VOL. 80, NO. 35 JOURNAL OF GEOPHYSICAL RESEARCH DECEMBER 10, 1975

Hugoniot Sound Velocities and Phase Transformations in Two Silicates

DENNIS E. GRADY,[1] WILLIAM J. MURRI, AND PAUL S. DE CARLI

Poulter Laboratory, Stanford Research Institute, Menlo Park, California 94025

Rarefaction wave velocities have been used to estimate sound velocities on the Hugoniot for a quartz rock and for a perthitic feldspar. The Hugoniot states and rarefaction wave velocities were determined with multiple manganin stress gages placed between successive slabs of the sample material. Hugoniot stress states were produced by impact from explosively driven flyer plates. The sound velocity was determined from the transit time across gage planes of the initial characteristic of the rarefaction wave originating at the flyer plate free surface. Sound velocities (referred to Eulerian coordinates) measured in quartzite were 7.6, 8.1, and 10.5 mm/μs at Hugoniot stresses of 220, 250, and 355 kbar, respectively. Sound velocities measured in feldspar were 7.4, 8.7, and 9.2 mm/μs at Hugoniot stresses of 255, 345, and 460 kbar, respectively. These velocities are close to estimated bulk velocities and imply an almost complete loss of material strength behind the shock front. On the basis of our measured sound velocities and earlier observations by others we suggest that the Hugoniot yielding phenomenon is an adiabatic shear process resulting in partial melting behind the shock front. We further suggest that inhomogeneity in the adiabatic shear process may account for many details of the nonequilibrium mixed phase Hugoniot observed in silicates.

INTRODUCTION

Hughes and McQueen [1958] were among the first to demonstrate that shock wave measurements could be applied to the study of the earth's interior. Since that time, shock wave data have become generally accepted as constraints for models of the earth [*Press*, 1968; *Ahrens et al.*, 1969]. For geophysical purposes, isothermal or adiabatic equations of state are required. The reduction of the Hugoniot states measured in shock wave experiments to isotherms or adiabats requires knowledge of the dependence of the Grüneisen parameter on volume, and, in principle, this behavior can be determined through measurements of Hugoniot sound velocities. Care must be taken in using Hugoniots to generate isotherms for further use in modeling the earth. Although Hugoniot data apply to states achieved in shock compression, they may not apply to states achieved by pressure and temperatures inside the earth. It is important therefore to use all the available evidence to determine whether the Hugoniot states measured in experiments of microsecond duration are thermodynamically equilibrated states.

Wackerle [1962] and *Fowles* [1967] have noted an apparent total loss of strength in the shock compression of quartz above the Hugoniot elastic limit in contrast to the elastic-plastic behavior of most ductile materials. This loss of strength has been reported to occur in other brittle solids [*Graham and Brooks*, 1971] and has not been satisfactorily explained.

Numerous studies on recovered samples of quartz and feldspar after shock loading provide accounts of lamellar features and identification of amorphous and high-density polymorphs of the original sample [*De Carli*, 1968; *Carter*, 1968; *Chao*, 1968; *Bunch*, 1968]. The genesis of these petrographic details is apparently linked to the shock deformation process. The results of these studies have been summarized in an excellent review by *Stöffler* [1972]. The residual features observed in recovered specimens of silicate materials are (1) planar fractures, (2) planar elements (shock lamellae), (3) deformation bands, (4) irregular plastic lattice deformation (mosaicism), (5) high-density phase, and (6) fused glass and diaplectic glass.

In this paper we report measurements of sound velocity on the Hugoniot for a quartz rock (Arkansas novaculite, initial density of 2.63 g/cm^3) and for a perthitic feldspar (75% orthoclase, 25% albite; initial density of 2.58 g/cm^3) over the stress range of 220–460 kbar. The present data also suggest loss of strength on the Hugoniot and further suggest that this loss of strength persists for some duration after shock passage.

These and earlier data suggest to us a physical model for the shock yielding mechanism and the Hugoniot phase transitions in quartz and feldspars. We will describe this model and show that it appears to provide reasonable explanations for the curious Hugoniot and shock wave properties of silicates and certain other brittle materials.

EXPERIMENTAL METHOD

Each experimental assembly was constructed of four parallel plates of the sample material. Manganin foil stress transducers were placed between plates, and the assembly was bonded with epoxy. The four-terminal manganin transducers were supplied by constant current sources, and voltage outputs were observed with high-quality camera oscilloscopes. Hugoniot stress states were achieved by the planar impact of explosively accelerated metal flyer plates. The experimental arrangements and a set of voltage-time records for one experiment are shown in Figure 1.

Because of the constant current, these voltage-time records are equivalent to resistance-time records, which can be transformed to stress-time data by using the dynamic calibration for manganin of *Lyle et al.* [1969]. The reduced multiple stress-time profiles for one experiment are shown in Figure 2 to indicate the propagation characteristics of the stress wave.

These records can be interpreted from inspection of Figure 3, a distance-time plot of the loading and rarefaction waves in the experiment. At impact of the flyer plate with the sample a shock propagates into the sample, and another shock propagates back into the flyer plate. When the shock in the flyer plate reaches the rear surface of the flyer, it reflects as a relief wave that propagates through the flyer and into the sample, eventually overtaking the shock wave in the sample. Since the

[1] Now at Sandia Laboratories, Albuquerque, New Mexico 87115.

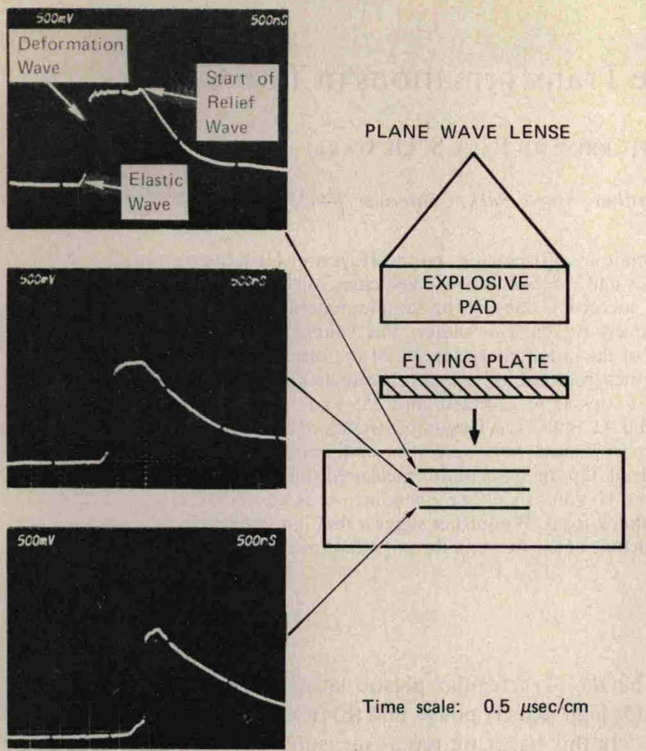

Fig. 1. Experimental stress profiles in feldspar obtained with manganin piezoresistant gage elements. Peak stress is approximately 350 kbar. Stress states are achieved by planar impact of the explosively accelerated metal flyer plate.

distances between transducer planes (usually about 3 mm) have been carefully measured beforehand, the gage records yield shock velocity and stress, which establish the Hugoniot state in each experiment.

The Lagrangian sound velocity on the Hugoniot is estimated by measurement of the transit time of the leading characteristic of the overtaking relief wave across the three transducer planes, as is indicated in Figure 2 and Figure 3. The relationship of the Lagrangian (initial length per unit time) velocity to the Eulerian sound velocity is the ratio of the initial density to Hugoniot density of the sample. The error in determining the Hugoniot density is conservatively estimated to be about 5% and is the major uncertainty in the present work. The finite thickness (about 0.025 mm) of the transducer plane slightly degrades the frequency response of the measurement but does not substantially limit the accuracy of determining the time of arrival of the relief wave. Special care in instrumentation (matched cable lengths, matched oscilloscopes and preamplifiers, a common *z* axis time mark, and careful calibration of instrumental time delays) was necessary to ensure proper time correlation among the oscilloscopes. The error bars on the data to be presented are believed to be conservative; the larger error bars are for experiments performed before all the time correlation problems were understood.

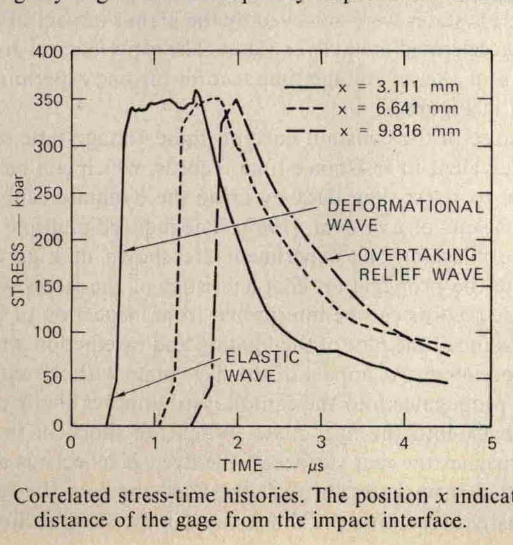

Fig. 2. Correlated stress-time histories. The position *x* indicates the distance of the gage from the impact interface.

EXPERIMENTAL RESULTS

The experimental data for quartz and feldspar are given in Table 1, and the sound velocities on the Hugoniot are plotted in Figure 4 as a function of the Hugoniot stress. These measurements ranged from 220 to 460 kbar in stress.

To understand the stress dependence of the measured sound velocities, it is instructive to consider two cases. First, if the silicate is assumed to have no mechanical strength and to behave as a fluid, it is possible to calculate the dependence of the bulk sound velocity on stress. A Murnaghan equation was used to estimate the compressibility of the low- and high-density phases and to determine the stress dependence of the bulk sound velocity. The results of this calculation are shown in Figure 4. The dashed lines represent extension into the mixed phase region. In these calculations we have assumed for each silicate that the low-pressure phase persists to 100 kbar, that the mixed phase region ranges from 100 to 400 kbar, and that the high-pressure phase occurs above 400 kbar.

In the second case, material strength is considered. A constant Poisson's ratio of $\gamma = 0.25$ was assumed for both low- and high-pressure phases. Use of Poisson's ratio allows a calculation of the variation of the longitudinal sound speed with stress. The results are curves labeled longitudinal sound speed in Figure 4.

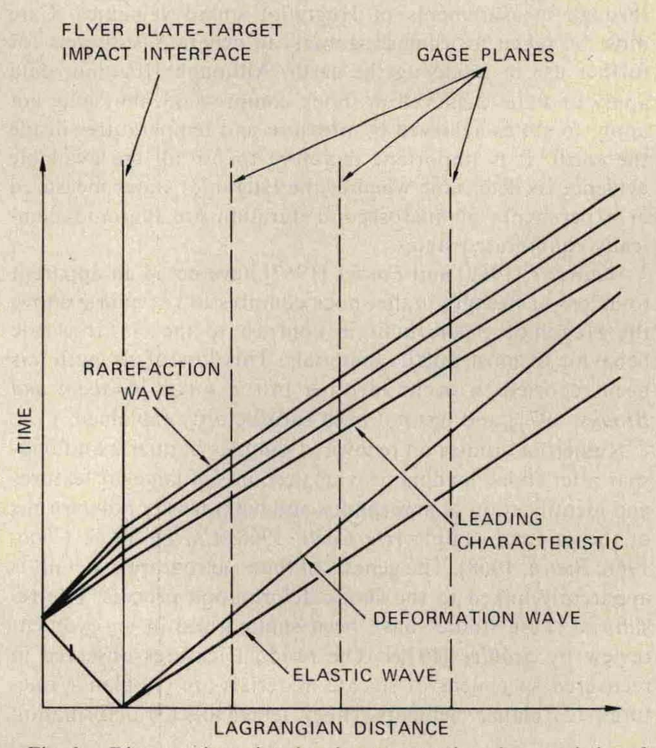

Fig. 3. Distance-time plot showing propagation characteristics of the stress wave and rarefaction wave produced by flyer plate impact. Sound velocity on the Hugoniot is determined from the transit time of the leading rarefaction wave characteristic across the gage planes.

TABLE 1. Hugoniot and Sound Velocity Data in Quartz and Feldspar

Material	Initial Specific Volume, cm^3/g	Hugoniot Pressure, kbar	Hugoniot Specific Volume, cm^3/g	Lagrangian Sound Velocity, $mm/\mu s$	Eulerian Sound Velocity, $mm/\mu s$
Feldspar	0.386	258*	0.257	11.1	7.4
Feldspar	0.386	345*	0.237	14.1	8.7
Feldspar	0.386	460	0.234	15.2	9.2
Quartz	0.380	222*	0.273	8.9	6.4
Quartz	0.380	252*	0.263	10.4	7.2
Quartz	0.380	352	0.233	21.0	12.9

* Precursor observed in these tests.

The data used to make the sound velocity estimates were obtained from *Anderson et al.* [1966], *Ahrens et al.* [1969], *Ahrens and Liu* [1973], and *Clark* [1966]. In the mixed phase region we assumed stress and particle velocity equilibrium but not temperature equilibrium. In addition we assumed that the sound velocity propagated as if the medium were one of frozen phase concentration; i.e., the sound velocity is given by the slope of the isentrope. The last assumption is justified by previous experimental work [*Grady et al.,* 1974] on quartz.

DISCUSSION

We conclude from the above calculations and our experimental data that sound waves on the Hugoniot in the materials studied travel at the bulk sound speed. This conclusion suggests an almost complete loss of shear strength in these materials behind the shock wave. *Graham and Brooks* [1971] observed a similar loss of shear strength in crystalline Al_2O_3 above the Hugoniot elastic limit. *Wackerle*'s [1962] data for *z*-cut quartz and those of *Graham and Ingram* [1969] for *x*-cut quartz also indicate a loss of shear strength above the Hugoniot elastic limit.

We suggest that the low values of the sound velocity measurements and the apparent loss of strength result from partial melting in the silicate materials behind the shock front. It is also possible that the thermodynamics of the phase change occurring over an extended stress range in the silicates may explain our observed data. However, since several of the data points lie well into the stress region in which a single phase exists, we consider this explanation less likely.

Over the stress range covered in the present experiments the increase in energy produced by shock compression is not sufficient to melt completely the silicate material. Furthermore, observations on samples recovered after shock loading also rule out complete melting in the stress range studied [*De Carli,* 1968; *Chao,* 1968; *Von Engelhardt and Stöffler,* 1968].

We believe that the melting is localized in shear deformation bands that result as the material is shock-loaded above the Hugoniot elastic limit and undergoes heterogeneous yielding. Specimens of silicate recovered after shock loading both in explosive experiments and in the vicinity of meteorite craters exhibit planar features commonly called deformation lamella [*Stöffler,* 1971, 1972]. These planar lamella attest to a nonuniform yield process. Such a heterogeneous yield process where energy transport is not sufficient to disperse the viscous energy generation has been called 'adiabatic' shear [*Zener and Holloman,* 1944]. In these shear bands a large portion of the localized plastic slip energy is converted to heat that causes the local temperature to increase (see also *Gruntfest* [1963] and *Nitsan* [1973]). Such localized melting has been observed in sandstone during frictional sliding in triaxial experiments by *Logan and Rigert* [1973]. *Giardini* [1974] observed rapid shear-strain-induced melting in granodiorite during triaxial compression experiments. Heterogeneous adiabatic shear would provide for a highly nonuniform distribution of thermal energy during yielding within the shock front. Calculations indicate that extreme temperature gradients of hundreds, even thousands, of degrees per micron can persist for several microseconds in the shear bands after shock passage because of the low thermal conductivity of silicate minerals. In these calculations we first estimated the dissipative energy resulting from the shock compression process. At a given Hugoniot stress this

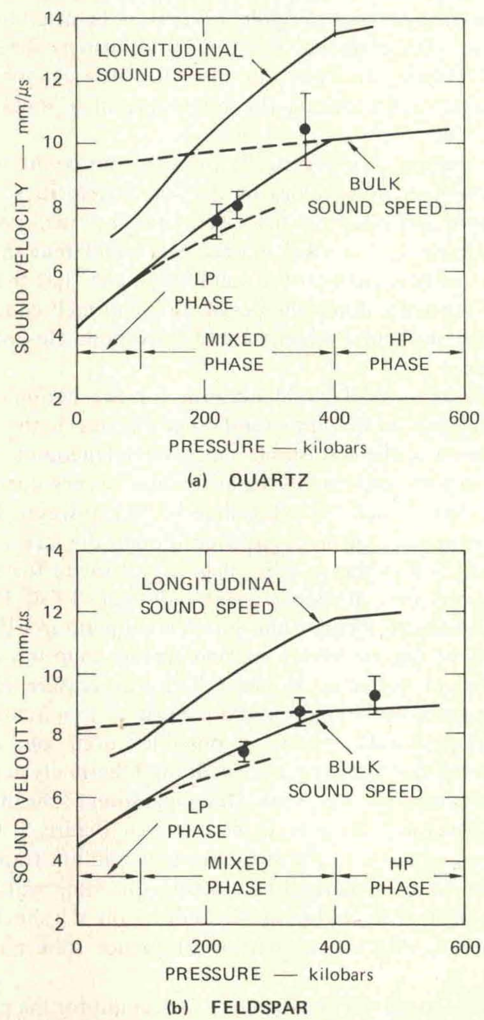

Fig. 4. Hugoniot sound velocities measured in quartz and feldspar. Approximate locations of phase boundaries on the Hugoniot are indicated. Solid lines show the estimated bulk and longitudinal sound velocity in the low-pressure, mixed, and high-pressure phase regions. Dashed lines are metastable extensions of the estimated sound velocity out of the stability field of the low- and high-pressure phases, respectively.

energy is the difference between the Hugoniot energy and the hydrostatic, compressional energy of α quartz, both of which can be determined with reasonable accuracy. The dissipative energy was then partitioned along planar regions in the material, and elementary heat flow solutions were used to estimate thermal evolution after shock-induced yielding. Ambient lattice thermal properties for silicate minerals were used in the analysis. Estimates of the radiative contribution to the heat flow were not significant in the time intervals of interest. The density of planar features can only be estimated roughly from inspection of recovered samples and depends on both shock amplitude and rise time [*Stöffler*, 1972]. This unknown distribution lends a qualitative aspect to the calculations performed; however, the general conclusion of high local temperatures and extreme temperature gradients appears to be correct if the proposed adiabatic shear process occurs during shock compression.

In Figure 5 we indicate the thermal state in the vicinity of a shear plane at some fixed time shortly after passage of the shock front. The ordinate is temperature which can approach several thousands of degrees in the center of the shear zone. The abscissa is distance from the shear zone. The distance between shear zones as suggested from the petrographic details of recovered specimens [*Stöffler*, 1972] is in the neighborhood of 2–10 μm. The extremely low thermal diffusivity for silicate minerals (about 1 $\mu m^2/\mu s$) will allow for little change in the temperature profile during the brief time of a shock wave measurement.

Partial melting is energetically possible and could account for the observed low values of the sound velocities. *Walsh* [1968, 1969] has analyzed the case of random penny-shaped liquid inclusions in a solid matrix. He found that the bulk modulus remains close to the solid value and that the shear modulus is greatly diminished even for small melt concentrations; hence the sound velocity could correspond closely to the bulk value.

The present model could account for the curious phase transition behavior of quartz (and other silicates) in the 'mixed phase' region of the metastable shock wave Hugoniot. Partial transformation, presumably to stishovite, occurs during the rise time of the shock front (less than 10^{-7} s); however, further transformation is not observed even though the stress is sustained well within the stability field of stishovite for several microseconds after shock passage [*Grady et al.*, 1974]. Heterogeneous adiabatic shear would provide temperatures that are thousands of degrees hotter in shear regions than in immediately adjacent material. In these high-temperature regions, transformation to the high-pressure phase or to a liquid form of the high-density phase is possible, even on a submicrosecond time scale, by a conventional thermally activated nucleation and growth process. Our suggestion of the distribution of transformed material is shown in Figure 5. Cooler regions not adjacent to the shear zones would not transform, and owing to slow thermal conduction this state will persist and give the illusion, within the short duration of a shock wave measurement, that an equilibrium Hugoniot state has been attained.

The model outlined above may also account for the proportions of low-density, high-density, and amorphous material identified in recovered specimens subject to shock loading in this pressure range. In Figure 5 we indicate qualitatively the change in material state with increasing distance from the shear zone. Melting will occur in the extreme temperature region of the shear zone. The low-density phase will persist in

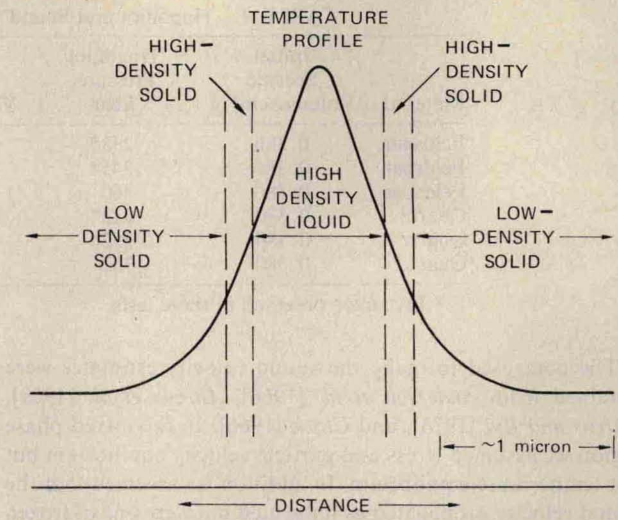

Fig. 5. Schematic temperature-distance profile based on heat flow calculations in the neighborhood of an adiabatic shear zone shortly after passage of the shock front. Indicated are the degree and state of phase transformation determined by the local temperature.

the region where the temperature is low and the thermal activation barrier prevents transformation within the time scale of the shock wave experiment. Finally, there would exist a small intermediate region where the temperature is sufficient to allow transformation to the high-density solid state within this brief time span. Quenching of the phases during rapid unloading would account for amorphous material and traces of the high-density phases observed [*De Carli and Milton*, 1965].

This work suggests that caution should be exercised when shock wave data are used to deduce high-pressure equilibrium thermodynamic properties of rocks and minerals. The apparent problem is thermal nonequilibrium, which is due to low thermal conductivity, and a heterogeneous deposition of thermal energy during the yielding process. A possible solution may be to study samples prepared from a fine powder, which would provide for a more homogeneous generation of thermal energy during the shock process.

REFERENCES

Ahrens, T. J., and H. Liu, A shock-induced phase change in orthoclase, *J. Geophys. Res.*, *78*, 1274–1278, 1973.

Ahrens, T. J., D. L. Anderson, and A. E. Ringwood, Equation of state and crystal structures of high-pressure phases of shocked silicates and oxides, *Rev. Geophys. Space Phys.*, *7*, 667–707, 1969.

Anderson, O. L., The use of ultrasonic measurements under modest pressure to estimate compression at high pressures, *J. Phys. Chem. Solids*, *27*, 547, 1966.

Bunch, T. E., Some characteristics of selected minerals from craters, in *Shock Metamorphism of Natural Materials*, edited by B. French and N. Short, Mono, Baltimore, Md., 1968.

Carter, N., Dynamic deformation of quartz, in *Shock Metamorphism of Natural Materials*, edited by B. French and N. Short, Mono, Baltimore, Md., 1968.

Chao, E. C. T., Pressure and temperature histories of impact metamorphosed rocks—Based on petrographic observations, in *Shock Metamorphism of Natural Materials*, edited by B. French and N. Short, p. 149, Mono, Baltimore, Md., 1968.

Clark, S. P., Jr. (Ed.), *Handbook of Physical Constants*, The Geological Society of America, 1966.

De Carli, P. S., Observations of the effects of explosive shock on crystalline solids, in *Shock Metamorphism of Natural Materials*, edited by B. M. French and N. M. Short, p. 129, Mono, Baltimore, Md., 1968.

De Carli, P. S., and D. J. Milton, Stishovite: Synthesis by shock wave, *Science*, *147*, 144–145, 1965.

Fowles, R., Dynamic compression of quartz, *J. Geophys. Res.*, *72*, 5729–5742, 1967.

Giardini, A. A., A review of rock behavior to shear over approximately 100 kbar of confining pressure and a speculative model for seismic disturbances, *J. Geophys. Res., 79*, 1183–1195, 1974.
Grady, D. E., W. J. Murri, and G. R. Fowles, Quartz to stishovite: Wave propagation in the mixed phase region, *J. Geophys. Res., 79*, 332–338, 1974.
Graham, R. A., and W. P. Brooks, Shock-wave compression of sapphire from 15 to 400 kbar: The effects of large anisotropic compressions, *J. Phys. Chem. Solids, 32*, 2311–2330, 1971.
Graham, R. A., and G. E. Ingram, Piezoelectric current from *x*-cut quartz loaded from 25 to 75 kbar, *Bull. Amer. Phys. Soc., 14*, 1163, 1969.
Gruntfest, I. J., Thermal feedback in liquid flow, plane shear at constant stress, *Trans. Soc. Rheol., 7*, 195–207, 1963.
Hughes, D. S., and R. G. McQueen, Density of basic rocks at very high pressures, *Eos Trans. AGU, 39*, 959–965, 1958.
Logan, J. M., and J. A. Rigert, Partial melting of sandstone during frictional sliding in triaxial experiments (abstract), *Eos Trans. AGU, 54*, 465, 1973.
Lyle, J. W., R. L. Shriver, and A. R. McMillan, Dynamic piezoresistive coefficient of manganin to 392 kbar, *J. Appl. Phys., 46*, 4663–4664, 1969.
Nitsan, U., Viscous heat production in a slab, *J. Geophys. Res., 78*, 1395–1397, 1973.
Press, F., Density distribution in the earth, *Science, 160*, 1218–1221, 1968.
Stöffler, D., Coesite and stishovite in shocked crystalline rocks, *J. Geophys. Res., 76*, 5474–5488, 1971.
Stöffler, D., Deformation and transformation of rock-forming minerals by natural and experimental shock processes, *Fortschr. Mineral., 49*, 50–113, 1972.
Von Engelhardt, W., and D. Stöffler, Stages of shock metamorphism in crystalline rocks of the Ries basin, Germany, in *Shock Metamorphism of Natural Materials*, edited by B. French and N. Short, Mono, Baltimore, Md., 1968.
Wackerle, J., Shock-wave compression of quartz, *J. Appl. Phys., 33*, 922–937, 1962.
Walsh, J. B., Attenuation in partially melted material, *J. Geophys. Res., 73*, 2209, 1968.
Walsh, J. B., New analysis of attenuation in partially melted rock, *J. Geophys. Res., 74*, 4333, 1969.
Zener, C., and J. H. Hollomon, Effect of strain rate upon plastic flow of steel, *J. Appl. Phys., 15*, 22–32, 1944.

(Received June 29, 1974;
revised August 7, 1975;
accepted August 29, 1975.