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ON METAMICTIC DISINTEGRATION OF  
THE ZIRCON GROUP OF MINERALS

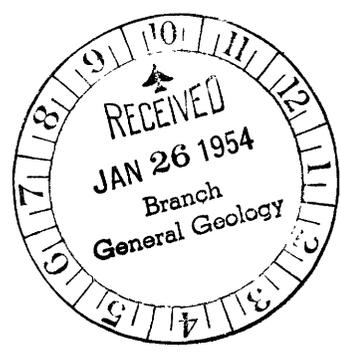
By  
E. E. Kostyleva

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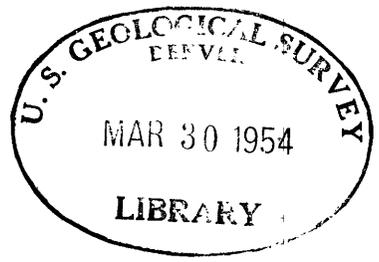
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Translated by Taisia Stadnichenko from p.27-35  
of Voprosy mineralogii geokhimii i petrografii,  
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#### GEOLOGY AND MINERALOGY

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## FOREWORD

The article on "Metamictic disintegration of the zircon group of minerals," by E. E. Kostyleva is one of the articles in the memorial volume dedicated to A. E. Fersman (1883-1945) by his pupils, friends, and coworkers. It appeared in a book entitled, "Voprosy mineralogii geokhimii i petrografii," published by the USSR Academy of Science, Moscow, 1946.

The translation was made in 1951 for Miss Jewell Glass of the Geological Survey who at the time was studying metamict zircons from San Bernardino County, California.

As the problem of metamictization and related phenomena are evoking such widespread interest at present, it was decided to make available in English this contribution to the problem of metamictic disintegration, especially with its original interpretations of the role of water in crystal structures.

Every effort has been made to insure the accuracy of the translation, but the responsibility for the accuracy of the data and the conclusions is the author's and does not belong to the Geological Survey nor to the translator.

July 27, 1953

Taisia Stadnichenko

ON METAMICTIC DISINTEGRATION OF THE ZIRCON  
GROUP OF MINERALS

E. E. Kostyleva

The term "metamictic" mineral was first introduced by Brögger in 1896, as an additional term to Breithaupt's classification of amorphous minerals into "porodins" and "hyalins". Brögger showed the existence of a third group: the metamictic group of minerals, which were first formed as crystalline substances, but later were transformed into glass-like isotropic substances with conchoidal fracture, preserving their original composition and the exterior crystalline form.

Metamictic alteration was shown in many minerals such as allanite, gadolinite, fergusonite, samarskite, euxenite, pyrochlore, polymignite, aeschinite, cyrtolite and others, most of which are rare-earth silicates and niobates. The phenomenon of metamictic disintegration is connected with changes of many properties of minerals: specific gravity, birefringency and refraction, hardness, cleavage, color, etc.

The capacity to regain the original crystalline state on heating to 500 -700 C is a characteristic property of the metamictic minerals.

The studies of the phenomena dealing mainly with fergusonite and gadolinite comprise an extensive literature (Th. Barth, Peters, Mügge, Scheteling, Liebisch).

The results of a fairly large number of observations and descriptions of the metamictic state of minerals were summarized by V. M. Goldschmidt in 1924 as follows:

1. Metamictic minerals are glassy, amorphous substances, which are optically isotropic, or very nearly isotropic.

2. The metamictic state is observed in compounds which have a weak chemical bond, compounds of weak acids and bases.

3. Metamictic minerals always contain large quantities of water.

4. On heating to 500-600 C metamictic minerals lose water and return to the original crystalline state frequently exhibiting luminescence, as they do so.

Brögger regarded the cause of the metamictic changes of minerals as due to insufficient stability of the complex crystalline "molecules" constituting metamictic minerals. Other authors (Hamberg, Scheteling, and especially Mügge, 1922) saw the radioactive radiation of U and Th as the cause of metamictic changes. Goldschmidt, as has been pointed out above, regarded the weakness of chemical bonds as the principal cause of the metamictic changes.

The essential features of metamictic change, according to V. M. Goldschmidt, lie in the change of charge of compounds. For example,  $YNbO_4$  changes into  $Y_2O_3$  and  $Nb_2O_5$ . A. E. Fersman assumes that "annealing of pegmatite" had some part in metamictic disintegration; metamictic minerals which are stable at high temperatures at which they are formed become unstable at the lower temperatures in the process of annealing of pegmatite and readily disintegrate especially under the effect of irradiation.

The data on the study of the metamictic state of zircon group of minerals which provide new material for explaining the basic principles of the process itself and establishing the causes of its rise are given below. Zircon, because of the simplicity of its composition, its formula, and its wide distribution is a very convenient mineral for the study of this process.

Two types of metamictic state have been established in the zircon group of minerals:

1. Metamictic state in water-free zircons of almost theoretical composition

2. Metamictic state in zircons containing water and having composition differing considerably from theoretical.

Both types of process are described in detail below.

I. Ceylon zircon pebbles derived from a rare-earth pegmatite in the area of the City Balongoda 1/ were used as material for study.

Metamictic zircons were represented by individual, considerably rounded crystals of 1 to 1 1/2 cm in diameter. The crystals are slightly dull on the surface, but in the fracture planes they are bright and have a fresh appearance; they are green colored of different shades from dark drab brown to black. The green varieties are transparent, the black varieties are barely translucent in thin fragments. The fracture plane is highly conchoidal. In the fracture planes the crystals, particularly the black varieties, seem to be amorphous. On breaking the crystals noticeable viscosity is shown. The specific gravity of metamictic zircons is very low. It varies from 3.9 to 4.2-4.3. Thin sections of the minerals in transmitted light have very coarse shagreen surfaces; the texture of many specimens resembles disintegration texture. The minerals are optically isotropic or have low birefringency. On heating in platinum crucible to red heat many crystals showed unusual luminescence which begins in a single area, rapidly spreads out through the entire crystal, and disappears. On repeated heating no luminescence is observed.

X-ray study of the powder pattern, together with the determination of the specific gravities of the fresh and ignited material permit us to recognize among metamictic zircons the following groups:

1. Highly altered metamictic zircons. Specific gravity very low; it varies from 3.8 to 4.0. Color: green, very dark drab brown, or almost

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1/ Collected by G. P. Chernik

black. On heating to red heat the crystals always glow. After heating the specific gravity either remains the same or is slightly lowered.

Powder patterns of the common unignited material give no lines; after ignition the powder patterns show distinct  $ZrO_2$  lines of pseudo-cubic type with  $a = 5.091 \text{ \AA}$ , several weak lines of  $\beta$ -quartz, and weak lines of  $ZrSiO_4$ . In these samples the distortion of the bonds in the lattice reached complete disintegration of  $ZrSiO_4$  into  $ZrO_2$  and  $SiO_2$ . It is so complete that on heating in the range of temperatures between 700 to 800 no reconversion into the zircon lattice takes place, but even more complete disintegration into the component oxides may be seen in powder patterns.

The products of the metamictic disintegration are no longer zircons, as their physical properties are quite different. They represent a solid solution of  $ZrO_2$  and  $SiO_2$  and small amounts of  $ZrSiO_4$  and were classed by the author in 1936 under the name of zirconoids.

The composition of the water-free zirconoids, approaching the theoretical composition without the water, shows that the lowering of the specific gravity parallels the disintegration. Slight swelling of the crystal is a result of the disintegration because of the larger volume of the unit cells of  $ZrO_2$  [ $a^3 = 131.49 \text{ \AA}^3$ ] +  $SiO_2$  [ $6sc = 161.1 \text{ \AA}^3$ ] =  $295.59 \text{ \AA}^3$ . A comparison with the volume of the unit cell of  $ZrSiO_4$  ( $a^2c = 232.27 \text{ \AA}^3$ ), i.e., the volume of the crystal on complete disintegration, must increase in the ratio of  $\frac{296}{232} = 1.27$ , whereas the specific gravity should become lower in the same ratio.

The heating curve at 920 shows a sharp exothermic bend produced by the evolution of energy during the transformation of the mineral from the amorphous into the crystalline state (fig. 1).

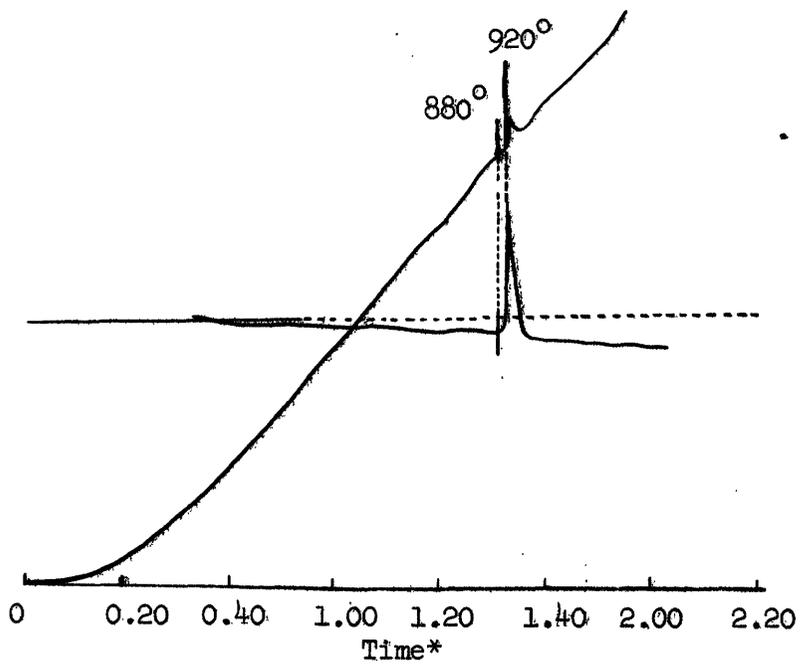


Figure 1.--Heating curve of zirconoid from Ceylon.

\*Time unit not shown, but it probably is hours.

T. S.

2. The less altered metamictic zircons. Their color is green, specific gravity 4.1 to 4.3. On heating the specific gravity increases. Thus, a zircon with specific gravity of 4.01 became 4.19 after ignition. Luminescence is not always observed. In the natural state no powder pattern is formed, but after ignition the  $ZrSiO_4$  line appears; the dimensions of the unit cell are:  $a_0 = 0.59 \text{ \AA}$ ,  $c_0:a_0 = 0.923$ . The heating curve also shows an exothermic bend.

For these zircons the distortion of the bonds in the lattice of  $ZrSiO_4$  is not very great and on heating the regeneration of the zircon lattice takes place.

The metamictic disintegration of the described type, as follows from analysis, depends on the presence of  $U_3O_8$  (0.86 percent). Individual determinations of  $U_3O_8$  made by V. I. Baranov for the different metamictically altered zircons are shown in table 1 in percent.

Table 1

<u>Name of the mineral</u>	<u>Color</u>	<u>Sp. gr.</u>	<u>Content of <math>U_3O_8</math></u>
Zirconoid	Black	3.9	1.19
Zircon	Green	4.1	0.61
Zircon	Colorless	4.5	0.21

Therefore, the larger content of  $U_3O_8$  corresponds to the more complete metamictic disintegration.

This type of metamictic disintegration is a new type, not previously found in the literature on metamictic disintegration of the minerals. It is characterized by:

(a) The simplicity of its composition, approaching the theoretical formula of zircon; absence of the isomorphic admixtures in the lattice (with the exception of U).

(b) The absence of water in the products of the disintegration, i.e., the metamictic disintegration is unaccompanied by the adsorption of water.

(c) The process proceeding to complete disintegration into the initial oxides, which do not regenerate on heating up to 1,000.

The described type of change definitely shows that the fundamental cause of the metamictic state of minerals is due to radiation from uranium present in the lattice.

II. Metamictic disintegration, accompanied by introduction of large amounts of water was studied in cyrtolites from Zap. Olenya Varaka in northern Karelia. A mineralogical description of this deposit has been made by A. N. Labuntsov.

Cyrtolite from this deposit is dark drab brown to honey yellow in color. It forms small crystals with forms (100) and (111) in the feldspar and biotite and large twinned radial aggregates with well-developed terminations. The fracture is fine conchoidal, luster slightly fatty; it is slightly transparent on thin edges. Optically it is isotropic to slightly anisotropic in separate areas. In thin section the mineral is clean without visible inclusions of foreign minerals, except specklike inclusions of uraninite. Specific gravity of the mineral is 3.76, after ignition it is 4.14; on ignition the mineral does not luminesce. Powder pattern of the unignited mineral gives lines which are not clear. After ignition  $ZrSiO_4$  lines appear. The sizes of the unit cells are:  $a_0 = 6.455 \text{ \AA}$ ,  $c_0:a_0 = 0.920$ . The mineral fuses with difficulty and does not readily decompose with acids. The chemical analysis of the mineral, made by L. B. Tumilovich in the laboratory of the Geological Institute, is given in table 2. The analysis shows that in addition to  $ZrO_2$  and  $SiO_2$  the mineral

Table 2.--Chemical composition of zircon from Ceylon and cyrtolite from Zap. Olenya Varaka, Karelia

Components	Zircon weight (percent)	Cyrtolite			
		Weight (percent)	Mol. ratio	atom.	ratios
SiO <sub>2</sub>	31.08	28.84	0.478	478	478
TiO <sub>2</sub>	0.00	0.02	--	--	--
ZrO <sub>2</sub>	67.14	47.82	388	388	--
HfO <sub>2</sub>	--	1.70	8	8	396
U <sub>3</sub> O <sub>8</sub>	0.86	1.27	1	3	--
Al <sub>2</sub> O <sub>3</sub>	0.00	0.71	6	12	--
Fe <sub>2</sub> O <sub>3</sub>	0.83	1.56	9	18	12
TR <sub>2</sub> O <sub>3</sub>	0.16	1.42	6	12	--
MnO	--	0.11	1	1	--
CaO	0.00	4.72	84	84	--
MgO	0.00	0.17	4	4	123
Na <sub>2</sub> O )	0.06	0.59	9	18	--
K <sub>2</sub> O )		0.28	2	4	--
SO <sub>3</sub>	0.00	0.72	9	9	--
P <sub>2</sub> O <sub>5</sub>	--	n.f.	--	--	--
H <sub>2</sub> O 110	0.12	1.56	--	--	--
H <sub>2</sub> O 110	--	8.52	473	--	--
Total	100.25	100.01			

Zr (Hf, TR, Ca, Mg, Mn, Na) = 519

Si (Al, Fe, S) = 517

n.f. - not found

also contains Y, Ca, U, Fe, Al, Mn, Mg, and a large quantity of water. On recalculation the molecular ratio  $\text{SiO}_2$  and  $\text{ZrO}_2$  is less than 1, showing an excess of  $\text{SiO}_2$ . However, the ratio of Zr (Hf, Y, Ca, Mg, Mn): Si (Al, Fe, S) is very close to 1.

The presence of the other elements in cyrtolite, such as Y and Ca, is undoubtedly primary, because these elements have been determined in all of the samples analyzed. Hevesy observed regular presence of TR (rare earths) and the presence of Y indicates high content of Hf in cyrtolite, which may be explained, on the basis of crystal chemistry, by the proximity of the two elements in the periodic table. Similar explanation could be given for calcium.

II	III	IV
Ca	Sc	Fe
Sr	Y	Zr
		Hf
		Th

The isomorphous substitution of Hf and Ca proceeds along the diagonal of the periodic table.

The introduction of Ca and Y, elements of lower valence and smaller atomic number than Zr, but with larger ionic radii (Ca 1.06; Y 1; Zr 0.87) into the crystal lattice is energetically less favorable. Consequently, the electrostatic balance is altered and the crystal becomes less perfect.

Therefore, it may be assumed that the primary entry of water into cyrtolite represents compensation in the electrostatic balance as well as replacement in the possible distortions and voids of the crystal. Hence, the determination of the character of water in cyrtolite is extremely important.

The heating curve, obtained by G. B. Shmakova (fig. 2), shows an endothermic bend at  $200^{\circ}$ , related to the loss of  $H_2O$ , and an exothermic bend at  $860^{\circ}$ , produced by the transformation of the mineral from the metamictic into the crystalline state.

The dehydration curve (fig. 3) was obtained by the author by heating the mineral in an electric furnace at different temperatures to constant weight. The temperature was measured by a thermocouple. The dehydration curve is in agreement with the heating curve. It also shows a sharp bend at  $200^{\circ}$  related to the loss of 5.22 percent of water. Above  $250^{\circ}$  the dehydration curve proceeds without an upward bend and gradually flattens out. At  $600^{\circ}$  a slight break is observed, and at higher temperature the dehydration curve becomes a straight line. At  $1000^{\circ}$  the dehydration is practically complete.

The character of the dehydration curve in the interval from 0 to  $250^{\circ}$  resembles the curve of Kuttlich's hydrates of silica. The dehydration curve from  $250^{\circ}$  to  $600^{\circ}$  corresponds to the loss of dissolved water and may be related to the dehydration of zirconium hydroxide, which, according to Weiser, has no definite hydrates, but contains water of solution; its loss is complete at about  $500^{\circ}$ .

The break in the dehydration curve at  $600^{\circ}$  and a flatter curve above  $600^{\circ}$  indicate a slower rate of water loss due to the more stable position of water in the lattice of the mineral than that of the water of hydration. High temperature of dehydration of this part of the water (1 to 1.5 percent) in the interval between  $600^{\circ}$  and  $800^{\circ}$  corresponds to the formation of cyrtolite mineral (phase B-C of the pegmatite process)<sup>2/</sup> and also indicates the entry of water into the lattice. The lack of a

<sup>2/</sup> Fersman, A. E., Pegmatites, vol. 1, Granite-pegmatites, 2d edition, pp. 712, Moscow, 1940. Chapter IV (pp. 37-39) deals with the concept of "geophase". Geophases B-C fall into the zone of temperatures from  $800$  to  $600^{\circ}$  and lower and correspond with the epigmatic zone (Becke) on one hand and true

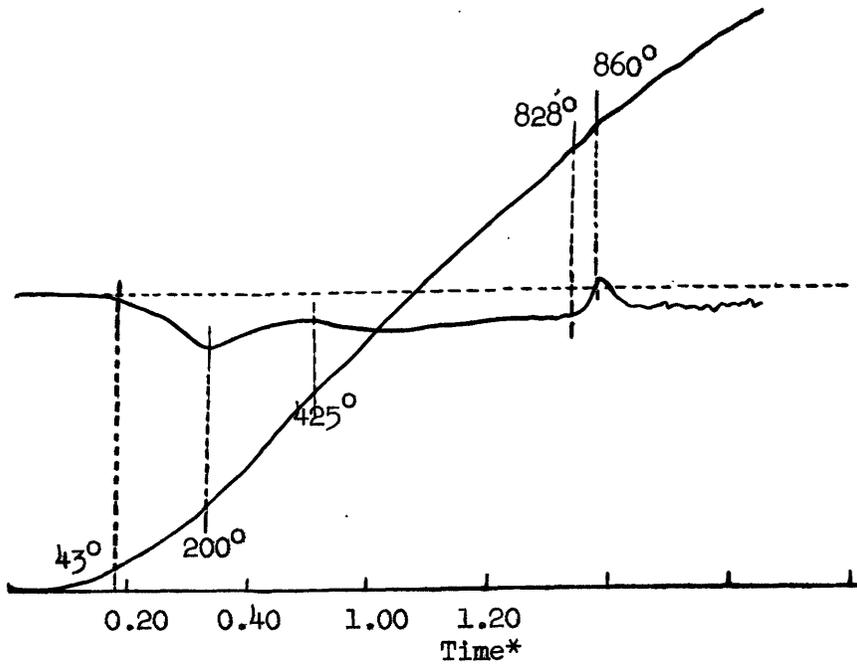


Figure 2.--Heating curve of cyrtolite. Zap. Olenya, Karelia.

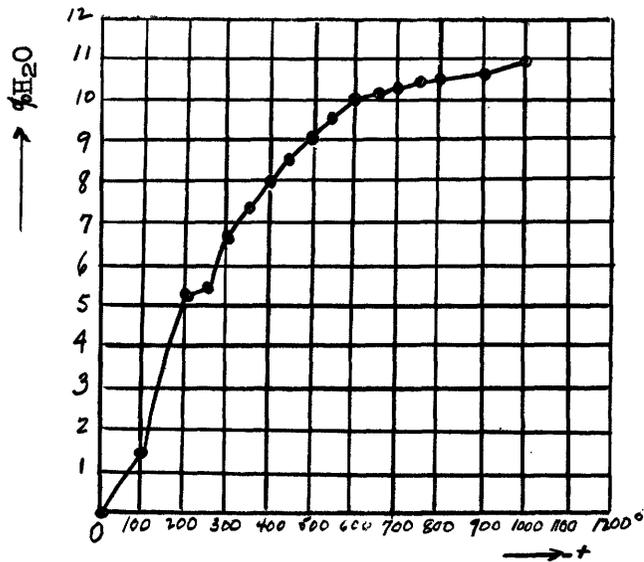


Figure 3.--Dehydration curve of cyrtolite.

\*Time unit not shown, but it probably is hours. T. S.

sharp bend in the curve above  $600^{\circ}$  explains the metamictic state of the mineral, which leads to a decrease in bond strength between the elements of the lattice and results in comparatively easy loss of the bound water.

Cyrtolite, as can be seen from analysis (table 2), contains 1.27 percent  $U_3O_8$ . Microscopic analysis showed microinclusions of uraninite; the problem of quantitative entry of uranium into the lattice of the mineral is not clear. The cause of metamictic disintegration besides  $\alpha$ -radiation may also be due to instability and nonhomogeneity of the cyrtolite lattice as a result of its complex composition and considerable deviation from the formula of cyrtolite. Nonhomogeneity of the lattice may also result in greater ease of hydration of the mineral during the metamictic disintegration.

The results of the study of the metamictic disintegration of zircon group of minerals discussed above may be summarized as follows:

1. Metamictic disintegration is the result of distortion in the lattice bonds produced by  $\alpha$ -radiation of radioactive substances present in the mineral lattice.
2. Metamictic disintegration is not always accompanied by entry of water. In a zircon with composition closely approximating the theoretical composition metamictic disintegration proceeds without adsorption of water.
3. Metamictic alteration may lead to complete disintegration of the mineral into oxides.
4. In minerals with complex composition greatly differing from the theoretical formula of zircon large amounts of water are found. Part of this water which is removed at high temperature enters into the lattice of the mineral. This type of metamictic disintegration requires further

study of other metamictic minerals and the causes of the water entry and its relation in the mineral of complex composition.

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