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SHOCK COMPRESSION OF POWDERED SiO_2, Mg_2SiO_4, $ZrSiO_4$ AND OTHER MATERIALS

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Phase-transformation in shock-compressed solids has been studied by many scientists in the last few years. Geologists hoped to apply these investigations to the theory of solid-state transformation in the Earth's mantle (DOBRETSOV *et al.*, 1968; DERIBAS *et al.*, 1966; RINGWOOD *et al.*, 1967; MCQUEEN *et al.*, 1967) but the specificity of shock compression prevents the realization of this idea at present. However, experiments in shock compression of geological materials are interesting in themselves. These experiments may be particulary useful for the general theory of solid-state transformation and for meteorite problems.

1. Methods of shock compression

The methods of shock compression with shocked material preservation have been described in BATSANOV *et al.* (1965) and DERIBAS *et al.* (1967). Theoretical investigations and direct observations show the possibility of the existence of a three-shock configuration in the axial part of the compressed material in the experiments with cylindrical containers (ADADUROV *et al.*, 1967). A photograph of shock configuration obtained by the optical method in (ADADUROV *et al.*, 1967) is shown in fig. 1. The existence of a steady three-shock configuration allows the determination of the pressure in the axial zone. For this case the Hugoniot's curve determines the pressure behind the plane shock wave propagating with the detonation velocity. The corresponding values of pressure for the two types of explosive used are given in table 1.

Evidently, the possibility of the existence of a three-shock configuration depends on the correlation of the sizes of explosive charge and that of the container, as well as of the composition and density of powder and other factors. In the case when there is no steady plane shock wave in shocked powder, the determination of pressure, temperature and density become very complicated.

Usually in shock-compression processes the pressure increases in a time of about 10^{-8} sec and decreases in

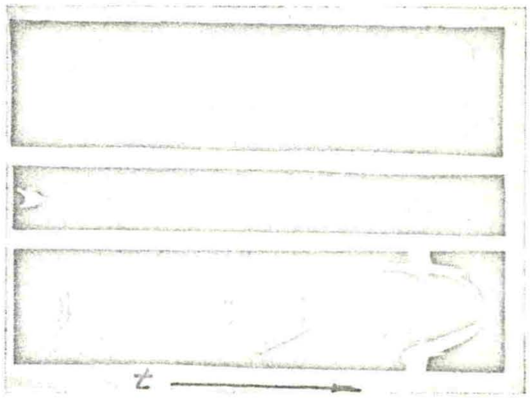


Fig. 1. Formation of three-wave configuration in cylindrical case.

TABLE 1

Pressure (in kbars) in the axial zone of containers in front of the head wave for different substances

Explosive	Explosive density g/cm^3	Rate of detonation km/sec	Substances and their density (g/cm^3)					
			SiO_2 (quartz) 2.60	SiO_2 (glass) 2.20	SiO_2 (powder) 1.6	Mg_2SiO_4 (powder) 3.05	$MgSiO_3$ (powder) 2.71	TiO_2 (crystalline) 4.25
Hexogene	1.1	6.6	480	490	420	—	510	—
Trotile/hexogene 50/50	1.6	7.6	680	680	—	660	—	800

a time of about 10^{-6} sec. The temperature decreases slower than the pressure in accordance with the thermoconductivity process.

2. Orthosilicates

2.1. *Forsterite*

The typical appearance of shocked powder is shown in fig. 2. The distinct clear zone is noticeable here in the axial part of the specimen. The dark and intermediate zones are observable on the periphery of the specimen. The insignificant changes of the initial powder are fixed in this zone. The observation of the specimens after compression is insufficient, evidently, for the single-significant determination of shock-wave configuration. Nevertheless, it is possible to compare the axial zone with the place of presumably three-shock configuration. No new phases are found in the experiment shown in fig. 2, but the structure of material in the axial zone suggests the formation of neogenic forsterite from the phase other than the initial one. The broadening of lines, the appearance of two new weak lines and the dissapearence of several weak lines, were observed in the X-ray pattern in the intermediate zone. The refractive index in the axial zone for natural olivine (N_g = 1.686, from kimberlite) was found to be equal to the pure forsterite (N_g = 1.670). Olivine in the dark border of the intermediate zone had a higher refractive index (N_g = 1.693). A redistribution of Fe from the axial zone into the intermediate one is probable in this process.

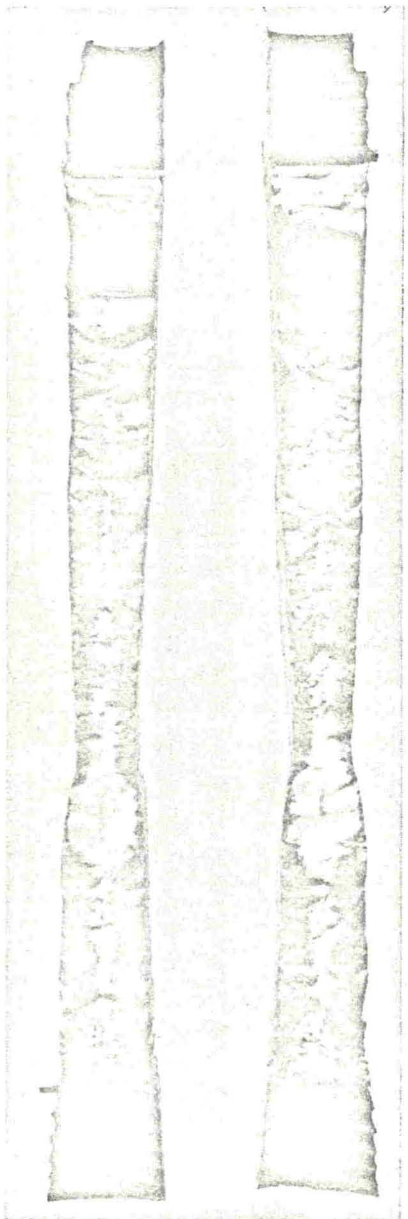


Fig. 2. Shocked powder of Mg_2SiO_4.

2.2. *Zircon*

The transformations in the powder of natural zircon ($ZrSiO_4$) are shown in fig. 3 (DOBRETSOV *et al.*, 1968). Distinctive axial zone 1, intermediate zone 2 and zone of the insignificant changes of initial powder 3 were observed in this experiment. The existence and width of these zones depend somewhat on the weight of explosive, but the composition of the material in zone 1 changes with weight of explosive. The relics of $(ZrSiO_4)^1$ with the destroyed lattice similar to the natural metamict zircon were found in zone 1. The amorphous glass-like phase of SiO_2, monoclinic ZrO_2 and some rhombic modification of ZrO_2, that is stable under high static pressure (BENDELIANI *et al.*, 1967), were also found in zone 1. It is necessary to emphasize that the last phase was definitely established in the experiments with the large charges of explosive. The quantity of "metamict" zircon $(ZrSiO_4)^1$ (lines in fig. 3 are marked by x), was decreased with the increase of the explosive weight.

Investigations of zone 1 by microsonde (fig. 4) confirmed the existence of the isolations of pure SiO_2. The particles of SiO_2 and ZrO_2 were very small in the ground part of zone 1 (less than 1–2 μ). These sizes are

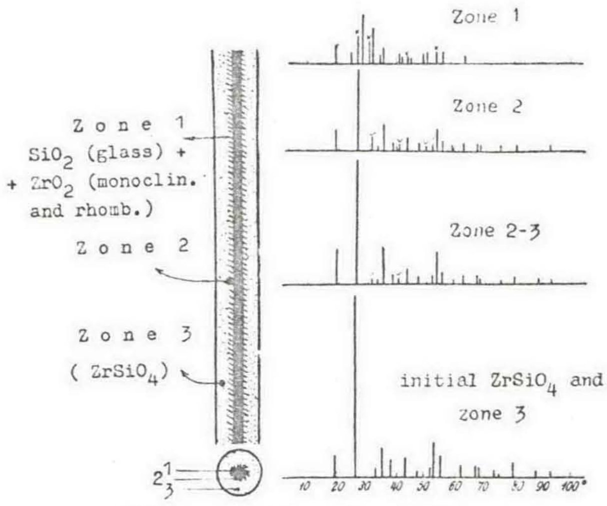


Fig. 3. Shocked powder of $ZrSiO_4$.

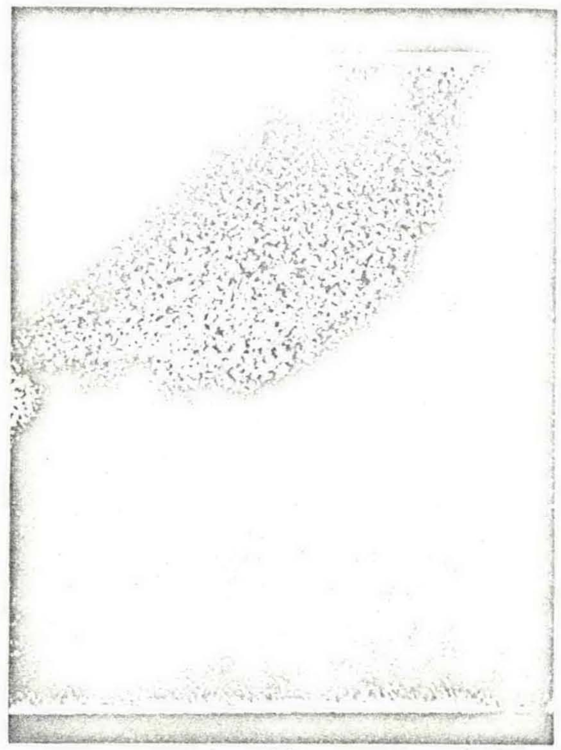
comparable with the accuracy of the microsonde, and the parts with a mixture of particles of SiO_2 and ZrO_2 are not distinguised in X-rays of SiKα and ZrLα from the relics of "metamict" zircon. These particles can be distinguished in an optical microscope.

The partial destruction of the lattice (broadening of the lines in the X-ray pattern and disappearance of the weak lines) was observed in zone 2. Sometimes the weak lines of ZrO_2 (marked by V in fig. 3) were found. The EPR-spectrums of zone 2 (fig. 5) reveal the characteristic effects similar to the partially metamict zircon. The broadening of line of EPR-spectra from zone 3 to zone 1, and the 10-fold decrease of its intensity were established.

In general, the behaviour of zircon powder is similar to the natural zircon with metamict destruction. The basic difference is that the high-pressure phase (rhombic ZrO_2) appears in shocked zircon and no intermediate states between the partially metamict zircon in zone 2 and the completely dissociated into oxides in zone 1 were found.

3. Framework silicates and SiO_2

As distinct from orthosilicates, we obtained the glass-like amorphous phases in framework silicates, often with heightened density and without the indication of melting. The appearance of shocked framework silicates differs from that of the othosilicates. The distinctive axial zone has not been observed in this case. Possibly it depends on the shock waves propagating in the frame-



(a)

Fig. 4. Photograph (0.1×0.1 mm) of central zone in X-ray radiation (a) SiK_α, (b) ZrL_α.

(b)

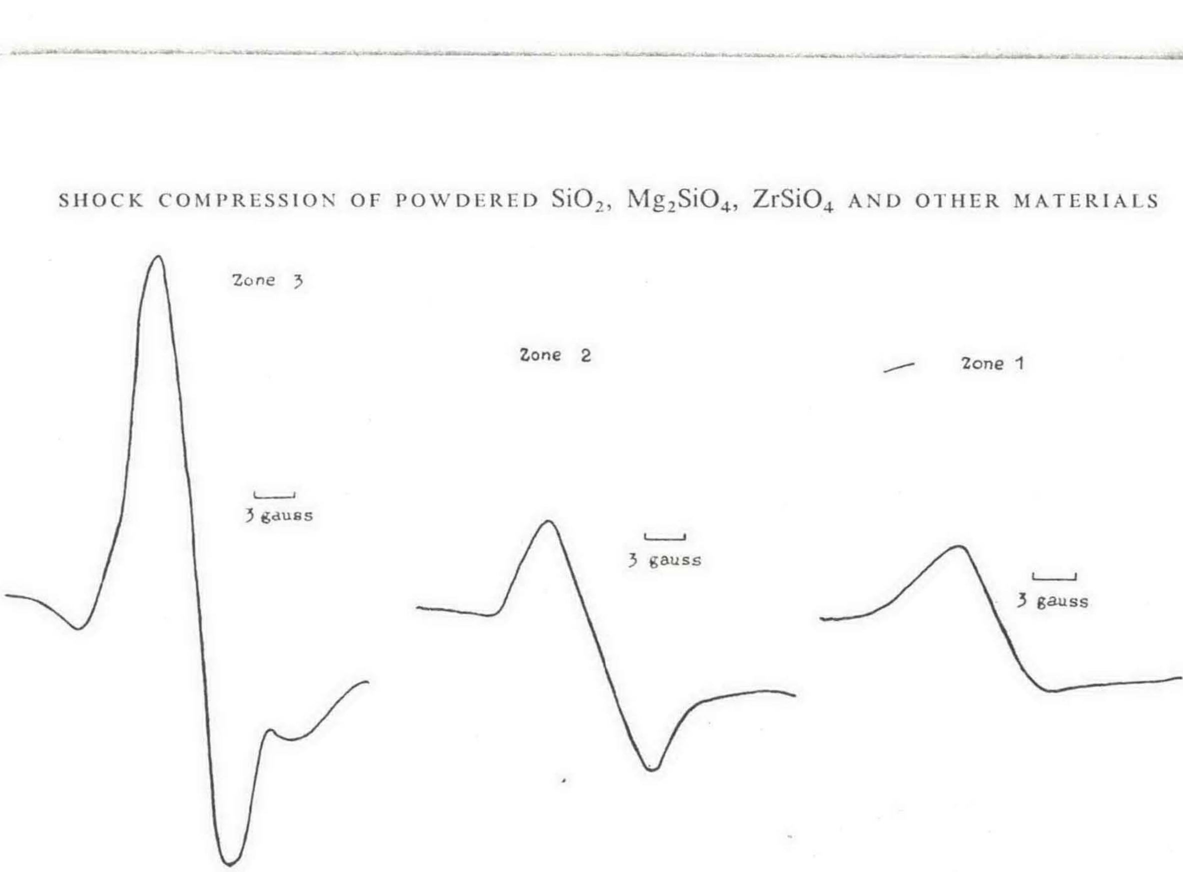


Fig. 5. EPR (electron paramagnetic resonance) spectra of the paramagnetic defect in shocked zircone of zone 3, 2 and 1.

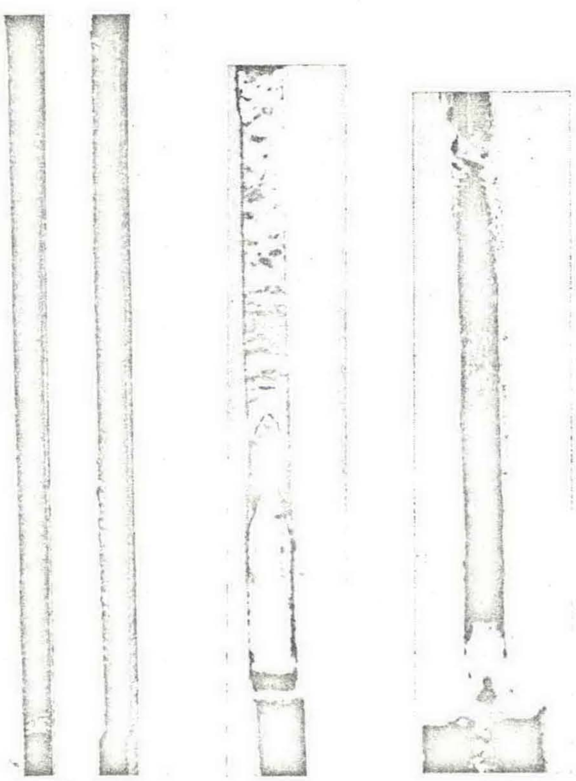


Fig. 6. Shocked powder of SiO_2 under different conditions: a – long container and large charge, size 0.5 of real size, b – short container and small charge, c – double shocked powder, b and c being twice their original size.

work silicates without formation of a three-shock configuration (fig. 6). Several cone-shaped zones are distinguishable in this case. The sizes of these zones essentially depend on the sizes of containers, explosive charge and initial density of powder.

It is possible to assume, that the absence of the three-shock configuration is connected with the "friable" structure of these silicates in comparison with the orthosilicates.

The situation and composition of phases are shown in fig. 7 for SiO_2 and $KAlSi_3O_8$ shocked in the equivalent conditions. The major part of the shocked products is the glass of normal density containing the great number of smallest bubbles in the lower part of a container. (Detonation moves from above.) The intermediate zones 2 and 3 are most interesting.

3.1. SiO_2

The fragments of grains of powder SiO_2 transit gradually with the preservation of form into the glass-like phase with the heightened density (N = 1.510 instead of N = 1.460 for normal SiO_2 glass). Simultaneously the relics of quartz grains acquired the lower refractive index (N up to 1.520) and the low double-refraction (0.001–0.003), the broadening of lines and disappearing of weak lines in X-ray patterns were observed. The appearance of the X-ray patterns indicates

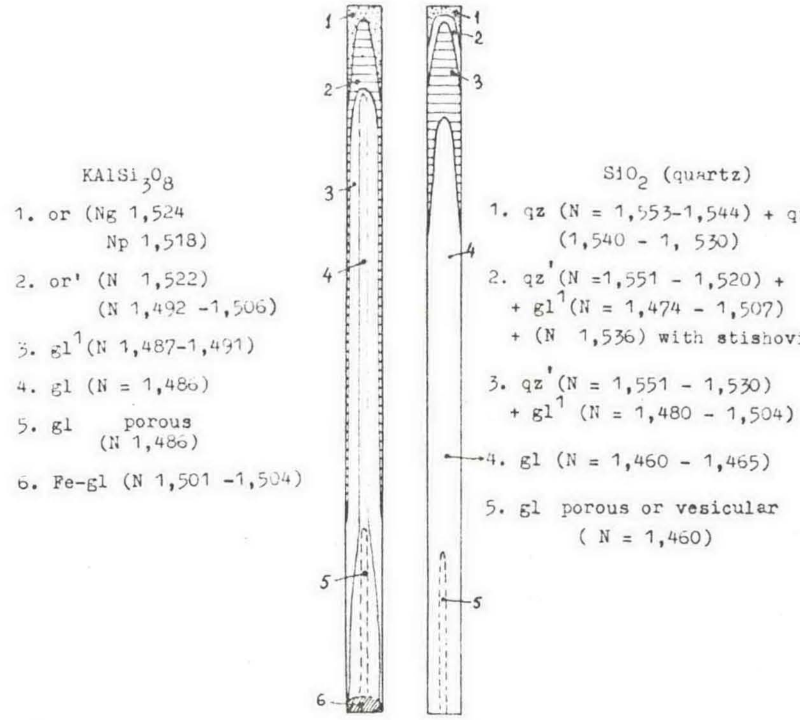


Fig. 7. Shocked powder of SiO_2 and $KAlSi_3O_8$ with zones of variable density.

the partial destruction of the lattice. The small quantity of the very dense glass (N = 1.536, constant density) was found in zone 2. This glass contained the needle-shaped grains which were hardly observed in the microscope, with these grain being possibly a coesite or stipoverite (stishovite). The stipoverite was found in SiO_2 after shock compression after treatment by a solution of HF and HNO_3 (DERIBAS *et al.*, 1967; DE CARLI and MILTON, 1965) and the coesite was found in some of our previous experiments (DERIBAS *et al.*, 1966). In the present experiments with large explosive charges (fig. 7) some coesite, tridimite (hexagonal) (coesite $\geq$ tridimite) and sometimes (in experiments with initial glass of SiO_2) neogenic quartz were found in zones 1, 2, 3. Some tridimite, traces of coesite and sometimes (in experiments with initial glass of SiO_2) α-cristobalite were found in zones 4–5. We suppose that the formation of tridimite and cristobalite is connected with the high residual temperature after shock compression. Zones 2 and 3 moved along the detonation and their sizes increased with explosive charge. Zones 1 and 2 disappeared with the largest explosive charges. Simultaneously, the appearance of stipoverite instead of coesite is possible.

According to this phenomenon, we considered in the previous paper (DERIBAS *et al.*, 1966) three different regimes of stability of quartz, coesite and stipoverite according to the weight of explosive charge. The present investigation shows that the detection of different zones in one experiment is more correct. It is necessary to note that the appearance of coesite instead of stipoverite depends on many factors little understood at present.

3.2. $KAlSi_3O_8$

The behaviour of $KAlSi_3O_8$ in shock experiments (fig. 7) is similar to that of SiO_2 in general. The glass-like phase (gl′) appeared in zones 2 and 3 with higher variable density (N up to 1.505). The relics of potassic feldspar with strongly destroyed lattice were observed. The presence of leucite and the variations of composition of glass were not found. The comparison of these data with the phase-diagram of a system K_2O–Al_2O_3–SiO_2 (SCHAIRER and BOWEN, 1955) shows that these effects are not simple melting at high temperature. The new high-pressure phase of $KAlSi_3O_8$ recently discovered (RINGWOOD *et al.*, 1967) was not found definitely. Probably a very small quantity of this phase was formed in our experiments.

3.3. *Other framework silicates*

A similar situation in shock experiments with other framework silicates was observed. Some effects were determined for albite ($NaAlSi_3O_8$) similar to those for $KAlSi_3O_8$. A small quantity of jadeite was also found in shocked albite. The paper (MILTON and DE CARLI, 1963) contains a description of the transformation of anorthite $CaAl_2Si_2O_8$ into an X-ray-amorphous phase, with preservation of the shape of grains and even cleavage, similar to mascelenite in stone meteorites.

4. Discussion

It is possible to distinguish two types of phase-transformation in silicates (table 2). Type I "without axial zone" corresponds to framework silicates and SiO_2, type II "with axial zone" is characteristic of ortho-silicates and some oxides. Type II may be divided into two subtypes: IIa "with decomposition", IIb "without decomposition". Naturally, this division is connected essentially with the conditions of shock compression, but in framework silicates and SiO_2 the axial zone has never been observed.

An intermediate picture was found in some other silicates. For instance, $MgSiO_3$ decomposed into Mg_2SiO_4 and X-ray-amorphous SiO_2, and the formation of glass $MgSiO_3$ with variable density was observed in the axial zone. In ferro-magnesian micas after shock compression, magnesian micas with the destroyed lattice, magnetite, native Fe and glass near to potassic felspatic composition were found.

Some transformation in shocked oxides are shown in tables 2 and 3. These transformations correspond to the high-temperature modifications (α-Al_2O_3), and to the high-pressure phases (Zr_2O_2, PbO). No transformations were found in some oxides (TiO_2) (BATSANOV *et al.*, 1967). However, a defect structure with change of colour was observed in this case. This type of transformation may be singled out as type III, and the relaxation and disappearance of X-ray lines were usually found in these experiments.

Broadening of Laue reflections in shocked single crystals of several materials was found in some experiments. It shows that the single crystals transform into a fine grained powder at a definite shock pressure.

The similarity between the shocked and "metamict"

TABLE 2

Transformations of silicate and oxide powders under shock wave treatment in the cylindrical case

Type	Characteristic features	Examples		
		Initial minerals	New phases*	
I	1. Indistinct or absent axial zone, i.e. unstable three-shock configuration	SiO_2 (quartz, glass)	Destroyed "quartz", s.r.o. phase of high density, traces of stishovite, rarely of coesite	
		Framework minerals: $KAlSi_3O_8$ (orthoclase)	Destroyed "orthoclase", s.r.o. phase of high density, traces of high pressure phase?)	
	2. Formation of glass-like phases of variable density (without fusion)	$NaAlSi_3O_8$ (albite)	s.r.o. phase, jadeite+SiO_2	
		$CaAl_2Si_2O_8$ (anortite)	s.r.o. phase (maskelinite)	
IIa	1. Distinct axial zone, corresponding to Mach's three shock configuration	Silicates: $ZrSiO_4$ (zircone)	Destroyed (metamictic) zircone, SiO_2+ZrO_2 (monoclin.), glass.	
	2. No glass-like phases, with partial or complete lattice deformation	$MgSiO_3$ (enstatite)	SiO_2 (s.r.o.)+Mg_2SiO_4, glass	
		$K(M,Fe)_3AlSi_3O_{10}(OH)_2$	Destroyed Mg-mica+$FeFe_2O_4$ or Fe+SiO_2+glass	
IIb	a. with decomposition to constituents	Non-complex silicates and oxides: Mg_2SiO_4 (forsterite)	Fine-grade fracturing and partial deformation of the lattice	Traces of new phase high pressure (?)
	b. with polymorphic transformations	Al_2O_3 (α and γ)		α-Al_2O_3
III	No phase transformations; partial lattice deformation	TiO_2		No new phases

* Destroyed – phase with partially or completely destroyed lattice; s.r.o. – short-range order (glass-like) phase.

TABLE 3

Comparison of the shock wave transformations and transformations caused by irradiative treatment (LASTMAN, 1963)

Minerals	Type of irradiative treatment	Type of transformation caused by shock wave treatment	Analogy with shock treatment
SiO_2 (quartz, glass)	Fast neutrons up to 2.10^{20} neutr./cm^2	I	Line broadening, decrease in SiO_2 density up to glass formation. Increase in glass density
$NaAlSi_3O_8$ $CaAl_2Si_2O_8$	Fast neutrons	I	Decrease in density up to formation of glass
ZrO_2 (monoclin.)	Fast neutrons up to 6.10^{19} neutr./cm^2	IIb	Decrease in the density and transformation to a new modification (to high temperature, cubic one with irradiative treatment; high pressure, rhombic one with the shock wave treatment)
$ZrSiO_4$	α-particles up to 3.10^{-4} α-particles/atom	IIa	Lattice deformation up to the X-ray amorphous state with decrease in density, decomposition to SiO_2 (X-ray amorphous) and ZrO_2 (various modifications)
	Fast neutrons up to 3.10^{20} neutr./cm^2	IIa	Decrease in density, disappearance of the far-order lines
Mg_2SiO_4	Fast neutrons	IIb	No observable change (except for disappearence of the weak lines)

$ZrSiO_4$, formed by natural radiation, was mentioned above. The same similarity can be stated for the other materials at conditions of shock compression (table 3). The radiation produced the basic effects of destruction of the lattice (LASTMAN, 1963). The main distinction of shock compression from radiation is the formation of high-pressure phases in shock experiments. It is possible to assume that the destruction of lattice in shock front is similar to that one produced by radiation.

Many investigations show that the basic processes characteristic of shock compression (destruction of lattice, formation of high-pressure phases, polymerisation) proceed in the short time of the existence of high pressure (about 10^{-6} sec) (BETSANOV *et al.*, 1965; DERIBAS *et al.*, 1967; ALTSHULER *et al.*, 1967; ADADUROV *et al.*, 1965). This is evidence of the abnormal speed of transformations in shock waves, exceeding by several orders the speed of the same processes under normal conditions. There is no common explanation of this anomaly in spite of some attempts in this direction (ALTSHULER *et al.*, 1967; ADADUROV, 1965).

Our conception is that the lattice is destroyed completely by a shock wave with energy exceeding a definite critical value depending on the properties of the powder.

In this case the material transforms into some "state of activation" similar to a strongly compressed gas (GLASSTONE *et al.*, 1941). This "state of activation" transforms into the glass-like phase for the framework silicates and SiO_2 and into the mixture of fine-grained crystalline phases for other materials under condition of high residual temperatures. In this case, destruction of the lattice and mixing of its elements creates the conditions for the formation of high-pressure and other phases. These phases form, possibly, in small quantities and transform partly into initial or metastable phases under the action of high residual temperature. As a rule, only the relics of these phases are observed, and the search of them is very complicated. The absence of high-pressure phases in the axial zone may be explained by the influence of residual temperature. Contrary to the axial zone, the intermediate zones are of the most interest. Possibly the using of oblique shock wave and the organisation of effective cooling will be useful for the increasing quantity of high-pressure phases after shock compression.

The absence of thermodynamic equilibrium in shock waves TROFIMOV, 1967 is the reason for the limited application of these experiments to geological problems, except possibly to the problem of meteorites. However, the principal possibility of obtaining diamonds, stipoverite, spinel-like modification of Mg_2SiO_4 and other high-pressure minerals by shock compression is very interesting. The destruction of the lattice, abnormal velocity of transformation and other phenomena of shock compression are also of interest in the general theory of solid phase transformations.

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