The Crystal Chemistry of Complex Niobium and Tantalum Oxides. IV. The Metamict State: Discussion

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Abstract

Graham and Thornber (1974b) have proposed a mechanism for metamictization in complex niobium-tantalum oxides in which complex compositions, rather than radiation damage, are the primary requirement. This note reviews the literature in support of radiation damage as a necessary condition for metamictization and suggests that the structural stability of the metamict "glass" relative to that of the crystalline pre-metamict material is an important consideration in predicting whether a substance will occur in the metamict state.

Introduction

Graham and Thornber (1974b) in an excellent study of complex niobium-tantalum oxides have proposed a new mechanism for the process of metamictization. Their model relies on the micro-exsolution of phases with similar structures in Nb-Ta oxides of complex compositions. The effect of radiation damage in the metamictization process is considered to only "accelerate the disproportionation." Although the process of metamictization is a complex one in which numerous factors must be considered, the purpose of this note is to reemphasize the importance of radiation damage in the metamictization process, particularly for the complex, orthorhombic, AB_2O_6-type Nb-Ta-Ti oxides, as well as to suggest that the structure of the metamict glass relative to that of the premetamict crystalline material is an important consideration in evaluating whether a substance may occur in the metamict state.

Metamictization in Complex, Orthorhombic AB_2O_6-type Nb-Ta-Ti Oxides

In Table 1, compositional data demonstrate the importance of uranium and thorium in the process of metamictization of complex AB_2O_6-type Nb-Ta-Ti oxides. Although the data in the literature are limited, in general those specimens of euxenite, fersmite, aeschynite, and lyndochite which are found in the crystalline state have distinctly lower uranium and thorium contents than their metamict euxenite and aeschynite counterparts. A similar relation has been demonstrated for zircons by Holland and Gottfried (1955). Graham and Thornber (1974b) have

rightly pointed to structural and compositional mechanisms for metamictization in complex Nb-Ta oxides; but these models cannot be separated from the necessary catalytic effect of radiation damage. The heart of the difficulty in understanding the process of metamictization lies in evaluating the interaction of alpha particles with different structures and compositions.

Hamberg (1914) was the first to suggest that metamictization is caused by irradiation of substances by particles which originate in the decay of radioactive isotopes of the uranium and thorium series within a crystal structure. Later work by Mügge (1922), Von Stackelberg and Rottenback (1940), Morgan and Auer (1941), Kostyleva (1954), and Holland and Gottfried (1955) supports this theory, but the mechanism of the interaction of alpha particles with the target material may vary.

Three effects are responsible for radiation damage: (1) a high velocity alpha particle may dissipate energy by excitation of electrons and ionization of atoms along its path, (2) a low velocity alpha particle may lose energy by collision, and (3) the energy of the alpha particle may be dissipated in the form of heat, resulting in a thermal spike which can reach temperatures of 10^4K for periods of 10^{-11} seconds along the path of the alpha particle. The last two effects are considered important in causing radiation damage (Chadderton, 1965). The collisions cause dislocations and Frenkel defects. Solidification of the material in the thermal spike area may result in: (1) a glass (Ueda, 1957); (2) finely crystalline component oxides (Ueda, 1957; Lipova, Kuznetsova, and Makarov, 1965; Makarov, 1970); (3) the original

TABLE 1. Uranium and Thorium Content of Non-Metamict and Metamict AB_2O_6-Type Nb-Ta-Ti Oxides

| | Weight percent | |
	U_3O_8	ThO_2
Non-Metamict		
Euxenite (Nefedov, 1956)*	--	--
Fersmite (Alexandrov, 1960)*	--	--
Aeschynite (Alexandrov, 1962; Zhabin et al 1962)	not det.	0.72
Aeschynite (Čech et al, 1972)	0.25**	2.26**
Lyndochite (Gorzhevskaya and Sidorenko, 1962)	0.08***	3.75
Metamict		
Euxenites (mean value of 28 analyses from the literature)	9.31	3.08
Aeschynites (mean value of 22 analyses from the literature)	1.21	10.73

*semiquantitative analysis, no U or Th reported.
**electron microprobe analysis by R.C.E.
***reported as UO_3.

phase with atoms in new lattice positions, e.g., a displacement spike (Brinkman, 1954); or (4) annealing of dislocations and Frenkel defects in the parent structure (Brinkman, 1954; Ueda, 1957). Primak (1954) has suggested that this ability of some materials to restore disrupted structure by thermally induced self-annealing is the main property which determines the degree of metamictization. Studies of radiation damage in reactor materials (Slater, 1951; Seitz, 1949, 1952; Dienes, 1953; Dienes and Vineyard, 1957; Whapham and Sheldon, 1965; Solomon, 1973) have shown that the nature and extent of radiation damage is a combination of all these effects, with the relative importance of each being dependent on the type of energy of the incident radiation as well as the structure and bonding of the target material. Also, some recovery usually occurs during or just after irradiation, and the magnitude of the effect is sensitive to the temperature of both the irradiation and observation.

It is the variation in the structure and bonding of geologic materials which caused early workers such as Goldschmidt (1924) and Faessler (1942) to note that the presence of uranium and thorium is a necessary but not sufficient condition for metamictization. There are minerals which maintain their structures against relatively high alpha-particle fluxes (e.g., xenotime, monazite, and thorianite) while others are found in a completely metamict state and yet contain trace amounts of uranium and thorium (e.g., gadolinite). The most striking example of this effect is seen in the dimorphous forms of $ThSiO_4$—thorite

and huttonite. Tetragonal thorite is nearly always found in the metamict state (Pabst, 1952) while monoclinic huttonite has been reported only in crystalline form. Thus, radioactivity, while important, seems but a partial explanation of the process of metamictization; and any theory must account for the "disposition" of structures toward the metamict state. This "disposition" has previously been variously attributed to: (1) alteration involving hydrolysis (Broegger, 1890; Dana, 1892; Lacroix, 1922), (2) extensive isomorphism particularly of the rare earths (Faessler, 1942; Pyatenko, 1970), (3) the weakness of chemical bonds of the original phase as compared to the chemical bonds of the simple component oxides (Goldschmidt, 1924), (4) the degree of covalency (Slater, 1951; Pellas, 1954; Lipova, 1966), (5) auto-oxidation (Ellsworth, 1925, 1932; Tomkeieff, 1946; Hutton, 1950; Povarennykh, 1956), (6) instability at lower pressures (Vegard, 1927; George, 1949), and (7) alteration resulting in pseudomorphic replacement (Zhieov, 1952). Graham and Thornber (1974b) have proceeded one step further, considering that "the metamict state in niobium-tantalum oxide minerals is not due to radiation damage, but to their complex chemical compositions." This becomes a difficult question to resolve as the presence of uranium and thorium is usually indicative of complex compositions (e.g., they may be accompanied by REE). In either case, it is important to consider the compositional and structural features that may contribute to the "disposition" of the orthorhombic, rare earth AB_2O_6-type Nb-Ta-Ti oxides to metamictization.

Because minerals of the euxenite-polycrase and priorite-aeschynite series are nearly always found in the metamict state, structural data is available for only two non-metamict natural compositions—aeschynite (Alexandrov, 1962) and fersmite (Alexandrov, 1960). The general features of both structures have been summarized by Graham and Thornber (1974a), but certain specific features of the structures that may make these Nb-Ta-Ti oxides susceptible to radiation damage are:

1. Compositions are characterized by extensive isomorphous substitution in the A site which results in variable bond lengths and charge distributions for the individual coordination polyhedra. Although the A-site cations of fersmite and aeschynite are in 8-fold coordination (Alexandrov, 1960, 1962), the variation in A-site ionic radii causes distortion of the coordination octahedra and smaller cations (Fe^{3+}, Y^{3+}) are probably more stable in

six-fold coordination. Also, the electrostatic charge distribution is irregular. For fersmite (Alexandrov, 1960) the oxygens are overbonded or underbonded by the following mean values:
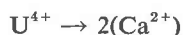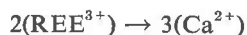
$$O_I = +1\ 1/3$$

$$O_{II} = +2\ 1/6$$

$$O_{III} = +2\ 1/2$$

This electrostatic imbalance is in part compensated by differences in the mean cation-anion distances (Alexandrov, 1960). As isomorphous substitutions increase, the electrostatic charge balance may show even wider deviations.

(2) Isomorphous substitutions in the A site of the types:

$$2(REE^{3+}) \rightarrow 3(Ca^{2+})$$

$$U^{4+} \rightarrow 2(Ca^{2+})$$

result in primary A-site deficiencies, and with hydration and replacement of O^{2-} by $(OH)^{1-}$, secondary A-site deficiencies are also formed (Pyatenko, 1959). Primary deficiencies in the A site are about 15 percent and may increase to 60 percent with alteration (Van Wambeke, 1970).

(3) For fersmite and aeschynite the coordination polyhedra of A- and B-site cations share edges as well as apices, with a subsequent decrease in crystal stability relative to structures in which only apices are shared. Although this is an admitted simplification, it may become an important factor when considering the stability of a metamict structure relative to the pre-metamict crystalline structure.

(4) The (Nb,Ta,Ti)–O bonds are not completely ionic (Bouška, 1970; Alexandrov, 1962). Slater (1951), Kinchin and Pease (1955), and Lipova (1966) have pointed out that substances with covalent bonds experience greater permanent radiation damage, since the restoration of the bond requires a greater activation energy than ionic bonds. As noted by Pellas (1954), the metamict state is characteristic only for minerals with partially covalent bonds. This feature agrees well with Smekal's view (see summary by Rawson, 1967) that "mixed" chemical bonds are required if a material is to form a glass. This correlation can be quantified by considering electronegatives (see Rawson's summary of Stanworth's work, 1967) or the field strength. High values of field strength are characteristic of glass forming oxides; and low values, of oxides that do not form a glass (Lipova, 1966).

The Structure of the Metamict "Glass" in Complex Nb-Ta-Ti Oxides

Another approach to the study of metamictization is to consider the relative stability of the glass to the crystalline structure and the kinetics of glass formation, particularly as it relates to understanding the factors which determine whether or not a particular substance is likely to form a glass. Here again the discussion must remain qualitative as efforts at developing a general theory of glass formation "are usually more in the nature of tentative guesses" (Rawson, 1967). Some substances readily form glasses (*e.g.,* SiO_2, GeO_2, B_2O_3) while others form glasses only with the addition of oxides of restricted compositional ranges (*e.g.,* TeO_2, SeO_2, Al_2O_3, V_2O_5). Aside from compositional constraints, the formation of a glass will depend on the rate of cooling and rate of crystallization. Compositions, bond strengths, melting point temperatures, rates of cooling, and kinetics of crystallization all interact and provide a complex picture of glass formation.

Modern ideas of the structure of inorganic glasses developed from observations by Goldschmidt (1926) who noted that the cation-anion radius ratio of glasses lie in the range 0.2 to 0.4. Goldschmidt was then led to the conclusion that a tetrahedral arrangement of oxygens around the cation is necessary for glass formation. Zachariasen (1932) amplified Goldschmidt's observations, assuming that the excess energy of the glass could not be much greater than that of the crystalline structure (else devitrification would occur). He envisioned the glass structure as being similar to the crystalline structure (*e.g.,* composed of the same types of coordination polyhedra joined in a similar manner) except with the coordination polyhedra in random orientations and without long range periodicity and without causing an increase in cation-cation repulsion. These considerations may be formalized, appropriately enough, into Zachariasen's Rules:

1. each oxygen atom is linked to not more than two cations,
2. the number of oxygen atoms around cations must be small, and
3. the oxygen polyhedra share corners with each other, not edges or faces.

Zachariasen's rules have been subject to criticism, and oxide glasses may be formed that do not obey the rules (Rawson, 1967), but there is an interesting feature of the rules that seems to bear on the metamict Nb-Ta-Ti oxides. Consider the general formula of the commonly metamict Nb-Ta-Ti oxides,

AB_2O_6 (euxenite, polycrase, priorite, aeschynite, polymignite, kobeite) and $A_{2-x}B_2O_7$ (pyrochlore, betafite, and samarskite [note, the formula for samarskite may be included in either category; Nilssen, 1970]). In all of these cases the B-site cations are in octahedral coordination, with each octahedron sharing at least two edges with neighboring B-site octahedra. According to Zachariasen's rules, glasses of the general formulas $A_mB_2O_6$ and $A_mB_2O_7$ must have the B-site cation in octahedral coordination. Such a glass consists of a random three-dimensional framework of B-site octahedra joined along their apices. A-site cations occupy the "holes" in the three dimensional framework. Conforming to Zachariasen's nomenclature, where the general formula of a glass is given as A_mB_nO, the B-site cation would be the "network forming oxide" and the A-site cation the "network modifying oxide." Nb_2O_5 and Ta_2O_5 are listed as possible network forming oxides. Simplistically, the metamictization of Nb-Ta-Ti oxides of types AB_2O_6 and $A_{2-x}B_2O_7$ involves the disruption of the periodic arrangement of the B-site octahedra, which results in: (1) a transition from edge sharing of octahedra to corner sharing, (2) an increase in volume and decrease in density, (3) microfracturing if the increase in volume is constrained, and (4) distribution of A-site cations throughout "holes" of the glass structure as well as absorption of molecular water. The stability of the glass may be only slightly less than that of the crystalline structure, because the extensive isomorphous substitution and A-site deficiencies are easily accommodated in the glass structure. Thus, there is little driving force for devitrification, recrystallization, or self-annealing of radiation damage. In contrast, for structures of simple compositions (*e.g.*, columbite) and no A-site deficiencies, the periodic arrangement of B-site octahedra is a much more stable configuration than the glass structure, and the driving force for continued self-annealing is greater. Although the ·argument here is qualitative, the important point is that structure of the glass may be as important as the structure of the crystalline material in determining why certain minerals persist in the metamict state (by a different line of reasoning, Primak (1954) has suggested a similar idea).

As with most qualitative pictures, detailed examination reveals inconsistencies. Zachariasen's rules have been criticized and exceptions documented (Rawson, 1967). In 1932, Zachariasen was not aware of the synthesis of glass-forming oxides of the type AO_3, A_2O_7, or AO_4 and therefore assumed, as Goldschmidt (1924) had, that network-forming oxides must have either trigonal or tetrahedral coordination, in contradiction with the suggested octahedral coordination of B-site cations in metamict Nb-Ta-Ti oxides. Additionally, although Zachariasen considered Nb^{5+} and Ta^{5+} as potential network-forming cations, he felt the network-modifying cations must be large and carry a small charge (*e.g.*, Na^+, K^+, Ca^{2+}). While this in part conforms to the composition of complex Nb-Ta-Ti oxides, one should note the presence of REE^{3+}, U^{4+} and Th^{4+}. Finally, although the complex Nb-Ta-Ti oxides of the general formula AB_2O_6 and $A_{2-x}B_2O_7$ conform to a model in which the coordination polyhedra of the crystalline structure form a random three dimensional framework in the glass structure, fergusonite (ABO_4) is an exception. According to Zachariasen's rules ABO_4 compositions should have the B-site network-forming oxides in octahedral coordination, but the B-site cations for fergusonite are in tetrahedral coordination. Thus, the transition from a crystalline to metamict state would involve a change in the coordination of B-site cations. A three dimensional glass could be formed from the B-site tetrahedra only for A_mBO_2 and $A_mB_2O_5$ compositions.

Conclusions

A substantial body of evidence supports the idea that metamictization is a result of radiation damage caused by alpha particles originating from constituent U and Th atoms within the crystalline structure. The main question lies in explaining why particular structures and compositions have a "disposition" toward the metamict state. The answer requires a consideration of the structural stability of the metamict material relative to that of the homogeneous crystalline pre-metamict material. Whether the metamict material consists of well ordered micro-domains as suggested by Graham and Thornber (1974b) or a three-dimensional random network of coordination polyhedra as suggested in this article, the catalytic role of the radiation damage cannot be discounted. Finally, one should note that the presence (Vance and Anderson, 1972; Lipova *et al,* 1965) or absence (Akhmanova and Leonova, 1961) of finely divided ZrO_2 in metamict zircons does not detract from the role of radiation damage as a mechanism for metamictization.

Note Added in Proof

For additional analyses of nonmetamict aeschynites see S. Rosenblum and E. L. Mosier (1975) Nonmetamict nioboeschynite-(Ce) from Alaska. *Am. Mineral.* **60,** 309–315.

Acknowledgments

References

AKHMANOVA, M. V., AND L. L. LEONOVA (1961) Investigation of metamictization of zircons with the aid of infrared absorption spectra. *Geochem. Int.* **5**, 416–431.

ALEXANDROV, V. B. (1960) The crystal structure of fersmite. *Dokl. Akad. Nauk. USSR,* **132**, 669–672.

——— (1962) The crystal structure of aeschynite. *Dokl. Akad. Nauk. USSR,* **149**, 181–184.

BOUŠKA, VLADIMIR (1970) A systematic review of metamict minerals. *Acta Univ. Carol.* **3**, 143–169.

BRINKMAN, J. A. (1954) On the nature of radiation damage in metals. *J. Appl. Phys.* **25**, 961–968.

BROEGGER, W. C. (1890) Die Mineralien der Syenitpegmatitgänge der südnorwegischen Augit - und Nephelinsyenite. *Z. Kristallogr.* **16**, 110; 122–126; 174–180; 389.

ČECH, FRANTISEK, S. VRÁNA, AND P. POVONDRA (1972) A non-metamict allanite from Zambia. *Neues Jahrb. Mineral.* **116**, 208–223.

CHADDERTON, L. T. (1965) *Radiation Damage in Crystals.* John Wiley & Sons, Inc., New York, 202 p.

DANA, E. S. (1892) *System of Mineralogy,* 6th ed., Vol. 1. John Wiley & Sons, Inc., New York.

DIENES, G. J. (1953) Effects of nuclear radiation on the mechanical properties of solids. *J. Appl. Phys.* **24**, 666–674.

———, AND G. H. VINEYARD (1957) *Radiation Effects in Solids.* Interscience Publishers, Inc., New York, 226 p.

ELLSWORTH, H. V. (1925) Radioactive minerals as geologic age indicators. *Am. J. Sci.* **209**, 127–144.

——— (1932) Rare element minerals in Canada. *Econ. Geol. Ser. Dep. Mines, Canada Geol. Surv. Br.* **11**, 81–104.

FAESSLER, A. (1942) Untersuchungen zum Problem des metamikten Zustandes. *Z. Kristallogr.* **104**, 81–113.

GEORGE, D. (1949) Mineralogy of uranium and thorium bearing minerals. *U. S. Atomic Energy Comm., Raw Mater. Operations* **563**, 198 p.

GOLDSCHMIDT, V. M. (1924) Uber die Umwandlung krystallisierter Minerale in den metamikten Zustand (Isotropisierung): *Norsk. Akad. Skr.* I, **1**, no. 5, *Geochemische Verteilungsgesetze der Elemente. III. (Anhang),* 51–58.

——— (1926) *Skrifter Norske Videnskaps Akad* (Oslo). I. *Math-naturwiss. Kl,* **8**, 7–156.

GORZHEVSKAYA, S. A., AND G. A. SIDORENKO (1962) A crystalline variety of lyndochite. *Dokl. Akad. Nauk. USSR,* **146**, 1176–1178.

GRAHAM, J., AND M. R. THORNBER (1974a) The crystal chemistry of complex niobium and tantalum oxides. I. Structural classification of MO_2 phases. *Am. Mineral.* **59**, 1026–1039.

———, AND ——— (1974b). The crystal chemistry of complex niobium and tantalum oxides. IV. The metamict state. *Am. Mineral.* **59**, 1047–1050.

HAMBERG, A. (1914) Die radioaktiven Substanzen und die geologische Forschung. *Geol. Fören. Förh.* **36**, 31–96.

HOLLAND, H. D., AND D. GOTTFRIED (1955) The effect of nuclear radiation on the structure of zircon. *Acta Crystallogr.* **8**, 291–300.

HUTTON, C. O. (1950) Heavy detrital minerals. *Bull. Geol. Soc. Am.* **61**, 635–710.

KINCHIN, G. H., AND R. S. PEASE (1955) The displacement of atoms in solids by radiation. *Rep. Prog. Phys.* **18**, 1–51.

KOSTYLEVA, E. E. (1954) On metamict disintegration of the zircon group of minerals. *U. S. Geol. Surv.,* **TEI-369**, 16 pp.

LACROIX, A. (1922) *Mineralogie de Madagascar,* Vol. I. A. Challamef., Paris, 624 p.

LIPOVA, L. M. (1966) Mechanism of metamict mineral alteration. *Geokhimiya,* no. **6**, 729–733. (*Geochem. Int.* **3**, 594).

———, G. A. KUZNETSOVA, E. S. MAKAROV (1965) An investigation of the metamict state in zircons and cyrtolites. *Geokhimiya,* no. **6**, 681–694 (*Geochem. Int.* **2**, 513–525).

MAKAROV, E. S. (1970) Physiochemical cause of metamictization of minerals and of zircon in particular. *Geokhimiya,* no. **1**, 54–58 (*Geochem. Int.* **7**, 200).

MORGAN, J. H., AND M. L. AUER (1941) Optical, spectroscopic and radioactivity studies of zircon. *Am. J. Sci.* **239**, 305–311.

MÜGGE, O. (1922) Über isotrop gewordene Kristalle. *Akad. Wiss. Gottingen. Math.-Phys. Kl. Nachr.* **2**, 110–120.

NEFEDOV, E. I. (1956) New data on fergusonite and euxenite. *Inform. Sbornik, Vses. Nauchn. Issled. Geol. Inst.* **3**, 82–85.

NILSSEN, BORGHILD (1970) Samarskites. Chemical composition, formula and crystalline phases produced by heating. *Norsk. Geol. Tid.* **50**, 357–373.

PABST, A. (1952) The metamict state. *Am. Mineral.* **37**, 137–157.

PELLAS, P. (1954) Sur la formation de l'etat metamicte dans le zircon. *Bull. Soc. fr. Mineral. Cristallogr.* **77**, 447–460.

POVARENNYKH, A. S. (1956) On the problem of the nature of metamict disintegration of minerals. *Proc. Mineral. Soc., USSR, 2nd Ser.* **85**, 593–597.

PRIMAK, W. (1954) The metamict state. *Phys. Rev.* **95**, 837.

PYATENKO, Y. A. (1959) Some aspects of the chemical crystallography of the pyrochlore-group minerals. *Kristallografiya,* **4**, 204–208 (*Sov. Phys. Crystallogr.* **4**, 184–186, 1960).

——— (1970) Behaviour of metamict minerals on heating and the general problem of metamictization. *Geokhimiya,* **9**, 1077–1083 (*Geochem. Int.* **7**, 758–763).

RAWSON, H. (1967) *Inorganic Glass-Forming Systems.* Academic Press, London, 317 p.

SEITZ, F. (1949) On the disordering of solids by action of fast massive particles. *Disc. Faraday Soc.* **5**, 271–282.

——— (1952) On the generation of vacancies by moving dislocations. *Adv. Phys.* **1**, 43–90.

SLATER, J. C. (1951) The effects of radiation on materials. *J. Appl. Phys.* **22**, 237–256.

SOLOMON, A. A. (1973) Radiation-induced creep of UO_2. *J. Am. Ceram. Soc.* **56**, 164–171.

TOMKEIEFF, S. I. (1946) The geochemistry of uranium. *Sci. Progr. (London),* **34**, 696–712.

UEDA, T. (1957) Studies on the metamictization of radioactive minerals. *Coll. Sci. Mem., Univ. Kyoto, Ser. B,* **24**, 81–120.

VAN WAMBEKE, L. (1970) The alteration processes of the complex titano-niobo-tantalates and their consequences. *Neues Jahrb. Mineral. Abhandl.* **112**, 117–149.

VANCE, E. R., AND B. W. ANDERSON (1972) Study of metamict Ceylon zircons. *Mineral. Mag.* **38**, 605–613.

VEGARD, L. (1927) The structure of xenotime and the relation between chemical constitution and crystal structure. *Phil. Mag.* **4**, 511–525.

Von Stackelberg, M., and E. Rottenback (1940) Dichte und struktur des zirkons, III & IV. *Z. Kristallogr.* **102,** 173–182; 207–208.

Whapham, A. D., and B. E. Sheldon (1965) Radiation damage in uranium dioxide. *Phil. Mag.* **12,** 1179–1192.

Zachariasen, W. H. (1932) The atomic arrangement in glass. *J. Am. Chem. Soc.* **54,** 3841–3851.

Zhabin, A. G., V. B. Alexandrov, M. E. Kazakova, and V. B.

Feklichev (1962) Aeschynite from arfvedsonite-calcite-quartz veins, Vishnevye Mts. Urals. *Dokl. Akad. Nauk. USSR,* **143,** 686–689.

Zhieov, K. K. (1952) Conversion of zircon into the metamict state. *Dokl. Akad. Nauk. USSR,* **85,** 889–891.