock experiments. No significant carbon deviation from stoichiometric calcite compositions (based on 6 oxygens) that would indicate CO₂ degassing had occurred was detected.