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Research Brief

INVESTIGATION OF SHOCK WAVE RESPONSE OF SILICATES

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INTRODUCTION

To permit accurate prediction of the effects of nuclear explosions, there is a current need for better knowledge of the response of common rock-forming silicates to transient stresses over the range extending from the negative (tensile) stress region to compressive stresses of over a megabar. This research brief describes a proposed joint SRI-Air Force Cambridge program of petrographic and mineralogic investigation designed to support and to increase the cost-effectiveness of current programs in which dynamic measurements are made of the response of geologic materials to compression and relief waves.

The program would consist of shock-loading and recovering selected rock or mineral specimens under carefully controlled conditions. The shocked specimens and control unshocked specimens would be examined by appropriate techniques, such as thin-section optical microscopy, electron microscopy, X-ray diffraction, and electron microprobe analysis. The objective of the examinations would be to obtain evidence of the details of material response to compression and relief waves. The results of these examinations would be interpreted with the aid of all available relevant information, including data from both shock wave measurements and static high pressure studies, thermodynamic data and calculations, and considerations of silicate crystal structure systematics.

It is expected that the proposed research would lead to an improved understanding of the microscopic phenomena, such as phase changes, that play an important role in the propagation of compression and relief waves in geologic materials. With this improved understanding it should eventually become possible to model stress wave propagation with reasonable accuracy for an arbitrary geologic medium. A more immediate goal of the proposed research would be to determine the validity or accuracy of various experimental data (and inferences from these data) upon which are based current models of shock propagation in rocks and minerals.

The proposed research program would be a joint SRI-Air Force Cambridge effort. SRI would be responsible for the shock wave experiments, and Air Force Cambridge would be responsible for studying the effects of shock loading on the recovered specimens. The planning of the experiments and the interpretation of results in terms of compression and release paths would be a joint effort.

BACKGROUND

During the past twenty years, computer codes for the prediction of shock wave propagation in solids have become increasingly complex and sophisticated, as have experimental techniques for the measurement of shock wave propagation. In the early 1950s the fundamental assumption of the computational models was that solid behavior could be treated as hydrodynamic, i.e., material strength effects were not important in the high stress region.

The essential input data for the computations were obtained by rear-surface measurements of shock velocity and free surface velocity of a material in laboratory shock wave experiments. With the aid of a few assumptions and the application of the conservation laws, each pair of shock velocity-free surface velocity points maps onto a point in the pressure-volume plane. The locus of states in the pressure-volume plane (or the equivalent pressure-particle velocity plane) that can be reached by shock compression of a material (from a given initial state) is called the Hugoniot equation of state or, simple, the Hugoniot.

By the early 1960s, the inadequacy of the hydrodynamic model had been conclusively demonstrated by the results of well-designed one-dimensional shock wave propagation experiments on metals; the hydrodynamic model predicted very much lower attenuation rates than were observed. With the development of improved stress wave generating techniques, higher resolution rear-surface measurements, and most recently, in-material stress and particle velocity transducers, progressively more refined computational models could be tested. It gradually became apparent that the propagation of stress waves in a solid is a complex phenomenon that can be modeled accurately only when all the complexities of actual material behavior are incorporated into the model. The realization of this complexity has led to the use of the general term "stress wave" in place of "shock wave," which implies narrowly restricted material behavior.

At present, there exist a variety of computer codes capable of predicting with satisfactory accuracy the outcome of both one-dimensional and two-dimensional laboratory wave propagation experiments with various metals. The common element in the successful predictions has been the development and incorporation into the computation of sufficiently accurate and comprehensive constitutive relations (a dynamic stress-volume-energy equation of state).

These material-specific constitutive relations quantitatively account for the effects on stress wave propagation of detailed material response including yielding, plastic flow, work-hardening, fracture (including the stress-time dependence of the nucleation and growth of fracture), stress relaxation, Bauschinger effect, heating, and cooling. The constitutive relations are based on Hugoniot measurements, static high pressure measurements, tests of mechanical properties at various strain rates, thermodynamic measurements and calculations, dynamic fracture experiments, elasticity theory, considerations of dislocation dynamics, and any other relevant data or theories that are needed.

The development of accurate constitutive relations for metals requires extensive collaboration among shock wave physicists, solid state physicists, physical and mechanical metallurgists, computer code specialists, and others. Rapid progress became possible only when the various specialists learned to communicate with one another.

One may presume that, at least in principle, the computational aspects of predicting the effects of nuclear explosions in geologic media are well understood. The heart of the prediction problem therefore appears to be the demonstrable inadequacy of present knowledge of constitutive relations for the geologic media of interest.

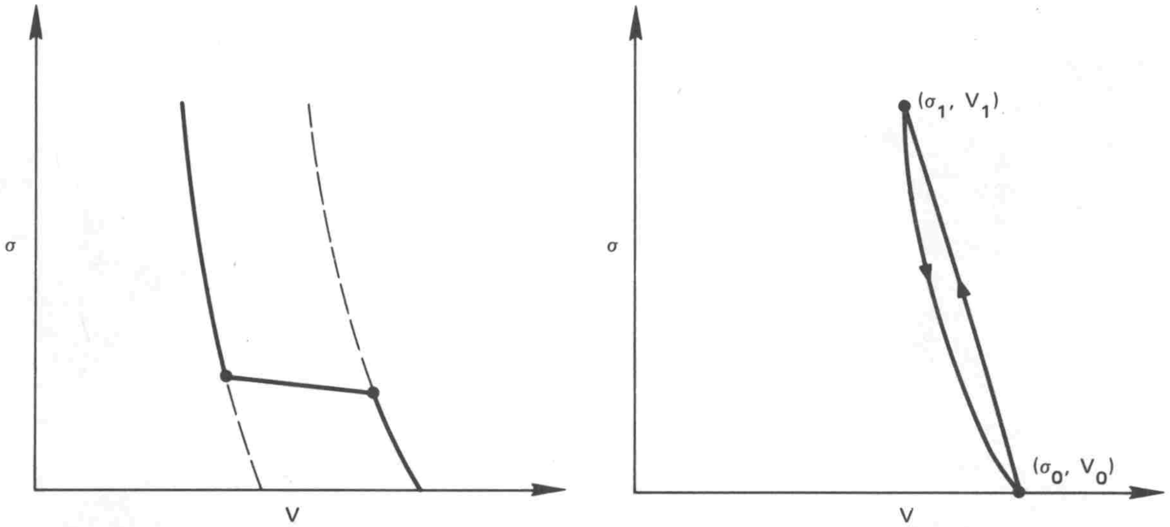
CONSTITUTIVE RELATIONS OF GEOLOGIC MEDIA

It is perhaps misleading to define the constitutive relations as a dynamic stress-volume-energy equation of state. Indeed, use of the term "constitutive relations" is one way of avoiding the implication that the states of interest are path-independent thermodynamically equilibrated states. It might be better to state that the constitutive relations are a detailed description of the response of a material to stress waves. A bare bones set of constitutive relations for a wave propagation calculation could be constructed from a set of compression and release paths covering the stress-time range of interest.

The variety of possible compression and release paths for geologic media is illustrated in the following examples. Assume the geologic medium to be a compact monomineralic rock composed of a mineral known to undergo a phase transition at high quasi-static pressures. The equilibrium stress-volume behavior of this material is schematically depiected by the solid line in Figure 1(a); the dotted lines represent metastable compression curves for phase I and phase II. Figures 1(b), 1(c), and 1(d) depict some possible responses of this material to stress wave compression and release.

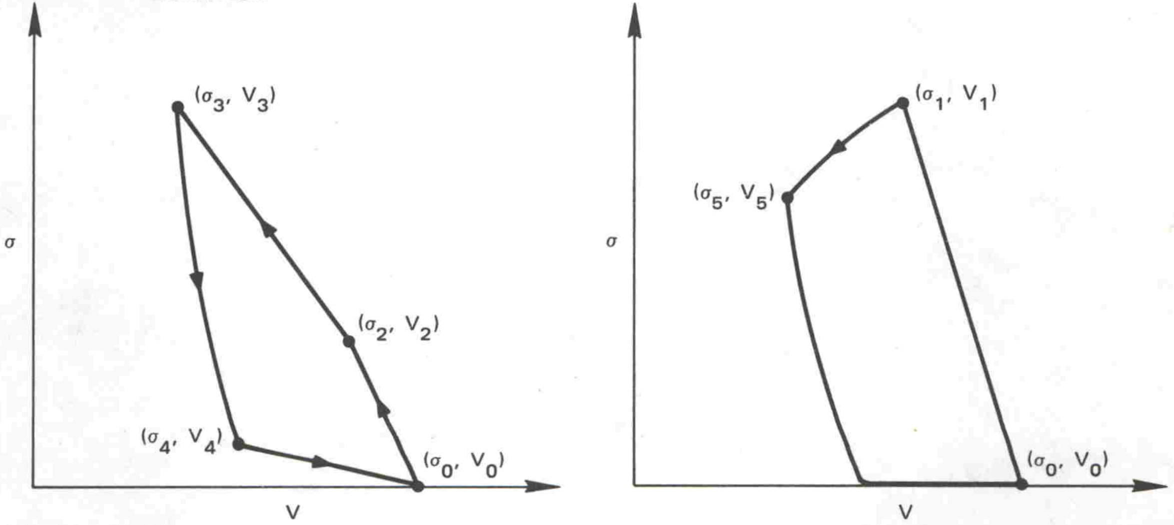
Figure 1(b) illustrates metastable response. The compression path is the Rayleigh line connecting the initial state (σ_o, V_o) with the state (σ_1, V_1) on the metastable extension of the phase I compression curve. The release path is the phase I isentrope. This type of response is experimentally observed for quartz single crystals and for compact quartzite loaded to peak stresses within the stability field of coesite.(1)

Figure 1(c) illustrates rapid (somewhat overdriven) phase transition behavior. A double shock forms in the material; the compression path is from the initial state (σ_o, V_o) to a state (σ_2, V_2) on the metastable extension of the compression curve of phase I and, in the second shock,



(a) EQUILIBRIUM STRESS-VOLUME BEHAVIOR

(b) METASTABLE RESPONSE



(c) RAPID PHASE TRANSITION BEHAVIOR

(d) TIME-DEPENDENT PHASE TRANSITION BEHAVIOR

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FIGURE 1 EXAMPLES OF POSSIBLE COMPRESSION AND RELEASE PATHS from (σ_2, V_2) to the state (σ_3, V_3) on the compression curve of phase II. The release path is along the isentrope of phase II down to a state (σ_4, V_4) in the stability field of phase I and thence to the initial state. This general type of behavior has recently been observed for quartzite loaded to peak stresses of about 500 kbar.(2) On the basis of petrographic evidence from recovered samples, I predict that the same type of behavior will be observed for feldspars loaded to similar high stresses.

Figure 1(d) illustrates time-dependent phase transition behavior in response to a stress pulse of relatively long duration, e.g., 10^{-3} sec. The initial compression path is to the state (σ_1, V_1) on the metastable compression curve of phase I. As the transformation proceeds, the material relaxes towards the state (σ_5, V_5) on the compression curve of phase II. The stress is relieved and the material expands along the isentrope of phase II down to zero stress before transforming back to phase I. There is a hint of this general type of behavior, on a microsecond time scale, in recent Lagrangian gage measurements of the response of Dolomite.(3) However, one can argue that this type of behavior should be fairly common on a millisecond time scale at high shock stresses (and concomitant high temperatures), invoking extrapolations of sparse static high pressure phase transition rate data.

The three examples, 1(b), 1(c), 1(d), of material response were presented in order of their effect on stress wave attenuation. If one recalls that the area enclosed by the compression and release paths is the internal energy increase of the material, one need not invoke the details of rarefaction wave propagation to realize that the stress wave would be much more attenuated by a material responding as in example 1(a) than by a material responding as in 1(b).

Unfortunately, current techniques for stress wave measurement in the high stress region (above 100 kbar) are adapted only to the microsecond time scale. We do not have a direct technique for measuring the course of a phase transition that might occur on a longer time scale (10 microseconds to 1 millisecond) comparable to the duration of the stress wave produced by a nuclear explosion.

Present constitutive models of silicate behavior in the high stress region are based largely on Hugoniot data obtained over the past 20 years by rear-surface measurement techniques. Rear surface measurements are subject to large experimental uncertainties and ambiguities of interpretation. These limitations have been largely circumvented, however, by the recent development of in-material gages to measure stress and particle velocity. A Lagrangian analysis of properly designed in-material gage experiments permits determination of complete compression and release paths. Although the recording time of such gages and the times at stress are short, compared with nuclear explosions, data can be obtained on at least the onset of a time-dependent phase transition at high stresses.

However, Lagrangian measurements are expensive (about $5000 per experiment under favorable conditions), few materials have been studied to date, and capabilities for performing such measurements exist in only a few laboratories. The diversity of natural geologic media, with respect to the parameters that affect constitutive relations, is very great. It has been experimentally demonstrated that even minor differences in porosity or in water saturation in otherwise identical media can lead to large differences in dynamic response.(4) A program that relied solely on Lagrangian experiments for determination of improved constitutive relations of all relevant geologic media would be a long-range and very expensive program. Furthermore, such experiments, unless techniques are developed to make close-in long duration measurements in nuclear tests, cover only a small portion of the stress-time region of interest.

The situation is not hopeless. Although geologic media are diverse, they consist predominantly of a relatively small number of mineral types. Given enough of the right kind of information on the response of the constituent minerals and taking into account other factors such as porosity and heat flow between adjacent regions that are heated unequally by rapid compression, it should be possible to make a reasonably accurate estimate of the constitutive relations of an arbitrary geologic medium.

Stress wave specialists appear to be generally ignorant of the contributions that could be made by mineralogists and petrologists to the determination of constitutive relations for geologic media. On the other hand, those mineralogists and petrologist who have studied shocked rocks and minerals have had the primary objective of developing a basis for inferring the history of meteorites and of lunar samples.(5) In only a few of these studies has any attempt been made to correlate petrographic observations with inferences based on Hugoniot measurements.

As a side-benefit of my past collaboration with petrologists and mineralogists in some studies of shock effects in minerals, I have acquired a patchy knowledge of their specialties. In the absence of a suitable collaborator, I will presume to apply this knowledge to illustrate the manner in which mineralogists and petrologists can contribute to the determination of constitutive relations.

In 1962 Wackerle reported results of rear surface shock wave measurements of the Hugoniot of single crystal quartz.(6) He inferred a phase transition to a denser form such as coesite, stishovite, or a dense glass. These data were reinterpreted by McQueen et al. as indicating the transition above 140 kbar to a phase containing silicon in sixfold coordination with oxygen, Either crystalline stishovite or a stishovite-like short-range-order phase.(7) Neither author commented on the possible release behavior of SiO_2. It may be instructive to attempt to deduce release behavior, using evidence from petrographic studies of shock loaded quartz.

The evidence obtained from petrographic studies of quartz, shock-loaded in laboratory scale experiments in which peak stress was fairly well known, includes the following observations:(5,8,9)

(1) Fractures, suspected to be the result of tensile iterations of rarefaction waves, are the sole feature discernible in specimens loaded to peak stresses below the Hugoniot elastic limit (HEL).

(2) Samples loaded to peak stresses above the HEL contain lamellar features, which I will loosely describe as deformation lamellae.

(3) Optically resolvable patches of isotropic material become discernible in samples shocked to peak stresses in the range of 200 to 250 kbar. With increasing peak stress, over the range of about 250-450 kbar, the proportion of isotropic material increases to 100%.

A fundamental assumption in interpreting these observations is that the crystalline quartz observed in recovered specimens represents material that did <u>not</u> transform to a high pressure phase during shock compression. There is no rigorous proof of this, except that it does not seem otherwise possible to account for the observation that the quartz retains the crystallographic orientation of the original pre-shock material. A second unprovable assumption, which is at least concordant with the Hugoniot data, is that the isotropic material represents material that did transform to a high pressure phase.

On the basis of these petrographic observations, made on specimens that were subjected to microsecond duration stress pulses, I would conclude that Wackerle's Hugoniot is an accurate representation of the response of quartz to microsecond duration loading. I can also use the petrographic observations to infer probable unloading paths in different regimes, as follows:

(1) Below the HEL, the response of single crystal quartz appears to be essentially elastic. I suggest that the error would be negligible if one assumed the release curve to be identical with the H ugoniot in this region.

(2) Between the HEL and 200-250 kbar, the response is essentially elastic-plastic. My best guess would be that the release curve is approximately parallel to the elastic portion of the Hugoniot. Although I believe that the material within some classes of "deformation lamellae" was probably transformed to a high pressure phase (under the influence of local high temperatures associated with adiabatic shear), the proportion of the whole represented by the material within the lamellae is insignificant in this stress range.

(3) Above about 450 kbar complete transformation to the stishovite-like phase has occurred. On thermodynamic grounds, one can predict that the release curve will approximately parallel the stishovite isentrope down to a stress well within the stability field of quartz.

(4) In the "mixed phase" region between 200-250 kbar and about 450 kbar the release behavior could be approximated by the average, weighted by the proportion transformed, of quartz release behavior and stishovite-like release behavior. We lack sufficient petrographic data to be more quantitative in discussing this region.

These deductions of quartz release behavior are generally confirmed by the results of recent Lagrangian gage measurements on compact quartzite. However, this is not quite a legitimate test, since I know of the dynamic results before I collected my thoughts on the implications of studies of recovered shock loaded mineral specimens.

However, I will now predict that feldspars, irrespective of composition, will behave much like quartz. On the basis of my own petrographic observations of shocked feldspars and on the crystal chemical argument that AlO_4 tetrahedra should transform at lower stresses than SiO_4 tetrahedra, I would lower the stress range for the onset of the transformation to 150-200 kbar. Otherwise my interpretation of feldspar release curves is identical to that of quartz. A reasonable structure for a high pressure feldspar could be described as a close-packed lattice of oxygen anions and large cations (Na, K, Ca), with the small cations (Al, Si) in octahedral sites. One could expect such a structure to become thermodynamically stable in the same range as stishovite, i.e., above about 100 kbar. The release isentrope for the high pressure feldspar phase should be very nearly parallel to the release isentrope of stishovite. Ahrens and Rosenberg, on the basis of rear-surface measurements, have inferred that such behavior is possible.(1)

Although the foregoing set of predictions would seem trivial to the well-rounded mineralogist, I fear that many shock wave specialists would consider them pure guesswork. Since Dennis Grady of SRI is currently planning Lagrangian measurements of the release behavior of feldspars, I thought it advisable to get my predictions on record before they are confirmed (as I fully expect) by experiment.

PROPOSED PROGRAM

One may readily envision a major research program in which geologic media of progressively increasing complexity would be studied, with the objective of developing the capability of accurately predicting the constitutive relations of an arbitrary geologic medium. The program would include shock recovery experiments, interpretation of results in terms of loading and unloading paths, wave propagation calculations, and Lagrangian measurements of wave profiles. Although we are convinced that the results of such a program would justify an estimated cost of $150,000 per year for three years, we accept that it will probably be necessary to begin with a smaller program.

Initially, a single mineral type will be selected for study. Samples will be shock loaded in carefully designed recovery experiments covering the peak stress range of about 50 kbar to about 1 megabar. The recovered samples will be examined for evidence of significant structural or microstructural alteration attributable to shock compression and release. Available Hugoniot data and calculations will be used as a guide in planning the shock loading experiments and subsequent specimen examination; the results of the specimen examination will serve as an independent check of the validity of inferences based on Hugoniot data. For example, in a material for which a phase transition is inferred on the basis of rear-surface Hugoniot measurements, one would expect to find microstructural evidence (such as structurally disordered material or cryptocrystalline material) indicative of the proportion transformed. If no such evidence could be found, the validity of the Hugoniot interpretation would be suspect, and alternate interpretations of the raw dynamic data (shock velocity-free surface velocity pairs) should be sought.

It is expected that thin-section optical microscopy will be the major method of specimen examination, although other techniques (e.g., X-ray diffraction, electron microscopy, electron microprobe analysis) will be used where warranted. The results of the examinations and other information (thermodynamic data, extrapolations of static high pressure studies, crystal chemical principles, and the like) will be used to infer a set of plausible shock compression and release paths for the material as a function of peak shock pressure. If suitable specimens from long-duration shock experiments (nuclear experiments) are available, it may also be possible to infer the dependence of compression and release paths on stress pulse duration.

If sufficient funds are available, it would be desirable to determine the accuracy of the compression and release paths inferred from the study of recovered specimens. This could be done by performing Lagrangian gage experiments in which the compression and release paths would be measured on a time scale commensurate with the recovery experiments.

We suggest that a pyroxene would be a good material to study initially. Ahrens and Gaffney(10) have inferred from Hugoniot measurements that Bamle orthoenstatite transforms to a garnet structure, beginning at shock stressess of about 135 kbar. The limited petrographic evidence at hand tends to indicate that their interpretation is erroneous, but more experimental evidence (from carefully designed recovery experiments) is needed to settle the matter. Pyroxene is an important constituent of some common geologic media; study of pyroxene would therefore be directly relevant to the prediction problem. Furthermore, differences in dynamic response of pyroxene on a much longer time scale could possibly be inferred from studies of the pyroxene in close-in basalt samples at the site of the 1962 Danny Boy nuclear experiment.

The proposed research program would be a joint SRI-Air Force Cambridge effort. SRI would be responsible for the shock wave experiments, and Air Force Cambridge would be responsible for studying the effects of shock loading on the recovered specimens. The planning of the experiments and the interpretation of results in terms of compression and release paths would be a joint effort.

The first year of the program outlined above might include six to twelve shock recovery experiments and probably two fully instrumented Lagrangian gage experiments to measure compression and release paths, to test the validity of the inferences based on studies of the recovered specimens. The cost of such a program depends on the details of the experiments to be performed, but we estimate about $20,000 for the first year for the SRI portion. We would expect Air Force Cambridge to handle the costs associated with the examination of the recovered specimens.

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