

A Shock-Induced Phase Change in Orthoclase¹

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New shock compression data to 340 kb for single-crystal orthoclase (along (001)) demonstrate the onset of a shock-induced phase change at ~ 115 kb. Along the Hugoniot a mixed-phase region extends to ~ 300 kb, above which the data are believed to correspond to the properties of a high-pressure phase having the hollandite structure (zero pressure density of 3.84 g/cm^3) reported by Ringwood et al. If the hollandite value for the zero pressure density is used, the zero pressure bulk modulus of this phase is approximately 2.8 ± 0.2 Mb.

The very high pressure equation of state of orthoclase is of importance both in describing the effects of intense shock waves on potassium-feldspar-bearing rocks on the earth and the moon [Hubbard et al., 1971; Drake et al., 1970; Chao, 1967; Kleeman, 1971; von Engelhardt and Stoffler, 1968] and in studying the earth's mantle. The latter is important because the orthoclase structure provides a model of the response of feldspar-bearing rocks to the high pressures of the earth's interior. Previously reported Hugoniot data for microcline [Ahrens et al., 1969a] demonstrated that this mineral, like plagioclase [McQueen et al., 1967], begins to transform to a new phase or phases at about 120 kb (along the Hugoniot). This phase change appears to go to completion for shock states above ~ 300 kb. Above this level the limited Hugoniot data for microcline suggested that the properties of a denser high-pressure phase were being sampled. The zero pressure density for the high-pressure phase inferred by Ahrens et al. [1969b] and Davies and Anderson [1971] of $\sim 3.5 \text{ g/cm}^3$ compares unfavorably and inconclusively with densities of 3.2 and 3.84 g/cm^3 expected for the possible high-pressure phases in the structures jadeite plus stishovite and hollandite. Because previous static high-pressure quenching experiments on both silicate and germanate (analog) potassium feldspar

yielded only the hollandite-structured phase [Ringwood et al., 1967a, b; Kume et al., 1966] and because the inferred high-pressure phase assemblage density for granite [Ahrens et al., 1969b; Davies and Anderson, 1971] is consistent with the formation of the hollandite phase (in KAlSi_3O_8), we assume that this phase is produced in our experiments.

To further study the equation of state of potassium feldspar, a series of Hugoniot experiments were carried out on a suite of single crystals of orthoclase from Madagascar (Table 1). These single crystals possess perfect cleavage along (001) and distinct cleavage along (010) [Winchell and Winchell, 1951]. The samples were prepared by mounting and polishing the crystals in a parallel lapping jig on the (001) cleavage planes. Thin sections of the same orientation were also prepared for microscope observation. Under conoscopic observation all thin sections showed slightly off-centered optical normal figures, which confirm that the sample faces are parallel to the (001) cleavage [Deer et al., 1966]. The experimental procedure used in impacting these samples is described by Ahrens et al. [1971] and Ahrens and Gaffney [1971].

In most of the experiments at least two shock arrivals were recorded at the specimen free surface when shock waves were driven into the sample assemblies. For final shock states below about 300 kb these initial shock arrivals, which we believe represent finite-amplitude elastic shocks, have an average velocity of 7.39 ± 0.06 km/sec (weighted mean and standard deviation). To substantiate this value, compressional

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TABLE 1. Orthoclase Formula Proportions

Element	Formula Proportion*
Na	0.022
Mg	0.0003
Al	0.192
Si	0.603
K	0.180
Ca	0.00015
Fe	0.0030
Total	1.003

Microprobe analysis by A. Chodos (California Institute of Technology). Orthoclase samples from Strongay, Madagascar.

*Based on eight oxygen atoms.

elastic velocity along the (001) direction was measured by ultrasonic interferometry [Spetzler, 1970] to be 7.53 ± 0.02 km/sec. Ryzhova and Alexandrov [1965] measured the ultrasonic velocities of a series of potassium-sodium feldspars. Their reported value of compressional velocity along the (001) direction of a feldspar containing 78.5% orthoclase is 7.01 km/sec. Because the other components of the feldspar, anorthite and albite, have lower velocities than orthoclase, this value agrees in trend with our measurement. The free-surface velocities resulting from the free-surface reflection of this elastic shock were used to determine the amplitude (Hugoniot elastic limit, HEL) of this wave (via the free-surface approximation [Walsh and Christian, 1955]). Observed values lie between 41 and 91 kb (Table 2). The data (with the exception of shots 179 and 164) suggest that the HEL value is related to the final shock pressure, not unlike the situation in single-crystal and polycrystalline quartz [Wackerle, 1962; Ahrens and Duvall, 1966]. For three shots with final shock pressures below 200 kb the average HEL value is 43.3 ± 1.0 kb. For shots with final pressures above this level a similar average yields 72.3 ± 7.7 kb (weighted mean and standard deviation). The present HEL values bracket the earlier data for microcline.

Above the HEL the Hugoniot states (Table 2 and Figure 1), representing final shock states, were calculated by the impedance match method [Rice et al., 1958]. An intermediate (6.4–6.8 km/sec) velocity wave was observed for shots with final states above 300 kb. We infer that

this shock front was due to the phase transition and corresponded to a shock state of ~ 300 kb and a density of ~ 4.0 g/cm³. The interaction of the elastic shock reflected at the free surface with the following second plastic shock was neglected. Figure 1 demonstrates that above ~ 115 kb the Hugoniot states achieved all lie at a greater density than the Hugoniot state inferred from the extrapolation of Bridgman's [1948] isotherm (to 39 kb) for orthoclase. These isothermal data were fit to a Birch-Murnaghan equation and yielded the zero pressure isothermal bulk modulus $K_{0i} = 539.5$ kb and $(dK_{0i}/dP)_T = 4.4$. Similarly, the Voigt-Reuss-Hill average of elastic constants for a series of potassium-rich feldspars reported by Alexandrov and Ryzhova [1962], Ryzhova [1964], and Ryzhova and Alexandrov [1965] gives a similar value for the (isentropic) bulk modulus K_{0s} , which varies from 470 to 574 kb. Isotherms based on the extreme values of the ultrasonic data are also shown in Figure 1. On the basis

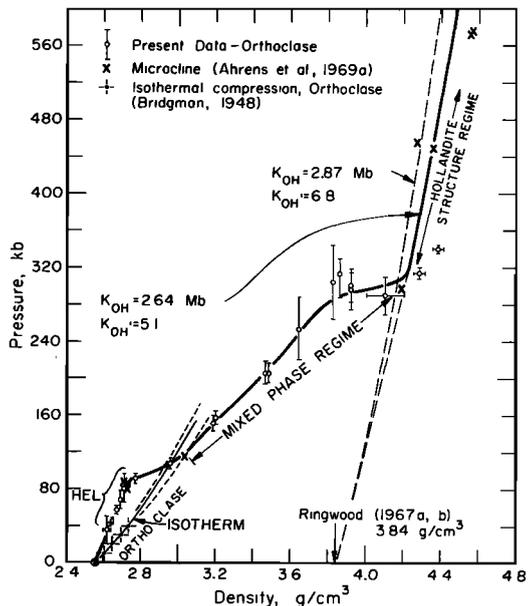


Fig. 1. Hugoniot data for single-crystal orthoclase. Shock data for microcline and the orthoclase isothermal compression data of Bridgman [1948] are also shown. Dashed curve above and below Bridgman's data represents the spread in bulk moduli observed ultrasonically for orthoclase-rich specimens by Alexandrov and Ryzhova [1962], Ryzhova [1964], and Ryzhova and Alexandrov [1965].

TABLE 2. Hugoniot Data for Single-Crystal Orthoclase Shocked along (001)

Shot No.	Projectile Velocity, km/sec	Initial Density, g/cm ³	Initial Thickness, mm	First Wave				Final Wave			
				Shock Velocity, km/sec	Particle Velocity, km/sec	Shock Pressure, kb	Shock Density, g/cm ³	Shock Velocity, km/sec	Particle Velocity, km/sec	Shock Pressure, kb	Shock Density, g/cm ³
175	0.868 ±0.023	2.557 ±0.002	3.588 ±0.003	7.25 ±0.04	0.242 ±0.006	45 ±2	2.645 ±0.001	4.99 ±0.02	0.735 ±0.021	107 ±6	2.95 0.05
178	1.25*	2.556 ±0.002	5.038 ±0.003	7.64 ±0.05	0.228 ±0.018	44 ±3	2.635 ±0.005	5.08 ±0.04	1.064 ±0.002	151 ±8	3.18 ±0.05
176	1.29 ±0.02	2.557 ±0.002	4.407 ±0.003	7.63 ±0.02	0.212 ±0.009	41 ±2	2.630 ±0.002	5.20 ±0.02	1.09 ±0.02	157 ±7	3.19 ±0.03
179	1.68 ±0.03	2.558 ±0.002	5.239 ±0.003	6.82 ±0.02	0.523 ±0.023	91 ±5	2.77 ±0.02	5.05 ±0.07	1.44 ±0.04	206 ±12	3.47 ±0.07
180	1.69 ±0.02	2.558 ±0.002	4.229 ±0.003	7.18 ±0.04	0.312 ±0.020	57 ±4	2.674 ±0.011	5.20 ±0.03	1.44 ±0.04	205 ±11	3.48 ±0.07
164	2.01 ±0.02	2.555 ±0.002	4.369 ±0.003	7.28 ±0.04	0.188 ±0.08	35 ±15	2.62 ±0.03	5.65 ±0.04	1.72 ±0.03	254 ±34	3.64 ±0.11
216	2.32 ±0.02	2.559 ±0.002	3.429 ±0.003	7.34 ±0.09	0.427 ±0.075	80 ±16	2.717 ±0.032	5.78 ±0.07	1.97 ±0.03	304 ±40	3.82 ±0.16
264	2.33 ±0.01	2.56† ±0.002	4.870 ±0.003	7.37 ±0.05	0.365 ±0.05	69 ±10	2.693 ±0.009	5.56 ±0.04	1.99 ±0.02	296 ±23	3.92 ±0.10
196	2.35 ±0.01	2.556 ±0.002	5.566 ±0.003	7.41 ±0.07	0.434 ±0.016	82 ±4	2.715 ±0.006	5.55 ±0.04	2.00 ±0.02	300 ±17	3.92 ±0.14
199	2.59 ±0.07	2.557 ±0.002	4.173 ±0.003	§	§	§	§	6.02 ±0.12	2.03 ±0.07	313 ±16	3.86 ±0.10
265	2.40 ±0.1	2.56† ±0.003	4.566 ±0.003	§	§	§	§	5.49 ±0.05	2.06 ±0.17	290 ±20	4.10 ±0.10
215	2.59 ±0.04	2.556 ±0.002	3.543 ±0.003	§	§	§	§	5.53 ±0.04	2.22 ±0.03	314 ±6	4.28 ±0.03
214	2.74*	2.559 ±0.002	3.353 ±0.003	7.11 ±0.06	§	§	§	5.64 ±0.04	2.35 ±0.04	340 ±3	4.39 ±0.03

*Single measurement.

†Assumed value.

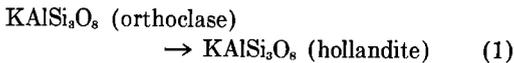
§Not measured.

TABLE 3. Calculated Shock Temperatures in High-Pressure Regime

Density, g/cm ³	Hugoniot Pressure,* kb	Isentropic Pressure,† kb	Hugoniot Temperature, °K	Isentropic Temperature,† °K
4.1	233	226	465	318
4.2	346	310	1138	325
4.3	472	401	1912	332
4.4	612	502	2795	338

*Birch-Murnaghan fit: $K_{0h} = 2869$ kb and $K_{0h}' = 6.8$.
 †Centered at zero pressure and 298°K.

of the intersection of the present orthoclase Hugoniot and the isothermal data at 115 ± 10 kb we infer that this pressure represents a minimum value for the onset for shock-induced phase change in orthoclase to the hollandite structure. This conclusion is based on the observations that the inferred pressure value for the transition agrees closely with the 120-kb value (at 900°C) obtained by Ringwood *et al.* [1967a, b] for the formation of the hollandite-structured phase from sanidine and that the present Hugoniot data, when they are taken with the earlier microcline results, imply a marked increase in the bulk modulus along the Hugoniot at densities greater than ~ 4.1 g/cm³ (~ 300 kb). The steep Hugoniot above 300 kb would presumably correspond to the properties of the hollandite structure. A minimum transition energy of 1.5×10^{10} ergs/g for



is implied by the observed transition pressure. In analogy to the case of shock compression of quartz and fused quartz [Wackerle, 1962; McQueen *et al.*, 1963] we infer that the Hugoniot between ~ 115 and ~ 300 kb represents a mixed-phase regime. Whether some phase other than the hollandite structure forms in this interval is uncertain; however, no other intermediate high-pressure phase or phase assemblage is currently known.

When the data of Ahrens *et al.* [1969a] are also used, a Birch-Murnaghan equation curve was fit through the eight raw Hugoniot data points, corresponding to the presumed high-pressure

phase, by using a zero pressure density of 3.84 g/cm³ [Ringwood *et al.*, 1967a, b]. This procedure gives the parameters $K_{0h} = 2869$ kb and $K_{0h}' = 6.8$. Excluding the lowest pressure, more uncertain datum at 290 kb, yields $K_{0h} = 2637$ kb and $K_{0h}' = 5.1$, which are our preferred values. Excluding the two highest pressure points from the fitting procedure yields $K_{0h} = 2959$ kb and $K_{0h}' = 6.6$. The sensitivity of these parameters to changes in the data indicates an uncertainty in the bulk modulus of the high-pressure phase of $\pm 8\%$ and of some 15% in the value of K_{0h}' . As a result both of using the new data and of making the outright assumption that the high-pressure phase has the hollandite structure, the bulk modulus obtained in this study is greater than that given by Ahrens *et al.* [1969b] by nearly a factor of 2.

For application to the study of naturally shocked potassium feldspar in rocks subjected to hypervelocity input, it is useful to calculate a series of shock temperatures (Table 3). These are calculated by the method of Ahrens *et al.* [1969b]. A constant value of the product of the Gruneisen parameter and a density of 3.84 and a transition energy of 1.5×10^{10} ergs/g was assumed. Although the equations of state of parameters of the high-pressure phase obtained in the present work are very different from those given by Ahrens *et al.* [1969a], the calculated shock temperatures, which depend critically only on the absolute increase in density upon compression, are rather similar to the earlier results.

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REFERENCES

- Ahrens, T. J., and G. E. Duvall, Stress relaxation behind elastic shock waves in rock, *J. Geophys. Res.*, **71**, 4319-4360, 1966.
- Ahrens, T. J., and E. S. Gaffney, Dynamic compression of enstatite, *J. Geophys. Res.*, **76**, 5504-5513, 1971.
- Ahrens, T. J., C. F. Petersen, and J. F. Rosenberg, Shock compression of feldspars, *J. Geophys. Res.*, **74**, 2727-2746, 1969a.
- Ahrens, T. J., D. L. Anderson, and A. E. Ringwood, The equation of state and crystal structures of high-pressure phases of silicates and oxides, *Rev. Geophys. Space Phys.*, **7**, 667-707, 1969b.
- Ahrens, T. J., J. H. Lower, and P. L. Lagus, Equation of state of forsterite, *J. Geophys. Res.*, **76**, 518-528, 1971.
- Alexandrov, K. S., and T. V. Ryzhova, Elastic properties of rock-forming minerals, 3, Feldspars, *Bull. Acad. Sci. USSR Geophys. Ser.*, **2**, 129-131, 1962.
- Bridgman, P. W., Rough compressions of 177 substances to 40,000 kg/cm², *Proc. Amer. Acad. Arts Sci.*, **76**, 71-87, 1948.
- Chao, E. C. T., Shock effects in certain rock-forming minerals, *Science*, **156**, 192-202, 1967.
- Davies, G. F., and D. L. Anderson, Revised shock-wave equations of state for high-pressure phases of rocks and minerals, *J. Geophys. Res.*, **76**, 2617-2627, 1971.
- Deer, W. A., R. A. Howie, and J. Zussman, *An Introduction to the Rock-Forming Minerals*, p. 306, Longmans, Green, and Co. Ltd., London, 1966.
- Drake, M. J., I. S. McCallum, G. A. McKay, and D. F. Weill, Mineralogy and petrology of Apollo 12 sample no. 12013: A progress report, *Earth Planet. Sci. Lett.*, **9**, 103-123, 1970.
- Hubbard, N. J., C. Meyer, Jr., P. W. Gast, and H. Wiesmann, The composition and derivation of Apollo 12 soils, *Earth Planet. Sci. Lett.*, **10**, 341-350, 1971.
- Kleeman, J. D., Formation of diaplectic glass by experimental shock loading of orthoclase, *J. Geophys. Res.*, **76**, 5499-5503, 1971.
- Kume, S., T. Matsumoto, and M. Koizumi, Dense form of germanate orthoclase (KAlGe₃O₈), *J. Geophys. Res.*, **71**, 4999-5000, 1966.
- McQueen, R. G., J. N. Fritz, and S. P. March, On the equation of state of stishovite, *J. Geophys. Res.*, **68**, 2319, 1963.
- McQueen, R. G., S. P. Marsh, and J. N. Fritz, Hugoniot equation of state of twelve rocks, *J. Geophys. Res.*, **72**, 4999-5036, 1967.
- Rice, M. H., R. G. McQueen, and J. M. Walsh, Compression of solids by strong shock waves, *Solid State Phys.*, **6**, 1-63, 1958.
- Ringwood, A. E., A. F. Reid, and A. D. Wadsley, High-pressure KAlSi₃O₈, an aluminosilicate with sixfold coordination, *Acta Crystallogr.*, **23**, 1093-1095, 1967a.
- Ringwood, A. E., A. F. Reid, and A. D. Wadsley, High pressure transformation of alkali aluminosilicates and aluminogermanates, *Earth Planet. Sci. Lett.*, **3**, 38-40, 1967b.
- Ryzhova, T. V., Elastic properties of plagioclase, *Bull. Acad. Sci. USSR Geophys. Ser.*, **7**, 633-635, 1964.
- Ryzhova, T. V., and K. S. Alexandrov, The elastic properties of potassium-sodium feldspars, *Izv. Acad. Sci. USSR Phys. Solid Earth*, **1**, 53-56, 1965.
- Spetzler, H. A., Equation of state of polycrystalline and single-crystal MgO to 8 kilobars and 800°K, *J. Geophys. Res.*, **75**, 2073-2087, 1970.
- von Engelhardt, W., and D. Stoffer, Stages of shock metamorphism in rocks of the Ries basin, in *Shock Metamorphism of Natural Materials*, edited by B. M. French and N. M. Short, pp. 159-168, Mono Press, Baltimore, Md., 1968.
- Wackerle, J., Shock-wave compression of quartz, *J. Appl. Phys.*, **33**, 922-937, 1962.
- Walsh, J. M., and R. H. Christian, Equations of state of metals from shock wave measurements, *Phys. Rev.*, **97**, 1544, 1955.
- Winchell, A. N., and H. Winchell, *Elements of Optical Mineralogy*, p. 303, John Wiley, New York, 1951.

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