Shock Effects in Certain Rock-Forming Minerals

Hypervelocity impacts by meteorites are reflected by the effects of shock and temperature on minerals.

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Impact metamorphism, a term recently introduced in geology, describes the changes in minerals and rocks resulting from the hypervelocity impact of a body such as a meteorite. A meteorite-cratering event is a large natural experiment, the effects of which closely resemble those of the detonation of a large nuclear device at or near Earth's surface. Many typical crater structures associated with remains of iron meteorites and identified as the results of hypervelocity meteoritic impact are being studied so that criteria can be established for identifying circular structures suspected to be of meteoritic rather than volcanic or tectonic origin. Many of the effects of extremely high transient pressures and temperatures, observed in minerals and rocks found at meteoritic craters, have never been observed in normal geologic environments and occurrences; they are recognized as unique (*1*). The surface of Moon is covered with craters whose origin has caused speculation for years. Possible detection of evidence of shock in samples brought from Moon would be of prime importance because it would provide definitive criteria for identifying the origin of the craters and the mechanism of cratering.

Experiments with cratering and shock waves and study of equations-of-state of various natural materials have been pressed for decades by investigators of high-energy chemical explosives and weapons and of nuclear devices. Static laboratory experiments with pressures exceeding 100 kilobars have been successful only within the last decade; they deal with problems of the structure and composition of Earth's interior (*2*). It is primarily in the study of shock-wave compression related to nuclear devices that pressures exceeding 100 kilobars—reaching even to several megabars—are attainable. Estimates of pressures and temperatures, and data on the shock equation-of-state, that may be applicable to impact-metamorphosed rocks are mostly derived from these sources.

The magnitude of a hypervelocity impact and cratering event caused by a body such as a meteorite is reflected by the transient peak pressure, peak temperature, residual temperature, and cooling history during and after the passage of the shock wave. The peak pressure may range from several hundred kilobars to many megabars; and the peak and residual temperatures may greatly exceed 1500°C; transient pressure probably rises and falls within a span of from several microseconds to seconds.

Besides introducing readers to this field of investigation, I shall describe, with examples, available information (from optical and x-ray diffraction observations) on shock effects in quartz, plagioclase, biotite, amphibole, and some accessory rock-forming minerals. These observations provide evidence for assignment of a sequence to the degree of shock metamorphism. With the help of experimental shock-wave data, some numerical limits can be placed on peak pressures and temperatures and on residual temperatures with respect to the time of passage of the shock wave; such estimates can then be used to place limits on the mass and velocity of the impacting object.

Meteorite Craters

Lists of craters certainly or possibly of meteoritic origin have been published (*3*). The most-widely known, best-preserved, and most-studied meteoritic crater in the United States is Meteor Crater, Arizona (*4*). The most-discussed recent crater in Europe is Ries Crater in Bavaria (*5*). Eleven probable meteorite craters at various stages of study (principally by the Canadian Dominion Observatory) are in Canada (*6*). Information on circular structures, including meteorite craters, in Africa has been compiled (*7*); there are several in Australia, South America, and Saudi Arabia.

Meteorite craters, with associated fragments of iron meteorites, occurring in nonvolcanic terrain include Meteor Crater (Arizona), Odessa Crater (Texas), Wabar Crater (Al Hadidah, Saudi Arabia), Henbury Craters and Wolf Creek Crater (Australia), and Campo del Cielo Craters (Argentina), which are accepted by most investigators. Those of most interest are craters large enough (100 to 1000 meters or more in diameter) to show the effects of high pressures and temperatures on the underlying rocks or the ejecta; the craters of Campo del Cielo are too small for study of impact metamorphism.

Craters such as Ries and the Lake Bosumtwi Crater of Ghana, Africa, of diameter greater than 5 kilometers but not associated with large fragments of iron meteorites, are identified as meteoritic by evidence of impact metamorphism. The circular Manicouagan structure of Canada and the Vredefort structure of South Africa, each more than 50 kilometers in diameter, are comparable in size to many lunar craters; their ejecta and fallout materials should show widespread evidence of shock metamorphism if the crater originated from impact.

Shock Effects in Rock-Forming Minerals

Several kinds of established evidence diagnostic of meteorite impact have been summarized (*1*): (i) evidence of deformation uniquely produced by shock under very high strain rates and pressures; (ii) partial and complete vitrification without melting; (iii) evidence of selective phase transition; occurrence of

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high-pressure polymorphs; (iv) occurrence of nickel-iron spherules; and (v) breakdown or melting of refractory, accessory, rock-forming minerals. These features are common in samples showing various degrees of metamorphism by shock or impact. Description and interpretation of various shock effects exhibited by selected rock-forming minerals, with increasing transient pressures and transient and residual temperatures, are based on mineralogic studies and petrographic observations. I have studied ejecta materials from the following craters: Meteor, Henbury, Lake Bosumtwi, Wabar, Aouelloul (Mauritania), and Ries.

Quartz and Plagioclase

Low to moderate shock effects in quartz. The first optically detectable diagnostic evidence of deformation by strong shock, with very high strain rates such as rates generated by the detonation of high-energy explosives or nuclear devices or by hypervelocity meteoritic impact, is occurrence of multiple sets of very closely spaced planar structures in quartz and feldspars. Such microstructures are observable with even a hand lens; they occur very commonly in ejecta of meteorite craters and have been studied (*8, 9*).

Carter (*9*) described in detail the distinctions of cleavages, fractures, and deformation lamellae, and the significance of their orientation in quartz that is deformed at ordinary geologic strain rates, as well as in quartz that is deformed by shock under extremely high strain rates. He concluded that the lamellae parallel to the basal plane (0001) in quartz grains, having nearly random spatial orientation, from several known or supposed meteoritic structures, must have been produced by a shock mechanism. He reasoned from observation of static tests that a stress difference in quartz, ranging between 35 and 60 kilobars (1500° to 700°C), would be required to produce the basal slips (the basal lamellae). Carter also pointed out the unique occurrence of planar features parallel to the form $\omega\{10\bar{1}3\}$, which were found in shocked specimens but have not been observed in static experiments with quartz; nor have they been described in quartz from other natural occurrences.

One must distinguish the various types of planar features: (i) fractures or cleavages resulting from yielding by fracturing when the elastic limit was exceeded; (ii) deformation lamellae, which are more clearly seen under phase contrast than under bright-field illumination and are asymmetric, being dark on one side of the discontinuity and light on the other, as a result of mechanisms such as translation gliding; and (iii) planar features that Carter thought might be shear fractures or tensile or extensile fractures, which show equally well under bright-field or phase-contrast illumination and lack the characteristics of deformation lamellae (*9*). Because of the close spacing and the inclination of more than one set of planes in the quartz of shocked rocks, it is extremely difficult to identify the planar structural elements with confidence, especially if partial phase transition has taken place. For the best results, each set of planar structures should be viewed under high magnification when it is vertically oriented under a petrographic microscope equipped with phase contrast, or under an interference microscope.

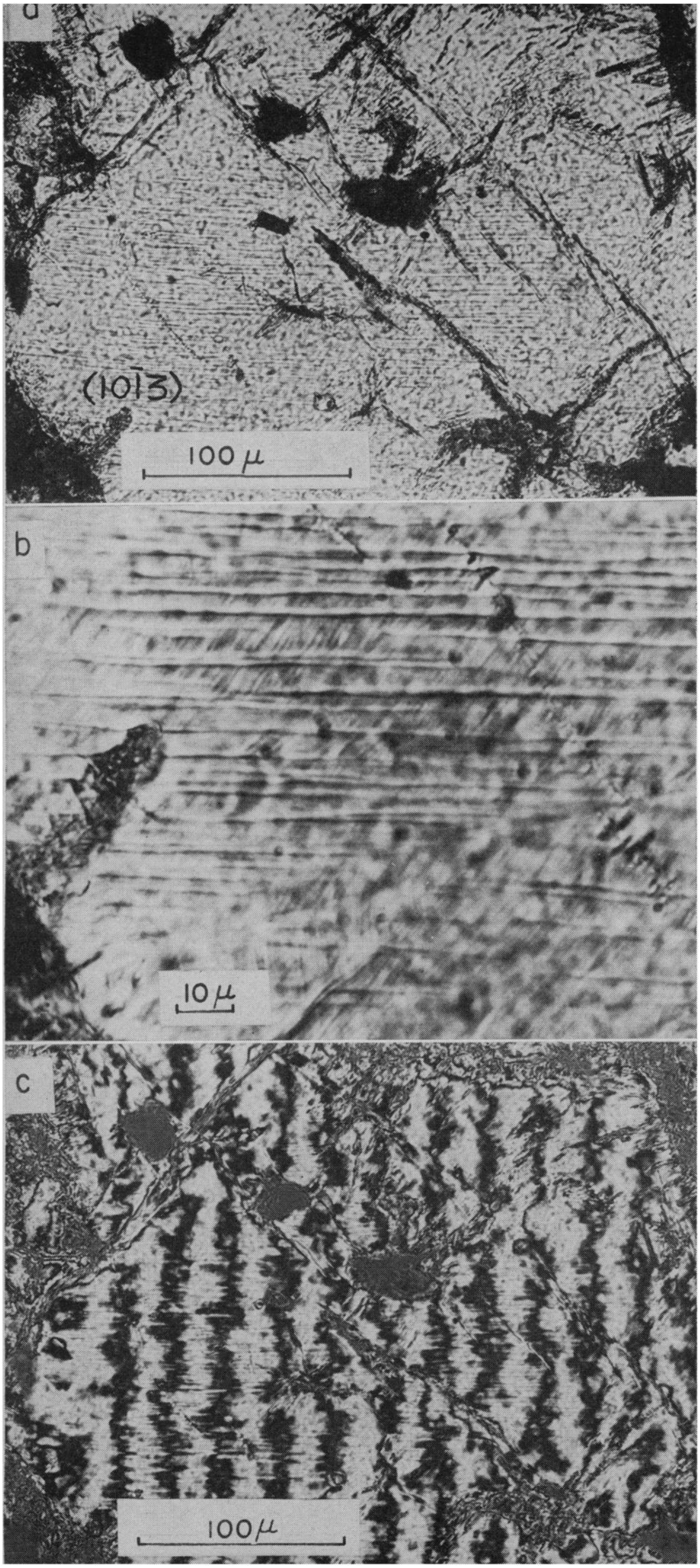
In Fig. 1a is a quartz grain, with well-developed sets of closely spaced planar structures, in a granite gneiss specimen from a fallout breccia known as suevite, from Ries Crater (*1*). The most pronounced set can be indexed as parallel to the form either $\{10\bar{1}3\}$ or $\{01\bar{1}3\}$; it consists of alternating bands of high and low mean index of refraction. The low-index bands are narrow, mostly between 1.2 and 1.8 microns in width; the high-index bands are broad, mostly between 4 and 11 microns. A broad band may contain several parallel lamellae, each about 0.7 micron wide. That these low-index bands are essentially isotropic under crossed nicols indicates that they consist essentially of siilca glass. Under higher magnification three sets of planar structures can be observed (Fig. 1b).

For confirmation that the rather pronounced low-index bands are predominantly silica glass and not openings between quartz, the same grain in the thin section was examined under a Leitz interference microscope. Figure 1c shows the bands parallel to $\{10\bar{1}3\}$, viewed under interference fringe contrast. The location of the low-index glassy quartz is clearly shown by the displacement normal to the interference fringe. Bands with higher index of refraction displace the dark fringe to the left. The difference in the index of refraction is proportional to the amount of the displacement. Observation under the interference microscope of glass along the planar features was reported by von Engelhardt during an April 1966 symposium on shock metamorphism, at Greenbelt, Maryland.

Detailed optical studies show that quartz with such planar features breaks with pronounced undulating surfaces and with easily recognized pearly luster and iridescence; such characteristic appearance probably reflects plastic deformation by some dislocation mechanism along the planar structures. Shocked quartz grains in a single specimen range widely in mean index of refraction, from the 1.548 of normal quartz to the 1.465 of nearly pure silica glass (*1*). Those having an index below 1.500 are translucent to transparent. X-ray studies of single grains show streaks instead of sharp spots on the powder pattern, with increased amount of vitreous or amorphous silica and reduced quartz intensity as the mean index of refraction of each grain decreases. Detailed studies of loose grains mounted in immersion oil also show that such planar features consist of bands of glassy quartz, with low index of refraction, alternating with untransformed or only partially transformed quartz. When the bands are slightly inclined, many of them appear to be discontinuous, separated by islands and irregular areas of less-transformed quartz within the plane of the band. Such studies show beyond doubt the transition of quartz to amorphous glass along the planar structures. These planar features are not fractures in the normal sense, with openings. Reduction of mean index of refraction has never been observed in tectonically deformed quartz.

Optical studies by Christie *et al.* (*10*) showed that the mechanism of formation of basal lamellae in quartz produced statically is due to translation-gliding parallel to the basal plane, along the *a*-axis. The lamellae areas that are sites of edge dislocations have been determined to be areas of localized strain, on the basis of the index and birefringence of the area adjacent to the lamellae being slightly lower on one side and higher on the other side than in the host quartz. In average lamellae, the measured birefringence is 0.0005 higher and lower than in the host (*10*); in the darkest lamellae, the difference is 0.002 (*10*).

The glassy bands in the shocked quartz shown in Fig. 1b in many ways resemble the basal deformation lamellae described by Christie *et al.* (*10*); they dif-



fer in that the glassy bands in shocked quartz are broader, and the difference in birefringence across them is greater. Furthermore, the mean index of refraction of a shocked quartz may be much lower than the mean index of refraction of quartz, than that of the statically deformed quartz of Christie *et al.*

Of interest in the study of shocked quartz is plastic deformation of solids due to the type of dislocations and kinking that produce notable changes in birefringence and concentrated areas of strain. On the basis of x-ray studies, the glassy bands or shock lamellae in quartz are localized zones in which long-range ordering in quartz has been reduced to short-range ordering. Unlike dislocation, such zones of vitrification or short-range ordering imply either that the network is severely distorted or that many bonds have been broken. The possibility that progression of vitrification sites may conceivably extend through the entire quartz crystal could account for the complete transition of alpha quartz to amorphous silica. While further proof is being sought, the similarity of glassy bands or shock lamellae in quartz to statically produced basal deformation lamellae produced under

Fig. 1. (a) A predominant set of closely spaced planar structures parallel to $(10\bar{1}3)$ in a single quartz grain of a granite gneiss fragment from suevite from Ries Crater (Bollstadt quarry). The planar structure, oriented perpendicular to the plane of the photograph, consists of bands of quartz having a higher index than the adjacent 1.2- to 1.8-micron bands or lamellae of partially to completely vitrified silica having a low index of refraction. Bright-field illumination. (b) Lower-left corner of same specimen [as in (a) and (c)] photographed under the universal stage, with the prominent E–W set parallel to $(10\bar{1}3)$ oriented perpendicular to the plane of the photograph. Shown is the detail of the narrow bands, having a low index of refraction, separated by the adjacent, broader, high-index bands and two additional sets of planar structures possibly parallel to the forms $\{11\bar{2}2\}$ (running NE) and $\{50\bar{3}2\}$ (running NNW). An inclined fracture cuts across the planar structures in the upper part. (c) Same field as (a) but viewed under an interference microscope with the interference fringes normal to the planar structure. The contrast of the indexes of refraction of the alternating bands is shown by the displacement of the dark fringes. Bands with a higher index displace the dark fringe to the left. The difference of the index is proportional to the amount of the displacement. Photographed in green monochromatic light; $\lambda = 546$ millimicrons.

great difference in stress, and the continuous range of lowering of mean index of refraction of shocked quartz suggest such a mechanism of transformation.

Moderate to strong shock effects in quartz: Effects in quartz of moderate to strong shock are represented by the complete solid-state transformation of crystalline alpha quartz to silica glass. Such glass, with an index of 1.46, which retains the morphology of the host quartz, is known as thetomorphic silica glass (*1*). Petrographic observations of moderately to strongly shock-metamorphosed specimens containing quartz confirm the lack of evidence of vesiculation or flowage due to melting (*1*); natural examples are the metamorphosed micaceous sandstone of the Henbury Craters and the biotite granites of Ries (*1*). Figure 2, a and b, shows a biotite quartz schist, also from Ries, in which all quartz grains have been transformed to silica glass while the biotites remained crystalline; without exception the silica glass retains the grain boundaries of the host quartz.

Strong shock effects in quartz: In Meteor and Ries craters the peak pressure generated by the impacts was great enough to form high-pressure polymorphs of quartz, such as coesite and stishovite. A summary of all natural occurrences of coesite and stishovite (*1*) shows them limited to rocks associated with meteorite craters. Without exception all coesite is embedded in silica glass (Fig. 3); none occurs outside former quartz grains, such as a reaction product of plagioclase under high pressure.

Intense shock effects in quartz: At still-higher shock pressures, the shock-induced residual temperature in the sample far exceeds the melting point of quartz. This fact is reflected by samples of fused rocks in which quartz occurs as stretched silica glass or lechatelierite filaments (Fig. 4). The low viscosity of the stretched lechatelierite indicates that the temperature exceeded 1700°C (*1*).

Shock-wave compression experiments on quartz: The first laboratory experiment illustrating the shock-transformation of quartz crystal to silica glass in the solid state was made by De Carli and Jamieson in 1959 (*11*). Specimens cut from natural quartz crystals to 25 by 25 by 6 millimeters (1 by 1 by ¼ inch) were struck by explosive-driven aluminum plates. Part of the quartz crystal was transformed to vitreous amorphous silica having a specific gravity of 2.22 and an index of refraction of 1.46; they calculated that the peak pressure slightly exceeded 600 kilobars; that the temperature of the quartz did not exceed 1400°K during shock or 1000°K immediately after. Wackerle (*12*) confirmed their results and concluded from temperature calculations that the fused quartz, recovered after shocking the crystalline quartz to 500 kilobars, probably did not result from melting of material at atmospheric pressure after the shot; he preferred the interpretation that the fused quartz resulted from direct transition from alpha quartz by shock. Apparently the spirals of (SiO_4) tetrahedra in quartz are thought to have been broken by the passage of the shock wave, with the result of random distribution or short-range ordering of silica tetrahedra.

The increase in amount of transformed glass may correlate with the increase in peak shock pressures. If the peak shock pressures are high enough to accomplish complete vitrification, the instantaneous process need not follow any of the observable steps that reflect crystallographic control. Under moderate to strong pressures, the shock effect in quartz, shown by the end product of quartz, is a silica glass having a normal index of refraction of 1.46—not a silica glass of higher index or density. If this were a compressed silica glass of high density, it would have had to revert quickly to the normal density of silica glass.

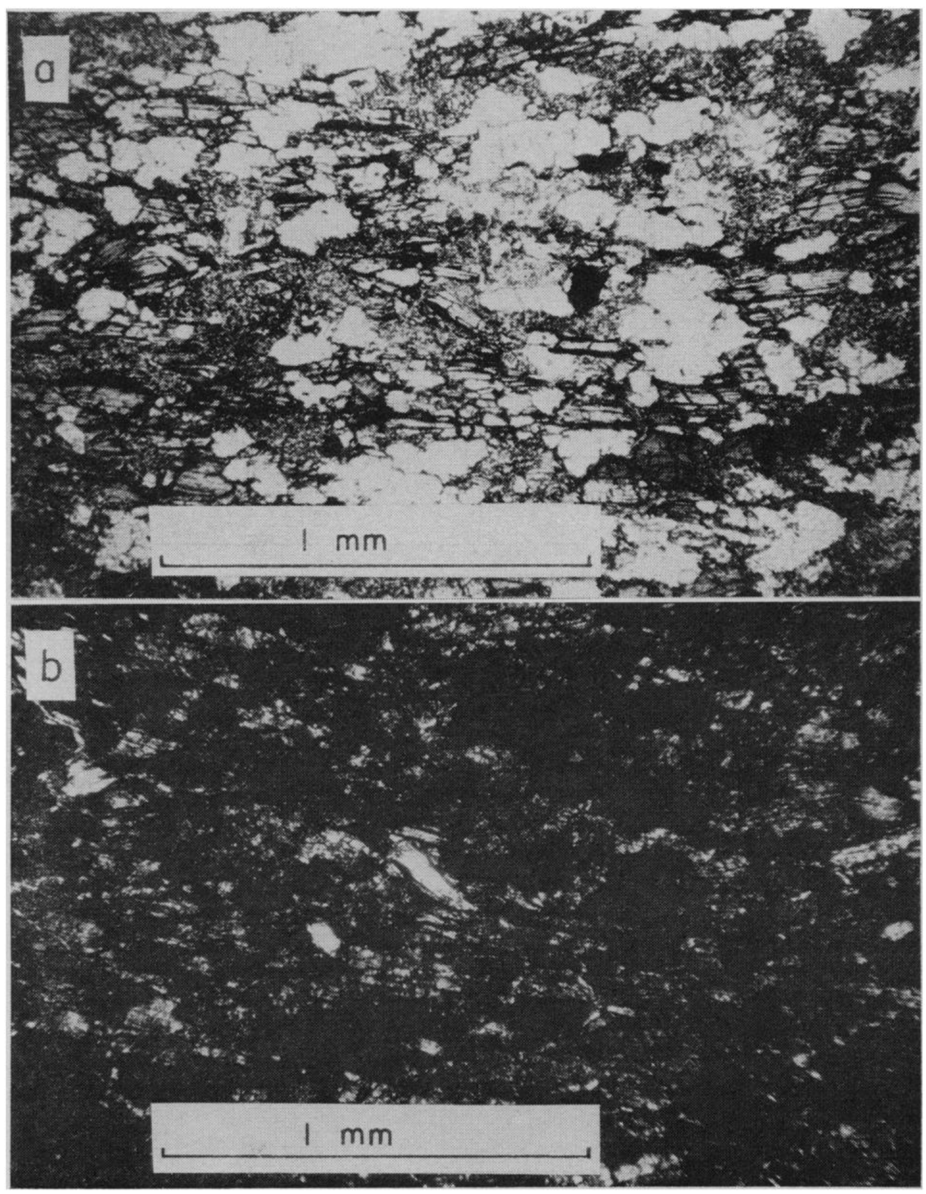


Fig. 2. (a) A shocked biotite-quartz schist. The quartz has been selectively transformed to thetomorphic silica glass (white areas); the biotite remains crystalline. Transmitted polarized light. (b) Same field as (a); crossed nicols. The silica glass is isotropic and biotite remains birefringent.

Unlike stishovite, coesite has not been recovered from shock-wave experiments in the laboratory (*13*). This fact is explained by the sluggish nature of the quartz-coesite transition, the pressure in these experiments not being sustained long enough, as in a natural meteorite-impact event (*12*).

Coesite is monoclinic, pseudohexagonal. The sluggishness of transformation from quartz to coesite under conditions of static high pressure seems to indicate that the transformation is reconstructive. Petrographic observations suggest that the formation of coesite follows the trend of vitrification, because in thin sections coesite coexists with silica glass in all observed instances. Under the high peak pressure, quartz possibly may be transformed to silica glass, but, locally, where the pressure was greater, stringers of coesite were formed. If the localized transient pressure is great enough the fourfold coordination of silica is transformed to a sixfold coordination leading to nucleation of the stishovite structure. A dense glass with silicon in sixfold coordination may exist, but no mineralogic evidence supports this view. It seems quite possible that stishovite may be derived from silica glass directly, so that the sequence is quartz–silica glass–stishovite. Stishovite occurs naturally in specimens containing a relatively high concentration of coesite; since it is submicroscopic, there is no evidence regarding its transformation from coesite or directly from the glass.

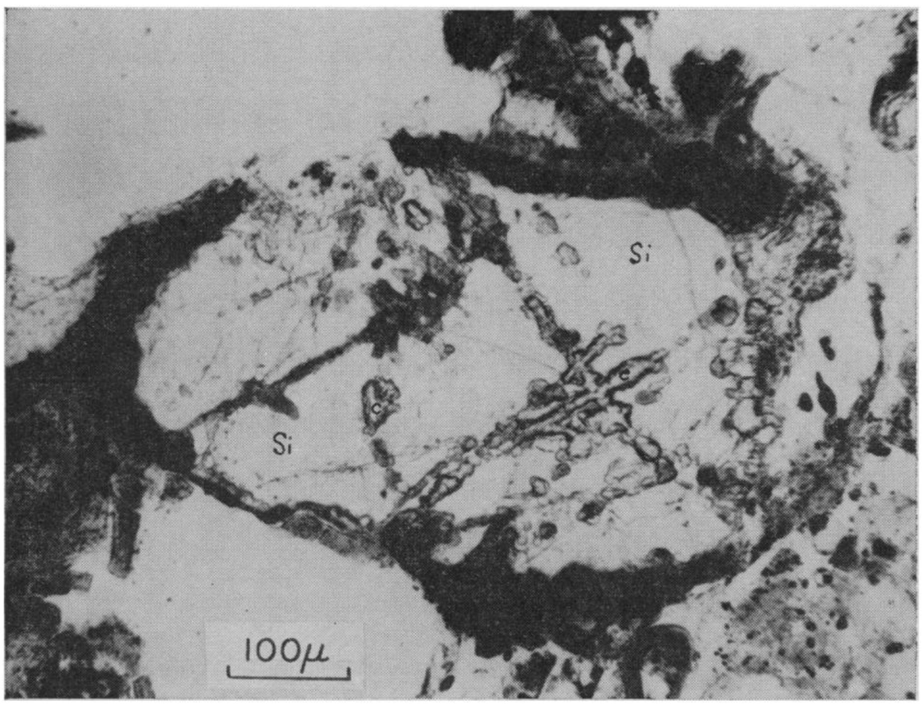


Fig. 3. A grain of silica glass (*Si*), with stringers of coesite (*c*), from a shocked, vesicular, biotite-granite gneiss. The silica glass is surrounded by a fused, opaque area of iron oxide.

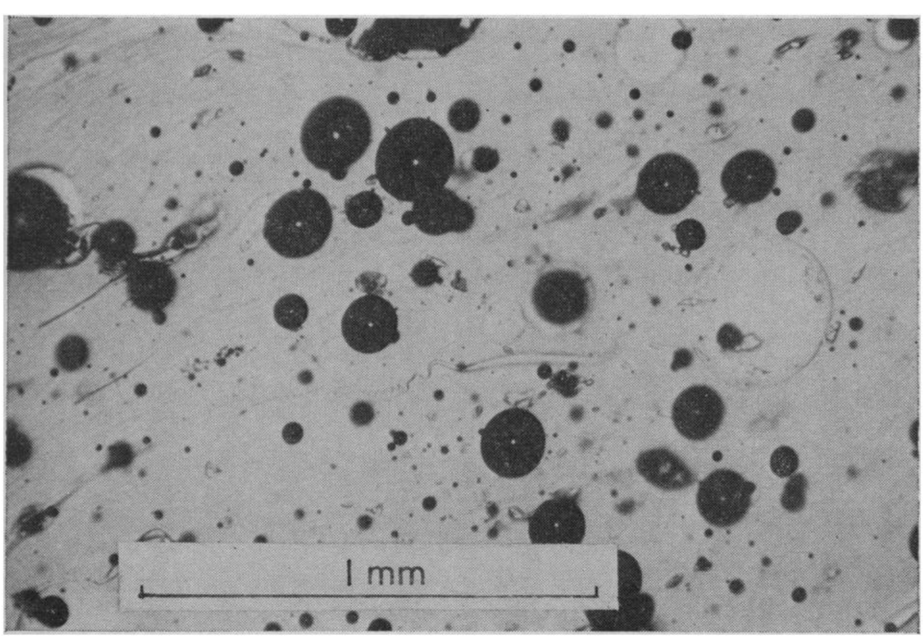


Fig. 4. A brown, transparent glass showing well developed schlieren and inclusions of serpent-shaped lechatelierite. There is no undissolved magnetite, and magnetic intensity of the glass is zero; black spherules are bubbles in the glass. Otting quarry, Ries Crater; plain polarized light.

Low to moderate shock effects in plagioclase: Deformation of plagioclase by low-to-moderate shock is closely related to complex partial vitrification of the host feldspar. Figure 5a shows a slightly fractured single plagioclase having seven sets of planar elements. Five of them appear in Fig. 5a; one is not shown because of its particular orientation. The seventh set can be seen only under oil immersion (Fig. 5b). The most prominent and broadest bands are 1 to 17 microns wide (trending NE in Fig. 5a). The widths of bands of the other five sets range from less than 0.5 to 3.5 microns. These seven sets of planar elements consists of alternating bands or platelets of plagioclase, with different mean indices of refraction. Under crossed nicols, the low-index bands have low birefringence or are locally totally isotropic (Fig. 5c). Platelets having reduced mean indices of refraction and birefringence are partially-to-totally transformed to plagioclase glass.

The orientation of these various sets of platelets is difficult to determine by use of the universal stage because of the narrowness of the platelets and the variable degree of reduced birefringence. In some instances the twin-composition plane in the part that is not effected by vitrification may be determined; traces of (001) cleavage can be observed. The most prominent set of bands or platelets follows the twin-composition plane (010) (*14*). The next prominent set, which runs from left to right in Fig. 5a, can be indexed as parallel to $(0\bar{2}1)$. The set that is parallel to (001) and nearly normal to (010) is clearly shown on the right side of Fig. 5a. A set near the lower-left corner of Fig. 5a probably can be indexed as parallel to (041). The three remaining sets have not been indexed. Platelets of the set parallel to $(0\bar{2}1)$ appear to be sharply cut off by bands of the set parallel to (010). However, platelets of the (001) and the (041) cut across the (010) bands without interruption. Because of the low mean index of refraction and low birefringence in one set of lamellae parallel to (010), the orientation of the platelets in them cannot be determined.

Conversion of the plagioclase crystal to glass occurs along these planar structures; three of them [(010), (001), and (021)] are also known twin-composition planes. The interaction of the plagioclase with the shock wave is thus closely controlled by the crystal structure; this finding is true from one individual plagioclase to the next, differently oriented, plagioclase in the same rock. Therefore the directions of these planar elements in a plagioclase cannot and do not reflect the direction of shock-wave compression.

Some planar elements cannot be indexed rationally. Figure 6 shows two sets of planar elements, predominantly fractures, that cut across the quartz and the embayed feldspar. The sets appear to be independent of the crystallographic orientation, yet these planar elements do not extend beyond the quartz grain.

Work on the plagioclase shown in Fig. 5a is being continued to determine its chemical composition, by the electron-microprobe method, and its structural state. The chemical composition cannot be determined from its optical properties because of the reduced mean index of refraction and birefringence. Electron microscopy and work on crys-

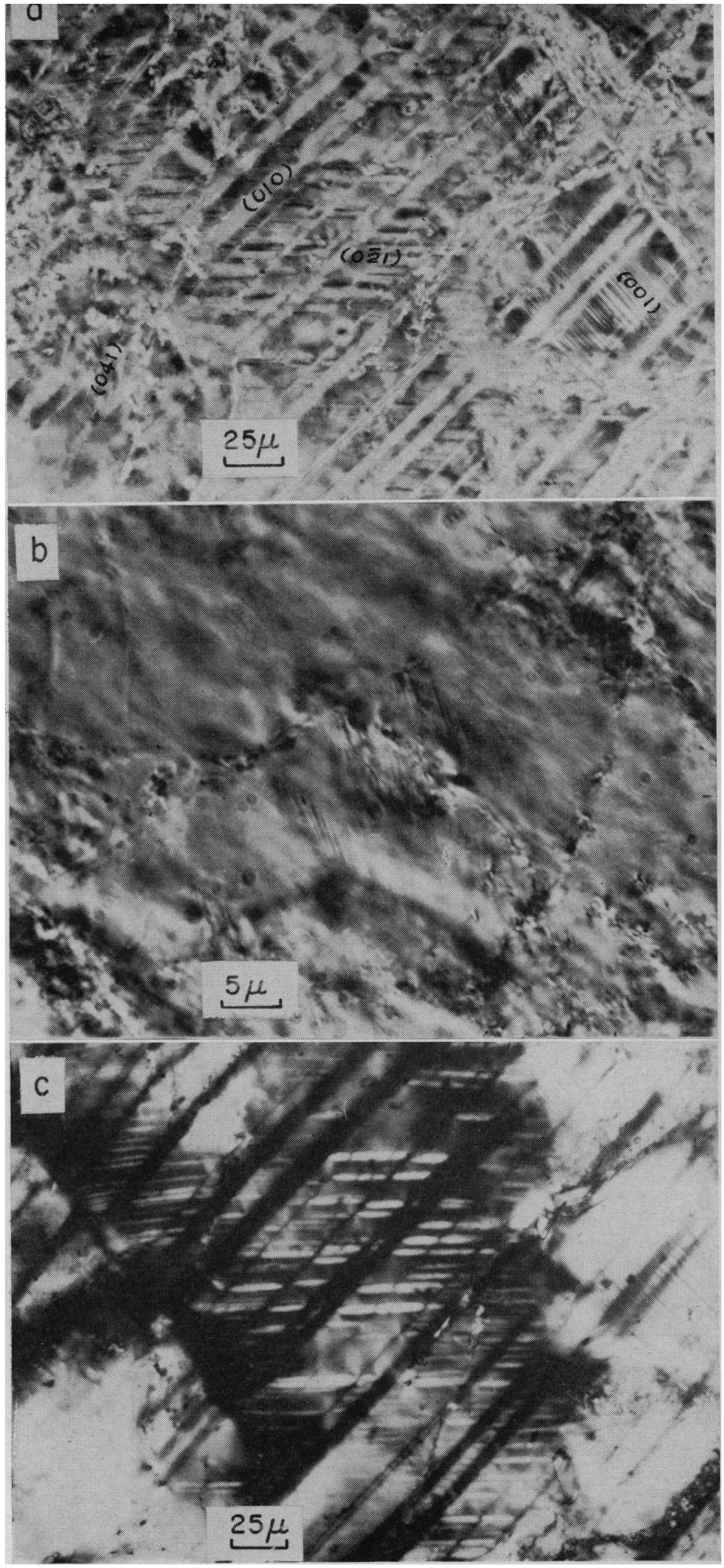


Fig. 5. (a) Plagioclase from a shocked granitic gneiss from Ries Crater (Zipplingen) having several sets of planar features. Four of these can be indexed as parallel to (010), (001), (0$\bar{2}$1), and (041). Those parallel to (010) consist of alternating bands of plagioclase of high (dark) and low (light-colored) mean index of refraction. Within these bands, platelets of contrasting mean indexes of refraction occur parallel to (0$\bar{2}$1). Platelets parallel to (001) also consist of alternating platelets of high and low mean indexes of refraction. The reduced index results from partial transformation from crystalline plagioclase to amorphous plagioclase glass. Phase-contrast illumination. (b) Same plagioclase as in (a) and (c) but with a different orientation. The closely spaced planar features occur within single (0$\bar{2}$1) platelets; they are not resolved in (b). Phase contrast, with oil immersion. (c) Same field as (a); crossed nicols. Dark areas are nearly completely isotropic; the gray areas are partly glassy and cover a wide range of mean indexes of refraction and reduced birefringence.

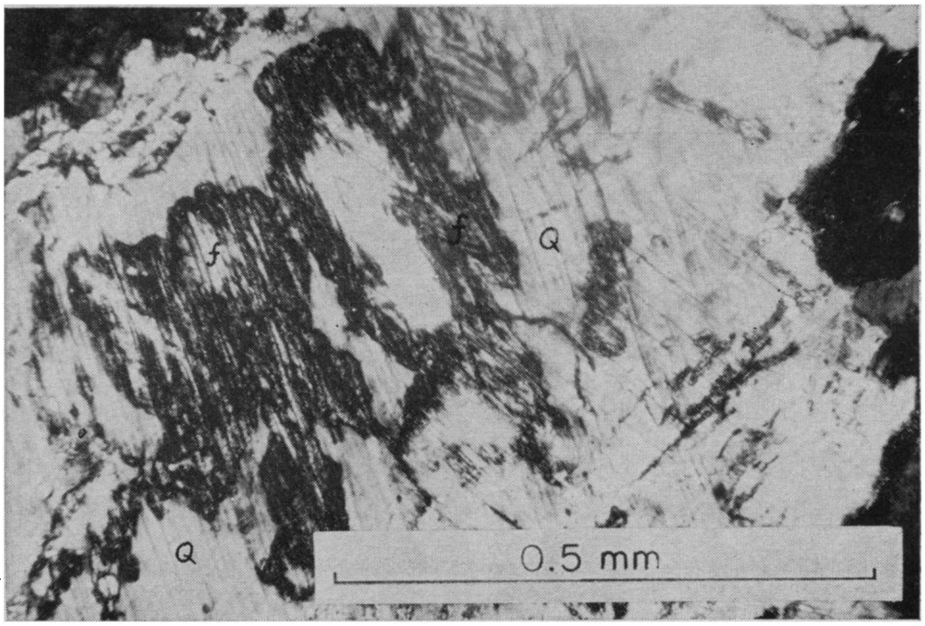


Fig. 6. Quartz, with embayed feldspar, from a granitic gneiss from Ries Crater (Bollstadt quarry), showing two sets of closely spaced fractures cutting across the quartz and the plagioclase but terminating at the boundary of the quartz grain.

tal structure may reveal whether vitrification follows specific shock-induced dislocations, the degree of disordering, and defects in the crystal.

Moderate to strong shock effects in plagioclase: A more striking example of such abrupt phase transition, typical of strong shock, is complete transformation of euhedral plagioclase to glass in a plagioclase-bearing amphibolite, also from Ries Crater. Figure 7, a and b, shows the euhedral outlines of the plagioclase, marked by the micaceous alteration products along the crystal faces and cleavage. The optical properties and crystal structure of the associated amphibole were not affected to any noticeable degree. Transformation of potash feldspar to a glass of the same composition has also been observed in many impact-metamorphosed granitic rocks from Ries.

The examples shown in Fig. 2, a and b, and Fig. 7, a and b, illustrate another characteristic feature of impact or shock metamorphism: phases that are lower in density and more compressible are selectively transformed; the denser biotite, or amphibole, with lower compressibility remained untransformed. In these two specimens the rise in temperature is probably not greater than the breakdown temperature of the biotite or the amphibole. Reaction between adjacent minerals is lacking.

Strong to intense shock effects in plagioclase: Unlike quartz, high-pressure polymorphs of plagioclase or potash feldspar have never been found in naturally strongly shocked specimens. A dense glass of the host-plagioclase composition may have been formed, similar to the dense maskelynite described by Duke (*15*) from the Shergotty achondrite. Vesiculation and flow in the plagioclase glass have been observed also. Evidence of reaction, in highly vesicular crystalline rocks, between silica or feldspar glass and the fused mafic component is very limited, possibly because of rapid heating and quenching during ejection and fallout.

The mechanism of transformation in low to moderately strongly shocked plagioclase in some respects seems to resemble that of quartz; that is, it shows a strong crystallographic structural control. Much of the mechanism remains unknown. One may postulate that, because of the lack of time for diffusion under shock, high-pressure phases such as jadeite, which requires the chemical breakdown of plagioclase, cannot form. The only type of polymorphic transition that prevailed under shock seems to be limited to minerals of simple composition. Glasses higher in density than normal glass of the same composition may be formed from minerals of complex compositions incorporating several oxides, such as feldspars.

Infrared-absorption and reflectance spectra of some artificially shocked rock-forming minerals have been studied (*16*). Infrared spectra of silica polymorphs including stishovite have been reported by Lyons (*17*). None of the glasses formed by shock transformation in the solid state has been studied by methods of thermoluminescence, electron spin resonance, low-angle x-ray diffraction, or infrared spectroscopy. Such studies may provide information on the defect and other structural characteristics of these glasses, as well as information regarding the density of packing, Si-O coordination, and the mechanism of nucleation of dense crystalline polymorphs.

Shock Effects in Mafic Minerals

In a shocked biotite granite or granite gneiss in which the quartz and feldspar display complex planar structures and partial or locally complete vitrification in the solid state, the biotites remain crystalline. The most pronounced change is development of strong kink bands and of reduced birefringence and pleochroism in the strongly kinked bands (*1*).

If the biotite-bearing rock is more strongly shocked, so that all the quartz and feldspars are transformed to glass, the quick rise in temperature is clearly reflected by the biotite. In such rocks the biotite crystals are oxidized; many show kink bands with indistinct pleochroism and low birefringence, and rims or concentrations of iron oxide along fractures. Also observed are examples of complete decomposition of biotite into iron oxides, and a silicate glass of feldspar, metasilicate, or orthosilicate composition—depending on the specific composition of the biotite. The decomposition is interpreted as having been caused by shock-induced temperature exceeding the breakdown temperature of the biotite.

In a moderately shocked plagioclase amphibolite in which the plagioclase feldspars are partially or completely transformed to a thetomorphic plagioclase glass, the associated amphibole or hornblende shows development of closely spaced planar structures. In another instance—the amphibole from a granodiorite gneiss from Ries Crater—a cummingtonite studied by x-ray methods showed partial vitrification. In more strongly shocked specimens in which the plagioclase glass shows vesiculation and flowage, the amphibole commonly shows rims of iron oxide, accompanied by gradual disintegration of the crystal into a slightly disoriented mosaic. Such fine-grained areas are distinctly lower in birefringence. In specimens that may reflect a higher shock-induced temperature exceeding the breakdown temperature of the amphibole, the amphibole decomposes into iron oxide and a glass whose composition depends on the composition of the host amphibole. The breakdown features are very similar to those of the biotite, but the required breakdown temperature may be higher for the amphibole, depending on the composition of the amphibole and the H_2O and oxygen fugacity (*18*). Much work remains to be done on the properties and composition of the glass resulting from the breakdown of mafic minerals.

The decomposed products of biotite and amphibole, consisting principally of fine particles of magnetite and a glass, contribute to the kinds of mixed fused glass derived from the parent rock. Two distinct types of mixed glass occur in the Ries material; one contains abundant magnetite dust while the other is free of it. The former glass is usually gray-to-black, magnetic, and nearly opaque (Fig. 8). Refractory accessory minerals in this glass show no evidence of fusion. The latter glass is brown, nonmagnetic, and transparent (Fig. 4). Refractory accessory minerals in the brown transparent glass do show evidence of fusion in some samples. The temperature of fusion of the gray-to-black magnetic glass probably ranges from 900° to 1200°C, whereas the nonmagnetic brown glass, with the iron dissolved in the glass, is probably formed at temperatures higher than 1400°C (*19*). Such estimates are subject to error because the effects of oxygen and water-vapor pressure were not considered.

A small amount of mixed glass, similar in composition to the parent rock, occurs in the suevite of Ries Crater; it normally contains relicts of unshocked, shocked, and partially fused fragments of mineral, indicating mechanical mixing. Development of diffuse-color banding and schlieren, and rims around silica-glass inclusions, indicate some degree of homogenization by diffusion.

Engelhardt and Hörz (*20*) described a dense glass from Ries as evidence of high pressure due to impact of the meteorite; in composition it resembles the bulk rock from which the glass derived. The dense glass was annealed at atmospheric pressure, with the result of a lower index of refraction, and so a lower specific gravity. The authors showed that the decrease in density by annealing under atmospheric conditions cannot be explained by the change in water content or the amount of crystalline inclusions.

Shock Effects in Accessory and Refractory Minerals

My petrographic observations indicate very few detectable shock effects at low to moderate shock pressures in minerals such as apatite, sphene, ilmenite, rutile, and zircon. All such accessory and refractory minerals remain unchanged in rocks in which the quartz and feldspars are transformed to thetomorphic glasses. When a granitic rock develops moderately to highly vesicular plagioclase glass, fused opaque minerals, such as iron oxides, occur along the vesicles. Sphene in such rocks shows planar structures locally, similar to those described for quartz and plagioclase.

The most-striking features revealed by the accessory and refractory minerals in the impact glasses are their decomposition and fusion products, which indicate a very high temperature. Such temperatures, generated by shock, are not attainable by normal geologic processes. Nickel-iron spherules and spheroids occur in impactites from Meteor (*21*), Wabar (*22*), and Aouelloul craters (*23*) and in tektites (*24*); they derive from the fusion of the impacting iron meteorites at temperatures exceed-

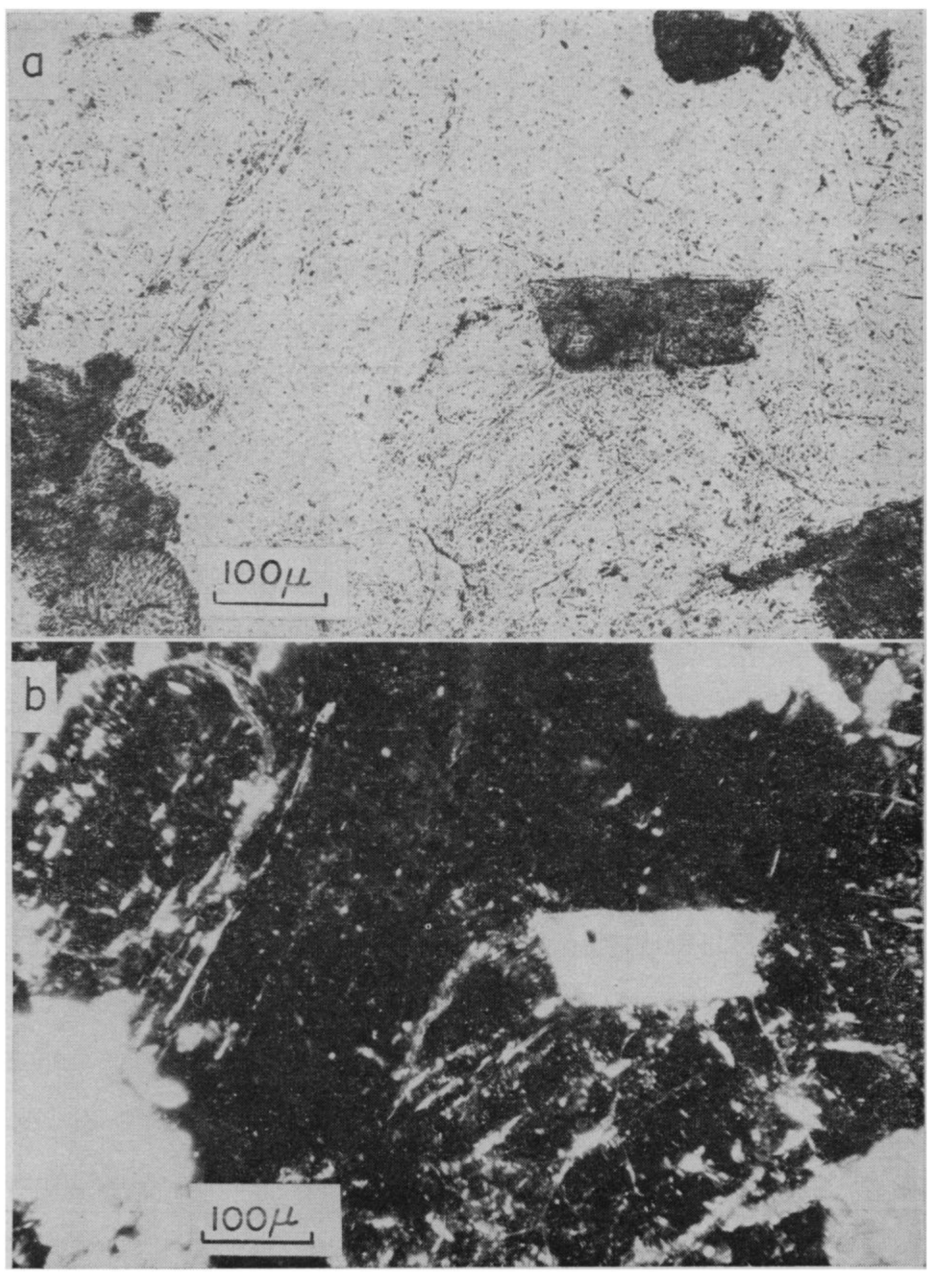


Fig. 7. (a) Plagioclase amphibolite showing the euhedral thetomorphic plagioclase glass in an anhedral feldspar glass; the amphiboles remain crystalline. Plain polarized light. (b) Same field as (a); crossed nicols. The euhedral thetomorphic plagioclase is revealed by the birefringent micaceous mineral along the crystal boundary and cleavages.

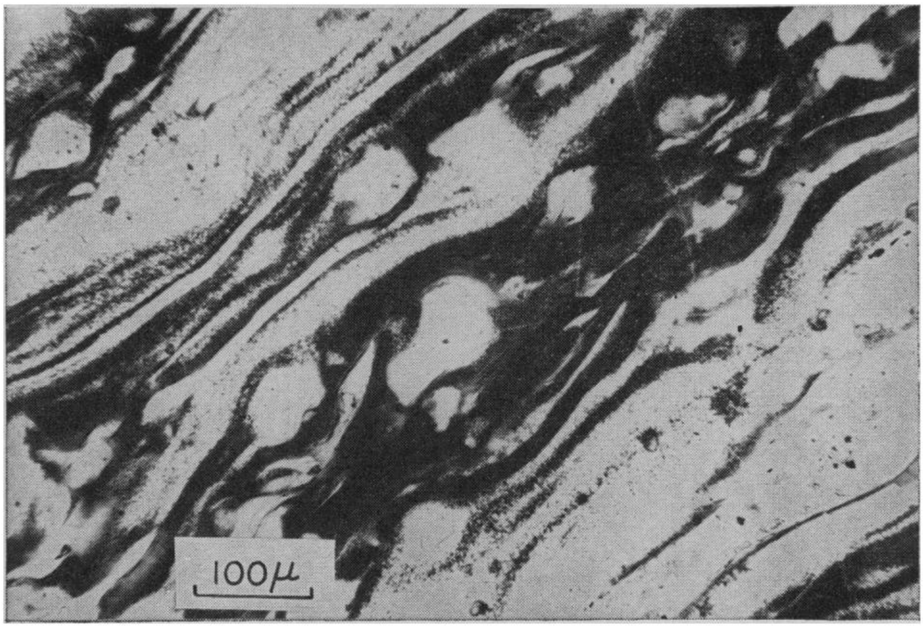


Fig. 8. A dark-gray, banded, magnetic glass in suevite from Ries Crater (Otting quarry). The dark bands contain many small particles of magnetite. Plain polarized light.

ing 1500°C. Chao (*25*) and Schüller and Otteman (*26*) have described metallic spherules from the impactites of Ries Crater and concluded that their presence indicates that the impactite glass was formed at temperatures similar to those of Meteor Crater impactites. El Goresy (*27*) described droplets of ilmenite, rutile, pseudobrookite, and baddeleyite from Ries glass, and nickel-iron and troilite spherules from Ries and Lake Bosumtwi glasses, with similar conclusions regarding the temperature of formation of these glasses. Glasses that contain droplets of pseudobrookite, baddeleyite, and rutile are largely transparent and generally free of magnetite dust; small amounts of wüstite may be present (*28*). Its identification requires further confirmation. The low viscosity indicated by the stretched lechatelierite, which is commonly observed in tektites and impactites, indicates that the temperature of formation of such glass exceeds 1700°C (*1*).

Pressures and Temperatures in Impact-Metamorphosed Rocks

The peak transient pressure and temperature during shock, and the residual temperature immediately after passage of the shock wave are characteristic of the magnitude of the impact event. Experimental data on the calculated peak pressures and temperatures and residual temperatures, from study of the equation-of-state of minerals and rocks, are extremely limited; those available are difficult to translate for application to natural events.

The physical conditions experienced by a particular natural rock under shock can be reconstructed to some degree from the following indications: (i) the degree of vitrification of a certain phase or phases accomplished in the solid state; (ii) the occurrence of high-pressure polymorphs; (iii) evidence of breakdown temperature of certain host minerals; and (iv) the solubility of iron oxide in and viscosity of the glass.

Under ideal conditions, by study of the degree of shock-metamorphism of a suite of rocks of the same parentage, the minimum peak temperature after shock may be estimated from evidence of the highest-melting refractory mineral. The peak temperature during shock is difficult to estimate because of the uncertainty of the time lag for the beginning of melting, which I shall discuss. The occurrence of high-pressure polymorphs gives some indication of the minimum transient pressure, whereas the peak pressure may be estimated from consideration that, in a shock event, a certain peak pressure is necessary for the estimated peak temperature to be attained immediately after shock. The residual temperature may be estimated from reactions produced during the cooling period after the passage of the shock wave.

This approach is at best crudely qualitative, since there are no two-dimensional experimental shock-wave data on slightly porous to porous natural minerals or rocks from which the pressure and temperature at any time of the shock event can be determined and calculated. Furthermore, from static high-pressure experiments with anhydrous and hydrous silicate systems, the stability field of a mineral, or the melting temperature of a particular phase, is sensitive to its composition and depends on the total pressure and, in some instances, on the oxygen fugacity and water-vapor pressure. The presence or absence of a change in phase during shock is an important factor in the temperature calculation, as was demonstrated by Wackerle on quartz (*12*) and Ahrens and Gregson on porous sandstone (*29*). The sluggishness of phase transformation is of critical concern, and the "time lag" for the beginning of melting (*30*), or the kinetic factor, is also implicated in a significant way. The kinetics of melting or phase change are pressure- and temperature-dependent. Thus the sluggishness of transformation of quartz to coesite in static and shock-wave experiments implies that a longer pressure pulse was necessary to produce coesite in a natural impact event. Overpressure, increased temperature, and possibly an unknown catalyst such as shearing stress might substitute for length of the pressure pulse. Because of the kinetic factor and the nonequilibrium condition, it would be difficult to apply the static high-pressure data to shocked rocks directly. For the same reason, the metamorphic-facies concept of Eskola, which is based on the principles of phase equilibria, is inappropriate and would not be applicable in most instances.

The above-mentioned factors concern only part of the problem. We also need to learn something about the effects of the interaction of reflected waves (rarefactions) with later shocks propagating through the heterogeneous geologic material, the relaxation of stress in the compressed rock material, and its cooling history.

It seems quite hopeless then to try to estimate or reconstruct the pressure and temperature history of shock- or impact-metamorphosed rocks. Nevertheless, let us first look at some shock-wave data and then try to extract as much information as possible from shocked natural mineral assemblages.

McQueen and co-workers (*31*) studied experimentally the residual temperature on the basis of the temper colors of shocked iron at various peak shock pressures. They show that the residual temperature of iron at a pressure of 400 kilobars is 265°C; at 785 kilobars, 465°C. The rise in residual temperature in the iron is thus approximately 80°C per 100 kilobars. Wackerle calculated the temperature in crystalline quartz and in amorphous quartz (after subjection to 383 kilobars) after the shock was relieved from a given Hugoniot temperature (*12*). At 400 kilobars the calculated temperature was 610°C; at 450 kilobars, 1080°C; and at 500 kilobars, 1580°C. Clearly the rise in temperature in amorphous quartz is much greater than in Fe for the same shock pressure. Ahrens and Gregson (*29*) calculated the temperature at various shock pressures for Coconino sandstone: at 42 kilobars the temperature was 265°C; at 64 kilobars, 411°C; at 89 kilobars, 598°C; at 113.5 kilobars, 815°C; and at 190 kilobars, 1452°C. The calculated rise in temperature in a porous sandstone is much greater than in crystalline quartz. These data suffice to indicate that, in order to compare the estimated peak shock pressure with temperature after passage of the shock wave, the equation-of-state of the mineral in that particular rock must be known.

In the case of a weakly to moderately shocked granitic rock, in which only the more-compressible quartz and feldspar show a range of shock effects and the mafic minerals remained essentially unchanged, the peak pressure and temperature can only be estimated from the strongest shock effects in them. The occurrence of a wide range of shock effects in quartz in a single rock suggests that either the attenuation of the shock wave is very large within a millimeter range, or the response to shock transformation in the solid state in a mineral aggregate is quite variable.

Let us use the complete transformation of quartz in the biotite quartz schist shown in Fig. 2, a and b, to illustrate the problems in estimating the pressure and temperature. In density an unshocked biotite schist is probably greater than a rock consisting essentially of quartz of equal porosity, and, if one uses Wackerle's data (*12*) on the rise in temperature of crystalline quartz as a rough guide, the expected temperature rise in a biotite schist at a peak pressure of 450 kilobars should be less than 1080°C. Since the biotite has not shown any sign of breakdown (one ignores the effect of the fugacity of water and oxygen), the increased temperature may not have attained about 700°C for any length of time (*32*).

An estimated peak shock pressure of 400 kilobars and an induced rise in temperature of less than 610°C seem reasonable. To accomplish the transformation from crystalline α-quartz to silica glass, a peak pressure of the order of 380 kilobars is required (*12*). If the precise composition of the biotite is known and if some estimates of the fugacity of water and oxygen are available, a more precise lower limit of the breakdown temperature may be deduced. Thus the minimum peak pressure required for a certain transition, and the breakdown temperature of another associated mineral provide a way for qualitative estimation of the minimum pressure and temperature experienced by this particular impact-metamorphosed rock.

Estimation of the temperature of formation of the Ries impact glasses (Figs. 4 and 8) is perhaps a little less hazardous. The solubility of iron oxide (magnetite) in the glass and the breakdown and melting features of accessory and refractory minerals are useful criteria, particularly if the composition, water content, and density of the glass are known. In some impactites that were raised to and held at very high temperature for a reasonable period, evidence of high pressure, as indicated by the relict inclusions with shock effects, high-pressure polymorphs, or dense glass, may have been erased. Such fused glass by itself may be very difficult to distinguish from glass formed by some other heating mechanism. In such instances the evidence of an impact event is based largely on evidence of extremely high temperature.

Metamorphosed minerals and rocks shocked by the detonation of a nuclear device, when the total yield is known, provide valuable information. Planar structures in quartz were widespread in such materials (*33*). Although the geographic location of the intensely shocked materials relative to the shock origin was not known, information on low to moderately shocked mineral assemblages, of known, calculated, peak pressure and temperature, should eventually clarify their environment of formation.

Keeping in mind the danger and limitations of applying experimental shock-wave data to naturally shocked mineral assemblages, one can extract some information regarding the pressures and temperatures of shock-metamorphosed rocks. I shall soon publish details of such a study based essentially on petrographic observations (*34*).

Summary

Shock effects in quartz, plagioclase, biotite, amphibole, and some accessory minerals have been observed in rocks subjected to various degrees of metamorphism by meteoritic impact. The shock features described are unique; they are never observed in rocks from normal geologic environments. Such features are described:

1) Multiple sets of closely spaced planar microstructures occur in quartz, plagioclase, and other rock-forming minerals. Those characteristic of shock consist of alternating platelets, with a range of reduced mean index of refraction and birefringence; they consist of platelets that have been partially or completely transformed to an amorphous phase.

2) Quartz and plagioclase are selectively and completely transformed to silica glass and plagioclase glass in the solid state, whereas the associated mafic minerals remained crystalline. There is no reaction between adjacent minerals.

3) High-pressure polymorphs occur, such as coesite or stishovite. Coesite occurs exclusively within silica glass; it has not been observed as a reaction or breakdown product.

4) Nickel-iron spherules occur in the fused glass or impactites.

5) The occurrence of droplets of ilmenite, rutile, pseudobrookite, and baddaleyite in impactites indicates a temperature of formation exceeding 1500°C.

6) Dense glass occurs, similar in composition to bulk rock, in which iron oxide, such as fine particles of magnetite, is completely dissolved.

All these features are characteristic of a process involving the rapid rise and fall of extremely high pressures and temperatures. Minerals and mineral assemblages experiencing such high strain rates and sudden changes of pressures and temperatures react and change independently to the bulk chemical composition, under nonequilibrium conditions.

Many aspects of shock features require careful study. Kink bands in biotite and deformation lamellae in quartz occur in tectonically deformed rocks. These features should be studied with great care in order to determine whether reduction in mean index of refraction and total birefringence along the planar structures have resulted from vitrification or phase transition; their presence is additional evidence in favor of a shock mechanism.

Vitreous phases or glasses formed by shock also have many unique properties; they have not been studied by such methods as thermoluminescence, electron spin resonance, low-angle x-ray diffraction, or infrared spectroscopy. Shock-fused glass of high density needs to be studied in detail in carefully controlled laboratory conditions.

Experimental shock-wave studies of the equation-of-state of single minerals and mineral assemblages, under carefully controlled conditions, must precede estimates of peak pressures and peak and residual temperatures of shocked natural mineral assemblages. Detailed petrographic and mineralogic studies, however, have provided useful and definitive criteria for characterization of impact events. Such data should be of paramount importance in the study of samples brought back from Moon.

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Biosynthesis of Polyketides and Related Compounds

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In 1907 Collie (*1*) suggested that orsellinic acid (I), a common lichen constituent, originates from two molecules of acetoacetic acid, as shown. This was part of a general suggestion that fatty acids, terpenes, and carbohydrates arise from acetic acid. He appears to have had the underlying idea that such compounds are polymers of ketene ($CH_2{=}C{=}O$) and called them first "polyketenes" and then "polyketides"; a close analogue is the later "isoprene" hypothesis for terpenes. Collie had some experimental evidence favoring his orsellinic acid hypothesis, since he had obtained this compound from "dehydracetic acid" (II), itself obtained from two molecules of acetoacetic ester. He implied that other natural phenols could be included in the scheme, but did not discuss examples; the hypothesis seems to have been largely forgotten, as was his related (correct) hypothesis for terpene biogenesis, and his (incorrect) hypothesis for carbohydrate biogenesis, on which he expended most of his effort.

There are a few bare mentions in the literature of the original hypothesis (for example, *2*) but the extent of its neglect is shown by the fact that the topics most affected—mold products (*3*), lichen products (*4*), and flavonoids and related plant products (*5*)—were completely unaffected as late as 1952. Robinson published for the first time in 1955 (*6*) an extrapolation of Collie's theory, but meanwhile we had considered the topic (*7*), starting from a different origin and with experimental support.

Collie's hypothesis was based on the biosynthetic use of organic-reaction mechanisms of the Claisen type (reactions involving an ester group and an activated CH_2, leading to β-polyketoesters or β-polyketones; for example, III) and aldol condensations involving a reactive methylene and a carbonyl (for example, reactions of the type leading from III to IV). He recognized the similarity, but did not identify them, except in the case of I, with natural products; hence he was led to the hypothesis. He was in essence postulating a relation between certain laboratory and biosynthetic processes on the implicit but unstated assumption that chemical mechanisms should be recognizable in biosynthetic processes, even though enzymes and coenzymes are clearly important. Great superficial differences in fact existed between laboratory conditions (for example, the necessary use of powdered sodium metal to produce ethyl acetoacetate from ethyl acetate) and any conceivable processes compatible with biological environments. Collie was nevertheless basically cor-

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