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Shock Compression of Dolomite

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Shock compression studies on a dolomite rock (ρ_0 = 2.84 g/cm^3) 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/cm^3, and the calculated porosity is 0.9%, based on the crystal density of dolomite, 2.866 g/cm^3. 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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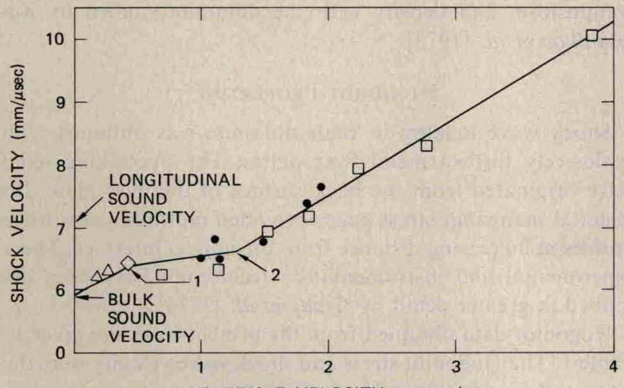
TABLE 1. Hugoniot Data for Blair Dolomite

Shot	Shock Velocity, mm/μs	Particle Velocity, mm/μs	Stress, kbars	Specific Volume, cm³/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

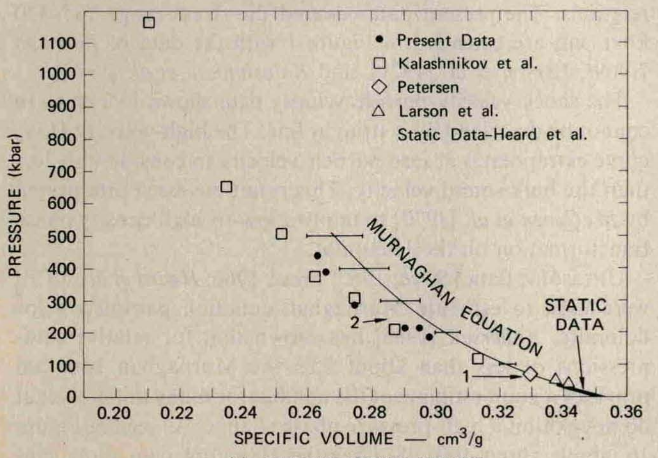
compressibility. Static compression data to 36 kbar for Blair dolomite [*Heard et al.*, 1973] is also shown in Figure 1*b*.

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