

SHOCK COMPRESSION OF $ZrSiO_4$ AND METAMICT DECAY¹N. L. Dobretsov, I. L. Dobretsova, Academician V. S. Sobolev
and V. I. MaliInstitute of Geology and Geophysics, Siberian Division,
Academy of Sciences, USSR

One of the main effects observed in silicates affected by shock waves is their conversion to a radioamorphous glassy state. This conversion was observed for SiO_2 [1-5], $CaAl_2Si_2O_8$ [6], $NaAlSi_3O_8$ and $MgSiO_3$ [7] both when a plane wave was passed through a single crystal [1, 2] and polycrystalline matter [4-6] and when powder was pressed into cylindrical ampoules [3, 7]. Clarification of the essence of this conversion is of great importance for understanding the processes in solid phases affected by shock waves and for determining the potential of phase transitions in silicates. This is considered in the present work.

The change to a vitreous state may result from disintegration during passage of the shock wave (which is irrefutable for a plane wave in single crystals of SiO_2 [1, 2]), although it can be interpreted in many cases as simple fusion under the action of the high temperatures persisting for some time after the shock wave has passed. The latter assumption can be expressed, in particular, for powder pressed into cylindrical ampoules. Certain indirect facts, in particular the formation of high pressure phases (coesite, stishovite), indicate that a special transition occurs here during passage of the shock wave instead of simple fusion [3, 7, 8]. V. S. Sobolev assumes that this special transition to a radioamorphous state may be analogous to metamict decay under the action of radioactive α -radiation. Natural metamict minerals are known to be radioamorphous and, probably, are subdispersed aggregates with a particle size of 30 to 60 Å, formed through disintegration of crystalline matter without its external form being modified [9-11]. This subdispersed state is detectable only on an electron diffractometer when waves with a length of about 0.06 Å are employed. In many cases the final result is dissociation into constituent oxides [9-12]. Scientists now envisage this dissociation as being due to the shift of ions (principally with covalent bonds) under the action of α -particles and, in part, to radioactive oxidation.

¹Translated from: Udarnoye szhatiye $ZrSiO_4$ i metamiktyny raspad. Doklady Akademii Nauk SSSR, 1968, Vol. 182, No. 4, pp. 910-913.

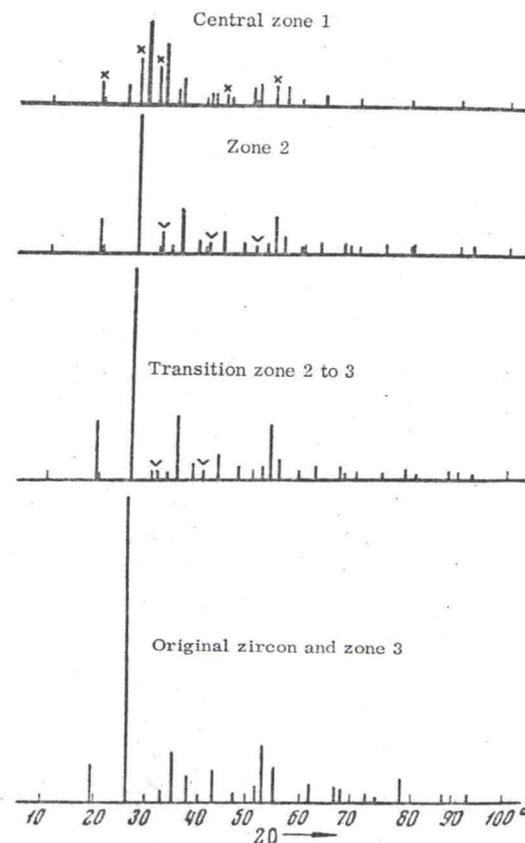


Fig. 1. Diffractograms for different zones of an ampoule with pressed zircon powder. In zones 2 and 2 to 3 ticks mark ZrO_2 lines, while in zone 1 crosses represent principal lines of the metamict zircon of [18] (No. 732 v). Test No. 2

To verify experimentally the assumption about the analogy with metamict decay and determine the essence of the vitreous transition, we selected zircon ($ZrSiO_4$) as the object of our tests since it is one of the most common natural

Central zone test No. 1	
I	$d_a/n. \text{ \AA}$
0.5	3.62
10	3.13
1	2.92
8	2.81
1	2.62
0.5	2.52
1	2.19
0.5	2.00
2	1.83
5	1.80
1	1.66
2	1.65
1	1.58
2	1.54
1	1.44
2	1.44
1	1.3

Note: C
3-No. 275
Asterisks

metamict mineral respect [12-15] diagrams for the original zircon powder of pale 0.2 mm in size the Kiya River zircon was free metamict decay. Ampoules with an 5 mm in diameter poured hexagonal 150 g. After 1 zones were observed of the charge 3) outer (in extent of zone substantially zone three is pattern and re zircon ($\omega = 1$ sintered, son ranging from The boundary

Table 1

Central zone, test No. 1		Central zone, test No. 2		Monoclinic ZrO ₂		Rhombic ZrO ₂		Central fritting zone		Original zircon	
I	d _α /n, Å	I	d _α /n, Å	I	d _α /n, Å	I	d _α /n, Å	I	d _α /n, Å	I	d _α /n, Å
0.5	3.62	2	4.47	3	3.67	w	3.66	1	4.45	1.5	4.47
10	3.13	3	3.67*	10	3.16			9	3.32	10	3.31
1	2.92*	7	3.32			s	2.97				
8	2.81	5	2.94*	8	2.83						
1	2.62*	8	2.84	8	2.83			0.5	2.66	0.5	2.66
0.5	2.52	2	2.64*	6	2.61	av	2.63	9	2.53	2	2.53
		4	2.53	4	2.54	w	2.55	1	2.35	1	2.34
1	2.19	2	2.21	5	2.20			0.5	2.23		
0.5	2.00	2	2.07			vw	2.08	5	2.08	1	2.07
		1	2.03	1	2.03						
2	1.83*	3	1.84	6	1.84	av	1.83	3	1.92	0.5	1.92
5	1.80*	3	1.81*	6	1.81	av	1.80				
		3	1.72*			w	1.72	2	1.76	1	1.76
1	1.69	2	1.69	5	1.69	w	1.70	10	1.72	2	1.72
2	1.65	3	1.66	5	1.65	w	1.66	0.5	1.70		
1	1.58*					av	1.58	6	1.66	2	1.65
								0.5	1.56		
2	1.54					av	1.54				
								0.5	1.51		
1	1.47	2	1.47	3	1.47	av	1.48	3	1.49	1	1.48
2	1.41					vw	1.42	8	1.39	1	1.38
						vw	1.39	2	1.37	1	1.36
1	1.32	1	1.33					1	1.30	0.5	1.29
								2	1.27		

Note: Operating conditions: 1—Co, 10 ma, 37 kv, URS—70; 2—Cu, 5 ma, 37 kv, URS—50 IM; 3—No. 275 of [18]; 4—of [19]; 5—Co, 10 ma 40 kv, URS—55; 6—Cu, 5 ma, 37 kv, URS—50 IM. Asterisks mark lines possibly representing rhombic ZrO₂ (test No. 1) or tetragonal ZrO₂ (test No. 2).

metamict minerals and has long been studied in this respect [12-15]. There are also experimental diagrams for the system SiO₂-ZrO₂ [16, 17]. The original zircon had an ω of 1.925 and was a powder of pale yellow transparent grains, 0.1-0.2 mm in size, from the Lower Cretaceous of the Kiya River basin (western Siberia). The zircon was fresh and almost unaffected by metamict decay. All tests were made in steel ampoules with an inner cavity 40 mm in length and 5 mm in diameter. The explosive used was poured hexogen with a weight of 80, 100 and 150 g. After pressing, the following same three zones were observed in all ampoules regardless of the charge weight: 1) axial, 2) intermediate, 3) outer (in cross section). The diameter and extent of zones along the ampoule do not vary substantially with the charge weight. Outer zone three is fully consistent in its X-ray pattern and refractive index with the original zircon (ω = 1.924). Zone two is a vitreous sintered, somewhat heterogenous substance ranging from dark to colorless and glass-clear. The boundary between zones two and three is so

indistinct that an intermediate zone two to three is recognizable. As can be seen from the X-ray patterns in Fig. 1, the principal lines become less intense and certain weak lines of long-range order (2θ > 70°) disappear on passing from zone three to zone two, but the intensities of some other weak lines increase. Zone two also exhibits the weak ZrO₂ lines characteristic of axial zone one. At the same time, in zone two, the refractive index of zircon decreases somewhat to 1.916. Studied preliminarily by M. Ya. Shcherbakova and V. A. Solntsev, the electron paramagnetic resonance spectra showed that the number of lattice flaws decreased from zone three to zone two, and that the electron paramagnetic resonance spectrum of zone two was qualitatively analogous to that of natural, partly metamict zircon. All these effects are analogous to the metamict conversion of zircon, although the degree of conversion is not very great. Axial zone one (cord), ~ 1 mm in diameter, is a metal-gray substance consisting mainly of crystalline ZrO₂ and amorphous SiO₂. The X-ray pattern (Fig. 1, Table 1) corresponds

AY¹

90 100°

of an amp- and 2 to 3 es repre- [18] (No.

tion about ermine ve se- our tests tural

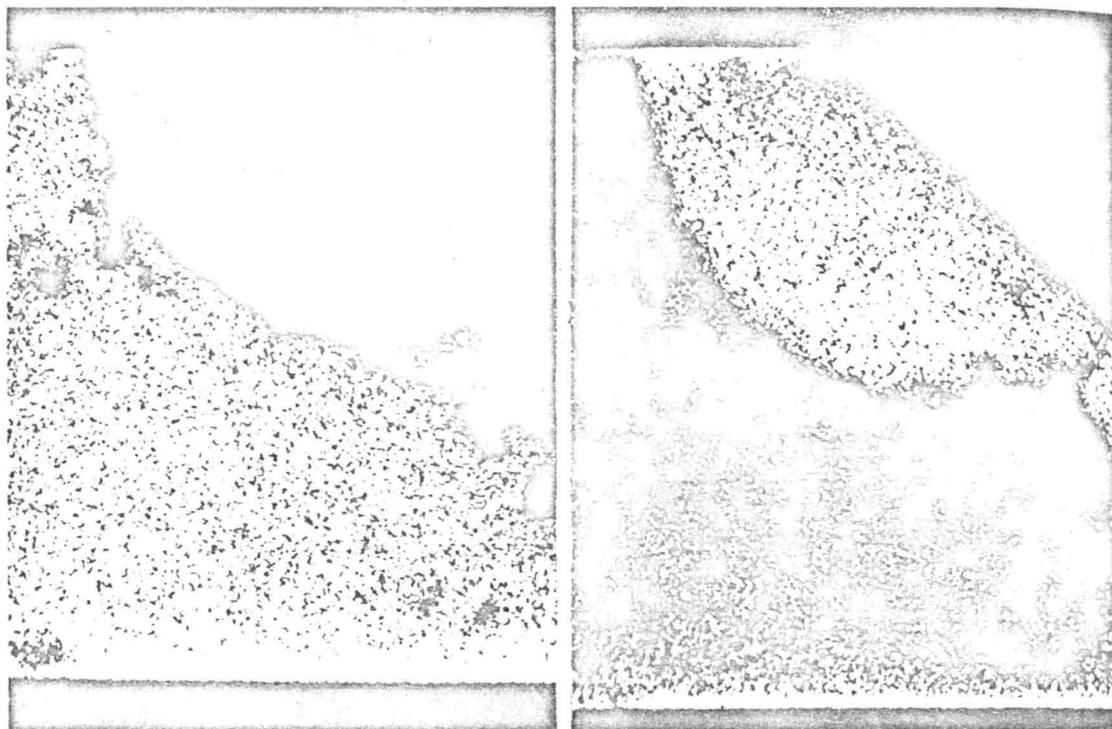


Fig. 2. Photograph of part ($100 \times 100 \mu$) of the central zone in X-radiation (SiK_α on the left, ZrL_α , on the right).

largely to that of the monoclinic modification of ZrO_2 . For test No. 1 representing the maximum charge (150 g hexogen) there are lines of another rhombic modification of zircon stable at high pressures [19]. The lines of crystalline SiO_2 phases are missing. In zone one there are round, bluish-white or glass-clear inclusions, the amount of which varies appreciably with the charge weight. At a maximum charge these bluish inclusions occur in small quantities, solely near the contact zones one and two. When the charge is increased (80 and 100 g hexogen) this phase becomes more plentiful, occurring throughout zone one; in this case the X-ray pattern (Table 1, test No. 2; Fig. 1) exhibits lines representing zircon of reduced density. The refractive index of this phase is very variable even within the same inclusion and ranges, on the whole, from 1.785 to 1.830. This phase, however, cannot be glass, for it remains markedly birefringent. Such low refractive indices are known for the most metamict zircon. Axial zone one was studied by Yu. G. Lavrent'yev on a MS-46 X-ray micro-analyzer. The central zone, including the bluish material, is not different in composition (within the limits of measurement precision) from the original zircon. Only the glass-clear round inclusions present in very small quantities near the edge of the axial zone are of pure SiO_2 (Fig. 2). Comparing the results of X-ray diffraction analysis, it can be assumed that the axial zone still consists mainly of a mixture of ZrO_2 and SiO_2 , although the particle size of

these phases is less than 1 to 2 μ , the area of the electron beam in the microanalyzer. Only a little of the SiO_2 was secreted as larger inclusions up to 100 μ in size. The bluish inclusions are relics of dissociated almost radioamorphous zircon. On the whole, zone one is a zirconoid representing the final product of metamict decay of zircon — a finely divided mixture of ZrO_2 , SiO_2 and the remains of radioamorphous ZrSiO_4 [12, 15]. The three ampoule zones are thus equivalent in a first approximation to different stages in the metamict decay of zircon culminating in the axial ampoule zone.

The degree of decay in the axial zone, in particular the amount of bluish inclusions of radioamorphous zircon, is a function of the charge weight. Like metamict zircon [15], after being calcined for 10 hr at 1200°, all zones (one, two, two to three, three) totally regained the zircon structure and their X-ray patterns became identical (Table 1). However, there are differences from the metamict decay of natural zircon. The chief difference is that there is a sharp transition between zones one and two (especially in the case of maximum charges) from a partly disintegrated lattice to total dissociation into oxides.

Another difference is that among the dissociation products of metamict zircon different authors mention all three modifications of ZrO_2 — pseudocubic, tetragonal and monoclinic [12-15]; whereas we have only the monoclinic.

It follows from experimental data on the

system SiO_2 - ZrO_2 above 1676°, zircon SiO_2 , after which formed almost in the separation of the tetragonal modification above 1170° and temperatures. The formation of (grated) zircon, modification of ZrO_2 , instead of glass are inconsistent or melting of Zr over, in static conditions requires very high temperatures of 1600°.

1. Wackerle, 1962.
2. Adadurov, Zhurn. p. 1962.
3. Deribas, Dokl. Akad. Nauk SSSR, 1962.
4. Ahrens, T. Geophys. Res. J., 1962.
5. Milton, D. 140, No. 1, 1962.

In the sum the multiple (Tadzhik SS which, when proved to be decided to ancient Cen The min equivalent made up of

system $\text{SiO}_2\text{-ZrO}_2$ [16, 17] that when heated above 1676° , zircon dissociates into ZrO_2 and SiO_2 , after which a SiO_2 -rich eutectic melt is formed almost immediately, at 1687° [17], with the separation out of ZrO_2 . Also, ZrO_2 forms the tetragonal modification at temperatures above 1170° and the monoclinic only at lower temperatures. The features mentioned above — the formation of defective (differently disintegrated) zircon, the epithermal monoclinic modification of ZrO_2 , and the secretion of pure SiO_2 instead of glass of intermediate composition — are inconsistent with the simple dissociation or melting of ZrSiO_4 when it is heated. Moreover, in static conditions, such dissociation requires very prolonged soaking even at temperatures of 1600 to 1700° [17].

Received June 19, 1968

REFERENCES

1. Wackerle, J. J. Appl. Phys., **33**, 922, 1962.
2. Adadurov, G. A., A. N. Dremine et al. Zhurn. prikl. mekh. i tekhn. fiz., No. 4, 1962.
3. Deribas, A. A., N. L. Dobretsov et al. Dokl. Akad. Nauk, **168**, No. 3, 1966.
4. Ahrens, T. J. and V. G. Gregson. J. Geophys. Res., **69**, 22, 1964.
5. Milton, D. J. and P. S. De Carli. Science, **140**, No. 3467, 670, 1963.
6. De Carli, P. S. and D. J. Milton. Science, **147**, No. 3654, 144, 1965.
7. Deribas, A. A., N. L. Dobretsov et al. Symposium H. D. P., Paris, 1967.
8. Goldschmidt, V. N. The Basic Ideas of Geochemistry, fasc. 1, 57, 1933.
9. Povarennykh, A. S. Zap. Vsesoyuzn. min. obshch., **85**, fasc. 4, 593, 1956.
10. Barsanov, G. P. Tr. Min. muzeya (Proceedings of the Mineralogical Museum), fasc. 10, p. 3, USSR Acad. Sci. Press, 1959.
11. Kostyleva, YeYe. In: Voprosy mineralogii, geokhimii i petrografii (Mineralogy, Geochemistry and Petrology), 1946.
12. Pabst, A. Am. Mineral., **137**, No. 3-4, 137, 1952.
13. Karyakin, A. V. Geokhimiya, No. 8, 1962.
14. Zyuzin, N. I. Dokl. Akad. Nauk, **154**, No. 5, 1964.
15. Toropov, N. A., V. P. Barzakovskiy et al. Diagrammy sostoyaniya silikatnykh sistem (Structural Diagrams of Silicate Systems), "Nauka" Press, 1965.
16. Toropov, N. A. and F. Ya. Galakhov. Izv. Akad. Nauk SSSR, otd. khimich. nauk, 1956, 158 (sic).
17. Butterman, W. C. and W. R. Foster. Am. Mineral., **52**, No. 5-6, 880, 1967.
18. Mikheyev, V. I. Rentgenometricheskii opredelitel' mineralov (X-Ray Identification of Minerals), Moscow, 1957.
19. Bendeliani, N. A. et al. Geokhimiya, No. 6, 677, 1967.

SOGDIANITE, A NEW MINERAL¹

V. D. Dusmatov, A. F. Yefimov, Z. T. Katayeva, L. A. Khoroshilova
and K. P. Yanulov

Institute of Mineralogy, Geochemistry and Crystal Chemistry
of Rare Elements; Geological Institute, Academy of Sciences, Tadjik
(Presented by Academician D. S. Korzhinskiy, April 30, 1968)

In the summer of 1964, while studying one of the multiple alkalic intrusions of the Alai Range (Tadjik SSR), V. D. Dusmatov found a mineral which, when subsequently studied by the authors, proved to be a new zirconium silicate. It was decided to call the mineral "sogdianite" after the ancient Central Asian state (Sogdiana).

The mineral occurs in pegmatite veins roughly equivalent to alkalic granite in composition, made up of microcline, quartz and aegirine. The

central parts of veins, where deposits of the mineral are the most frequent, consist of quartz nuclei with sporadically disseminated crystals of microcline and aegirine and accessory rare metal minerals like thorite, stillwellite, etc.

Sogdianite occurs as flaky grains up to $10 \times 7 \times 4$ cm in size, either included in quartz or (less commonly) confined to the spaces between microcline crystals.

The mineral has an elegant violet color of the kunzite type and a vitreous luster. It is often ideally transparent and less commonly turbid. The cleavage is perfectly parallel to (0001). There were no grains with clearly enough expressed crystal faces. The specific gravity of

¹Translated from: Sogdianit--novyy mineral. Doklady Akademii Nauk SSSR, 1968, Vol. 182, No. 5, pp. 1176-1177.