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Shock Compression of Dolomite

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Shock compression studies on a dolomite rock (ρ_0 = 2.84 g/cm³) have been conducted in the stress range 150–450 kbar. The entire loading and unloading history as well as the Hugoniot properties were investigated, using continuous recording piezoresistant stress gages. The following results were obtained: (1) The Hugoniot shock velocity–particle velocity curve shows deviation from linearity in a region corresponding to stresses between 100 and 250 kbar. (2) Comparison of the experimental Hugoniot with a Murnaghan pressure-volume relation extrapolated from low-pressure ultrasonic data indicates anomalous compressibility. (3) Unloading experiments from peak stresses between 180 and 300 kbar show excessive hysteresis in the stress-volume plane. (4) Shock compression to a peak stress in excess of 400 kbar is followed by immediate stress relaxation. (5) Overtaking relief wave velocities measured at the Hugoniot state are found to be considerably higher than extrapolated bulk sound velocities. Our interpretation of the results is a rate-dependent, low- to high-density phase transformation occurring in the stress range 100–500 kbar.

INTRODUCTION

Shock compression is an important geophysical tool for studying high-pressure properties of rocks and minerals. It is the only method now available to determine pressure-volume relations above about 300 kbar, and much of our current knowledge of the equation of state of the earth's interior has been obtained from shock wave studies. Extension of shock wave techniques offers potential methods for investigating the high-pressure and temperature elastic and thermal properties of minerals as well as the thermodynamics and kinetics of polymorphic phase transformations and melting.

Although a large body of shock wave Hugoniot data exists for many rocks and minerals, very little is now known about the mechanical deformation process by which the material reaches a Hugoniot state. It has been assumed, out of necessity, that the state attained by shock compression is an equilibrium thermodynamic state. This need not be the case. In fact, it is widely known that in a certain domain of the Hugoniot for silicate minerals the states achieved by shock compression are far from equilibrium. Recent studies have expanded our understanding of the shock deformation process in silicate minerals [*Grady et al.*, 1974; *Graham*, 1974] and have offered an explanation for why nonequilibrium states are achieved [*Grady et al.*, 1975].

For a thorough understanding of the shock deformation process it seems important to study minerals from other classes as well. In this work, shock compression characteristics of dolomite, an anhydrous carbonate rock, were studied. Using continuous recording piezoresistant stress gages, we investigated the entire loading and unloading history as well as the Hugoniot properties. The present effort was confined to the stress range 150–450 kbar. We found that the response to shock compression in this region is very complex and is inconsistent with the assumption of thermodynamic equilibrium behind the shock front. Large stress-volume hysteresis, stress relaxation, and anomalously high sound velocities were encountered on the Hugoniot. Our present interpretation of the results is a rate-dependent, low- to high-density phase transformation occurring in the stress range 100–500 kbar. Considerable work remains before a complete understanding of shock compression in this material will be available.

The rock studied in this work was Blair dolomite, a dark grey, fairly homogeneous fine-grained equigranular dolomite (>98% $CaMg(CO_3)_2$) obtained from Martinsburg, West Virginia. The measured dry density is 2.84 g/cm³, and the calculated porosity is 0.9%, based on the crystal density of dolomite, 2.866 g/cm³. This rock is the same material studied by *Petersen* [1969] and *Larson et al.* [1971] and agrees well in composition and density with the dolomite studied by *Kalashnikov et al.* [1973].

HUGONIOT PROPERTIES

Shock wave loading in Blair dolomite was obtained with explosively thrown metal flyer plates. The overtaking relief wave originated from the back surface of the flyer plate. In-material manganin stress gages provided multiple stress wave profiles at increasing distance from the impact interface. These experimental and instrumentation techniques have been described in greater detail by *Grady et al.* [1974].

Hugoniot data obtained from the present work are given in Table 1. The Hugoniot stress and shock wave velocity were the measured quantities, while specific volume and particle velocity were calculated by assuming validity of the Hugoniot jump relations. The present data covered the stress range 185–420 kbar and are extended in Figure 1 with the data of *Petersen* [1969], *Larson et al.* [1971], and *Kalashnikov et al.* [1973].

The shock velocity–particle velocity data shown in Figure 1*a* cannot be described by a straight line. The high-velocity U_s-u_p curve extrapolates at zero particle velocity to considerably less than the bulk sound velocity. This result has been interpreted by *McQueen et al.* [1970] to imply a low-to-high density phase transformation on the Hugoniot.

Ultrasonic data [*Birch*, 1960; *Press*, 1966; *Heard et al.*, 1973] were used to estimate Murnaghan equation parameters for dolomite. *Anderson* [1966] has shown that for relative compressions of less than about 0.85 the Murnaghan equation provides a good estimate of the adiabat for many minerals that do not exhibit a high-pressure phase change. As seen in Figure 1*b*, above about 100–200 kbar the Hugoniot data show substantial deviation to the left (larger volume change) of the Murnaghan equation prediction. A phase transformation on the Hugoniot is a possible explanation for this anomalous

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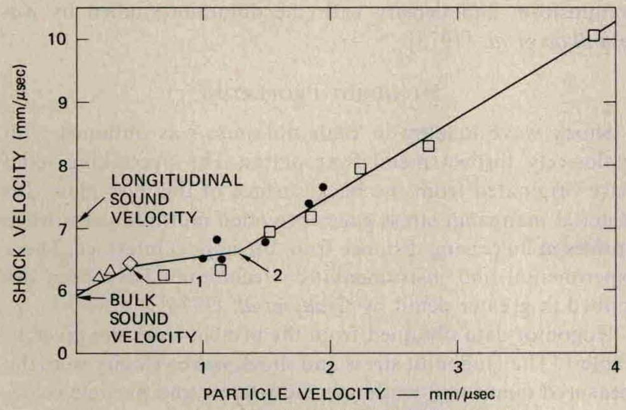
TABLE 1. Hugoniot Data for Blair Dolomite

Shot	Shock Velocity, mm/μs	Particle Velocity, mm/μs	Stress, kbars	Specific Volume, cm^3/g
1883-27	6.51 ± 2%	1.00	185 ± 5%	0.298
8909-4	6.50 ± 2%	1.15	212 ± 5%	0.290
1883-26	6.82 ± 2%	1.11	215 ± 5%	0.295
1883-8	6.78 ± 2%	1.49	287 ± 5%	0.275
1883-36	7.40 ± 2%	1.84	386 ± 5%	0.265
1883-3	7.65 ± 2%	1.94	420 ± 8%	0.263

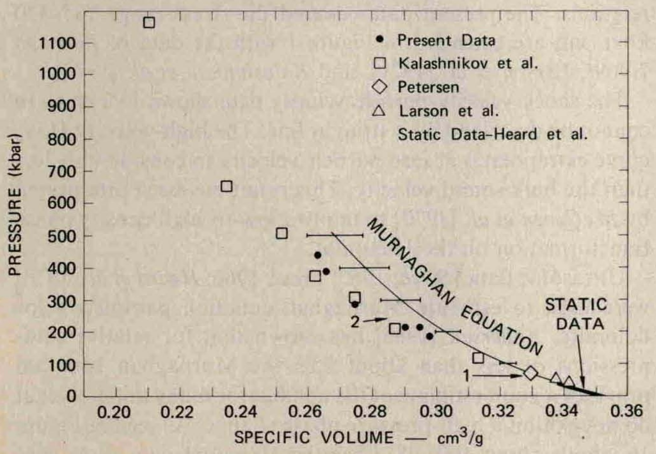
compressibility. Static compression data to 36 kbar for Blair dolomite [*Heard et al.*, 1973] is also shown in Figure 1*b*.

UNLOADING EXPERIMENTS FROM HUGONIOT PRESSURES BELOW 300 KBAR

Three experiments were performed in which the Hugoniot stresses achieved were less than 300 kbar. Manganin stress gage profiles for one experiment of this type are shown in Figure 2. The profiles show shock loading, a flat top portion of constant stress, and a slightly dispersive unloading wave. Unloading profiles from Hugoniot stresses exceeding 300 kbar were unusual and will be discussed in the next section. We believe that what appears to be a second unloading wave in Figure 2 is the result of incomplete expansion of the detonation products when the first relief wave originates at the flyer–detonation products interface. Thus a second reverberation wave after reflection at the dolomite–flyer plate interface brings the material closer to a zero stress state. We have not conclusively verified this point, however.



(a) SHOCK VELOCITY-PARTICLE VELOCITY



(b) PRESSURE-SPECIFIC VOLUME

Fig. 1. Hugoniot data for dolomite. Numbers correspond to equivalent Hugoniot points. Error bars on the Murnaghan curve are the maximum allowed by the ultrasonic data.

Unloading curves in the stress-volume plane were determined from the relief wave velocities by the method of analysis originated by *Fowles and Williams* [1970] and by *Cowperthwaite and Williams* [1971]. The relief curves determined from the three experiments are compared with the dolomite Hugoniot in Figure 3.

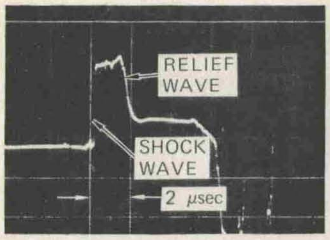
Thermodynamic stability requires that unloading isentropes for a single phase solid satisfying an equilibrium hydrostatic equation of state be shallower than the Hugoniot [*Duvall and Fowles*, 1963]. The unloading curves for dolomite shown in Figure 3 violate this condition. Material strength (a nonhydrostatic effort) could account for the hysteresis in the stress-volume plane. If a Hugoniot elastic limit (HEL) P_Y is observed in a shock wave experiment, then a stress hysteresis of $Y = \frac{2}{3}P_Y$ between loading Hugoniot and the unloading curve is expected for an ideally elastic-plastic material with a Poisson's ratio of 0.25. *Petersen* [1969] measured an HEL in Blair dolomite of approximately 30 kbar, and more recently one of the authors (D. E. Grady, unpublished manuscript, 1975) has measured an HEL of about 25 kbar. These data would imply a stress hysteresis of between 15 and 20 kbar, which is insufficient to explain the unloading hysteresis in Figure 3. We suggest that this stress-volume hysteresis is further evidence of high-pressure phase transformation in dolomite.

STRESS RELAXATION EXPERIMENTS

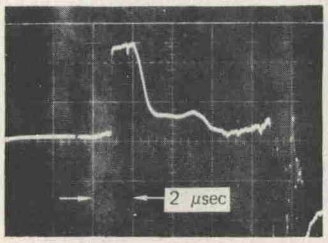
The results obtained from the first plate impact experiment exceeding a stress level of 400 kbar were unexpected. In Figure 4, three stress gage profiles from this experiment are shown. It is apparent from these gage profiles that the peak stress is followed by immediate stress relaxation. We were initially hesitant to accept these results because of their unusual nature and possible alternative explanations. We were concerned with possible misbehavior of the flyer plate system. Also, anomalously high relief velocities from the flyer plate free surface could conceivably have overtaken the wave front and produced the observed profiles. Another possibility was pressure-induced electrical conductivity in the dolomite or in the epoxy bonding agent, causing an anomalous piezoresistant response of the manganin gage. Three further experiments were designed and carried out, and all the alternative explanations were eventually eliminated. Observation of stress relaxation in each case forced us to conclude that it is a real effect. Again, we suggest that a phase transformation occurs, and the stress relaxation is evidence of a rate dependence of this transformation.

Seven successful gage profiles at four gage planes were obtained from the experiment, three of which are shown in Figure 4. Attenuation of the peak stress with propagation distance, stress relaxation, and two distinct breaks on unloading are features that could be seen in all seven stress profiles. The method of *Fowles and Williams* [1970] was used to determine the stress volume path implied by these stress-time data. Arrival times, distances, and amplitudes of peak stress and unloading features were determined from the seven gage records to analyze the stress profiles. These features were treated statistically, and smoothed stress-time profiles were reconstructed. The smoothed profiles and resulting stress–specific volume paths are shown in Figure 5.

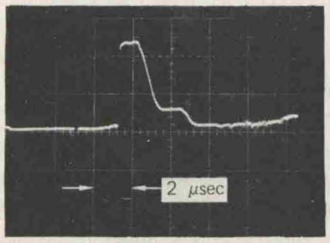
We suggest the following interpretation of the stress profiles and stress-volume unloading paths: From peak stress down to



1.72 mm FROM IMPACT INTERFACE



5.17 mm FROM IMPACT INTERFACE



8.49 mm FROM IMPACT INTERFACE

Fig. 2. Manganin stress gage profiles in dolomite. Peak stress is 287 kbar.

about 270 kbar, stress relaxation occurs due to a rate-dependent transformation of material from a low- to high-density phase. The first break in the profiles at about 270 kbar on unloading corresponds to first arrival of the relief wave from the flyer plate free surface. Details in the stress-volume path in the neighborhood of 270 kbar are questionable because the type of analysis used is subject to increasing error in regions where the stress profile shows increasing flatness. We believe that the second break on unloading at about 220 kbar corresponds to a reverse (high to low density) transformation of the volume fraction that was converted to the high-density phase during shock loading and approximately 1 μs of stress relaxation. This transformation is indicated in the middle figure of Figure 4 by a shallower stress-volume path on unloading below the break at 220 kbar.

SOUND VELOCITIES ON THE HUGONIOT

A previous study of the sonic velocity behind a shock wave in silicate rocks [*Grady et al.*, 1975] provided considerable insight into the mechanical processes accompanying shock deformation. A similar examination of the Hugoniot sound velocities obtained in the present work was attempted. As in the silicate work, the first characteristic of the overtaking relief wave provided an estimate of the Lagrangian sound velocity C_L at the Hugoniot state. Because of the immediate stress relaxation in the shots performed above 300 kbar, only those experiments shock loaded to a peak stress of less than 300 kbar were reduced in this manner. The Eulerian sound velocity C for the initial release wave refers to a material at rest and is given in terms of the Lagrangian velocity as $C = (\rho_0/\rho)C_L = (1 - u_p/U_s)C_L$ where ρ_0 and ρ are the initial and Hugoniot specific densities, respectively, u_p is the Hugoniot particle velocity, and U_s is the shock velocity. Since the shock velocity and stress on the Hugoniot are measured directly, the Hugoniot jump relations were used to calculate u_p and thus obtain the Eulerian sound velocities for comparison with equation of

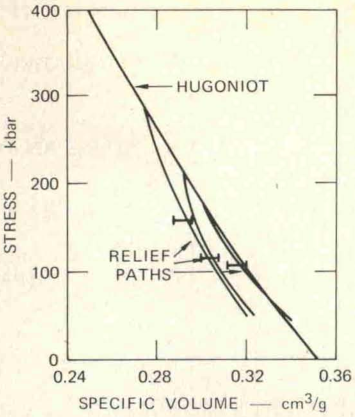
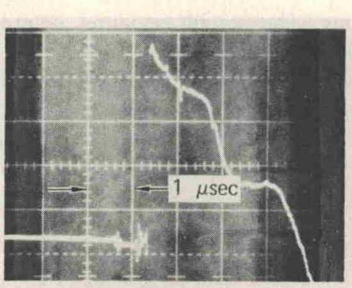
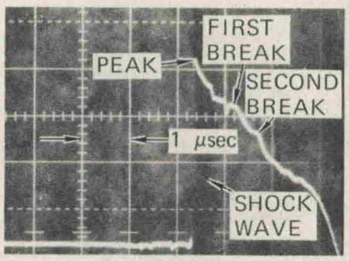


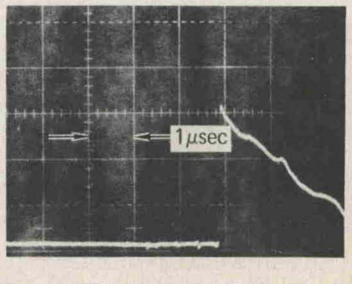
Fig. 3. Unloading paths in dolomite. Error bars are best estimate for unloading curves.



1.58 mm FROM IMPACT INTERFACE

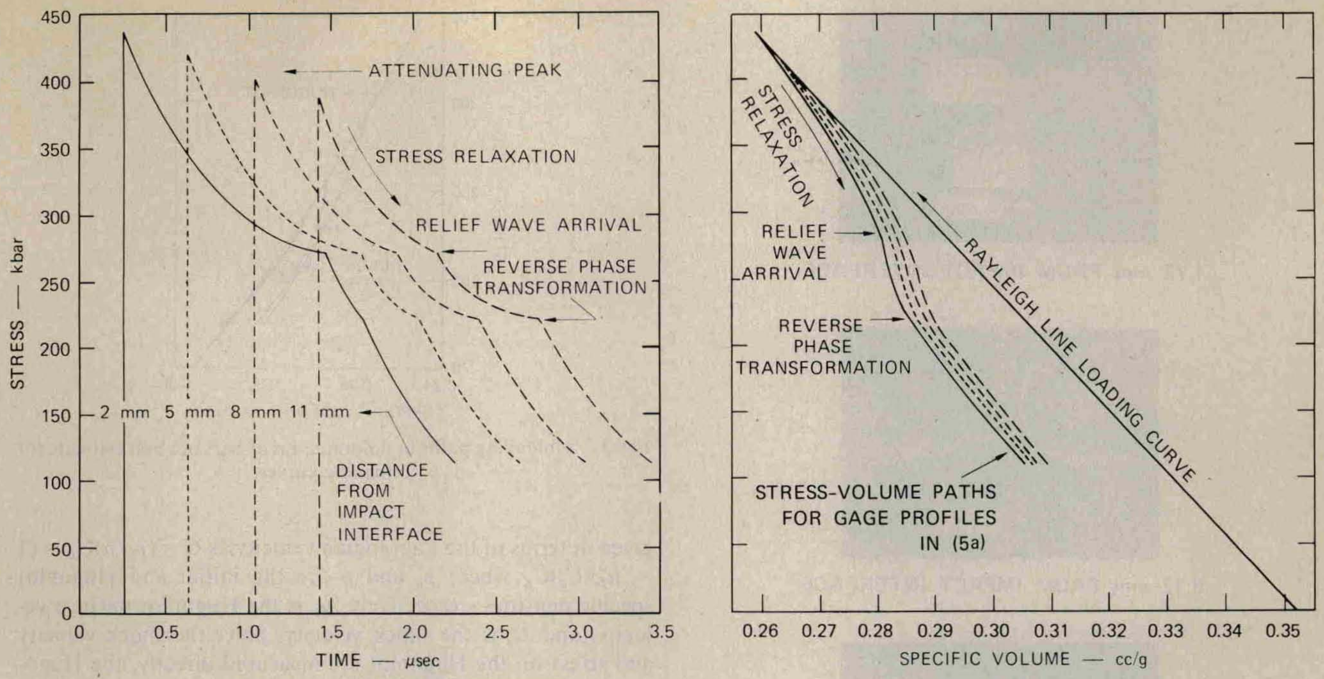


4.80 mm FROM IMPACT INTERFACE



8.17 mm FROM IMPACT INTERFACE

Fig. 4. Stress relaxation in dolomite. Peak stress is approximately 420 kbar. The figure shows three of seven successful gage records obtained in this experiment. In the 4.80-mm profiles, unloading features observed in all the profiles are indicated.



(a) SMOOTHED STRESS-TIME PROFILES

(b) STRESS-VOLUME PATHS

Fig. 5. Stress-time profiles and stress-volume paths for material elements corresponding to gage locations.

state predictions. The sound velocities determined by this method are shown in Figure 6.

The bulk sound velocity for dolomite determined from ultrasonic data [*Birch*, 1960; *Press*, 1966; *Heard et al.*, 1973] was extrapolated to high pressure and is also shown in Figure 6. The measured Hugoniot sound velocity is seen to be significantly higher than the extrapolated bulk sound velocity. If the material retains rigidity at the Hugoniot state, initial relief waves will propagate at a longitudinal velocity which will be higher than the bulk sound velocity by a factor $C/C_0 = \{[3(1-\nu)]/(1+\nu)\}^{1/2}$, where ν is Poisson's ratio and C_0 is the bulk sound velocity. In Figure 6 we have shown longitudinal sound velocity curves based on the extrapolated bulk sound velocity curves and assumed constant values of Poisson's ratio equal to 0.15 and 0.25. A value of Poisson's ratio for Blair dolomite measured at 1 atm and room temperature is 0.24 [*Petersen*, 1969]. The data agree best with a value of 0.15 for Poisson's ratio, which is not immediately unreasonable. However, studies by *Anderson et al.* [1968] on a number of rock-forming minerals indicate that both the pressure derivative and the temperature derivative of Poisson's ratio are positive in the large majority of cases. On the basis of the initial Poisson's ratio of 0.24, the lower value of 0.15 seems unlikely. We suggest that an alternative explanation for the unusually high Hugoniot sound velocities would be the occurrence of a partial or complete transformation during shock compression to a higher density and less compressible phase.

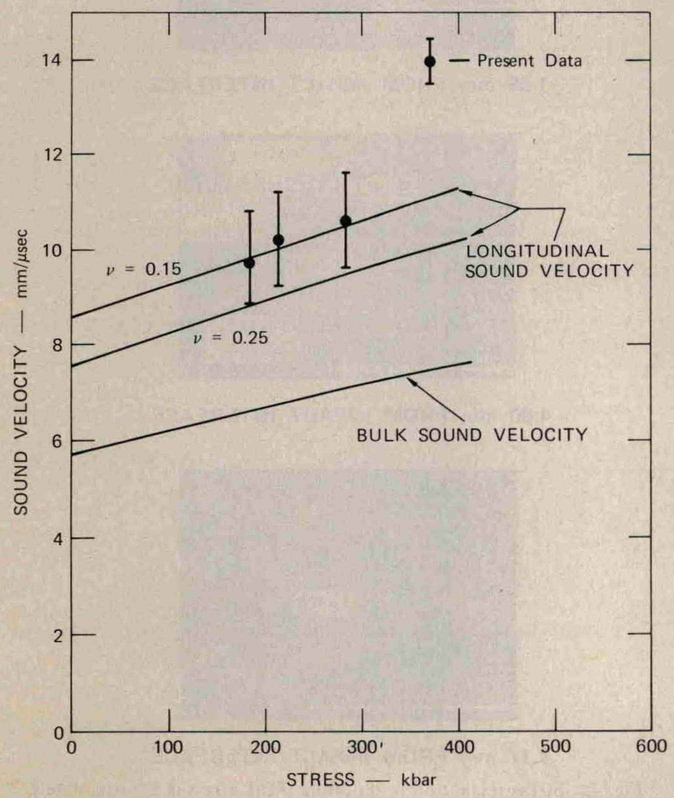


Fig. 6. Sound velocities on the Hugoniot for dolomite. Bulk sound velocity curve is extrapolated from ultrasonic data. Longitudinal sound velocity curves are estimated from the bulk sound velocity and a constant Poisson's ratio ν.

DISCUSSION

We currently believe that the unusual properties observed when dolomite is subjected to high-pressure shock compression are the effects of a rate-dependent low- to high-density phase transformation. A phase transformation is the simplest explanation for the variation from linearity in the shock velocity–particle velocity curve, as suggested by *McQueen et al.* [1970] and for the deviation of the pressure-volume Hugoniot from the Murnaghan curve extrapolated from ultrasonic data. Hysteresis in the relief curves from peak stresses of less than 300 kbar suggests that a phase transformation is occurring. The stress relaxation observed in the experiments performed at stresses above 400 kbar indicates a time-dependent phase transformation occurring during a time comparable to the shock wave transit time in the specimen. The large value of sound velocities measured on the Hugoniot, although possibly an indication of material strength at the Hugoniot state, most likely provides further evidence for a partially completed phase transformation.

This kind of time dependence has been observed by *Kormer et al.* [1965] in studies on alkali halides, notably with sodium chloride. In these experiments they found anomalies in their shock velocity–particle velocity data, which they suggested were caused by a change in coordination number with a relaxation time approximately equal to the wave transit time across the specimen.

More recently, *Horie and Duvall* [1968] and *Duvall* [1971] have described numerical calculations which predict the wave propagation characteristics of a solid undergoing a rate-dependent phase transformation. Their results indicate that for a constant stress driving force, a propagation time of at least several times the transition time must pass before relaxation effects subside and conditions approximating a steady state two-wave structure occur. *Hayes* [1972] has shown that stress relaxation necessarily occurs at the impact interface and behind the shock wave, if one makes the reasonable assumption that the transformation rate is a function of the thermodynamic states of the constituents and that the shock velocity is constant and propagates along a characteristic. In the present work, stress was not measured immediately at the impact interface; however, it is unlikely that the profile measured at the first gage plane (approximately 1-mm propagation distance in several experiments) differs considerably from the impact interface profile.

The stress propagation characteristics of dolomite appear to be consistent with these earlier studies. Of particular interest is the explanation suggested by *Kormer et al.* [1965] of a change in coordination number in the material undergoing shock compression. In the present carbonate material at a pressure favoring higher coordination number, it is legitimate to raise the possibility that carbon may be assuming a CO_4 tetrahedral coordination similar to the SiO_4 groups in silicates [*Verhoogen et al.*, 1970]. This condition, however, has not been produced experimentally, and the present work provides no evidence for such an occurrence other than that a fairly substantial volume change transition must be occurring to produce the observed wave propagation effects.

Unfortunately, considerable detail in the shock compression process of dolomite is not yet understood. We have no indication of a high-pressure phase boundary. Extrapolation of the high-pressure data to zero pressure, as has been done by other authors, would be of little value in this case, since there is no clear indication of which data correspond to the completely transformed high-density phase. No experiments were performed to recover and isolate the high-density phase.

We do not know with precision at what threshold stress the phase transformation initiates on loading. The shock velocity–particle velocity curve suggests that it may start as low as about 90 kbar. The experiments conducted in the neighborhood of 200 kbar certainly show evidence of partial transformation, and the higher-pressure experiments show evidence of crossing the phase boundary on unloading at about 220 kbar.

Stress relaxation at about 420 kbar implies that the phase transition has not yet reached completion. Why stress relaxation is not observed in the experiments below 300 kbar is not clear. Possibly the relaxation time is a function of the overdriving stress.

Further study of the remaining interesting and extremely important details is required. The present results, however, certainly show an unexpected complexity in the high-pressure shock compression properties of dolomite.

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