

Natural and Artificial Minerals as Matrices for Immobilization of Actinides

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Received January 22, 2007

Abstract—The possibility of insulation of long-lived actinides for the entire period of their potential hazard, i.e., over a virtually infinite time, is the crucial problem in safe disposal of high-level radioactive wastes (HLW). The reality of such a possibility is corroborated by the study of natural radioactive minerals that firmly retain U, Th, and REE, which are close in geochemical properties to transuranic actinides, for millions of years despite the effects of groundwater. The natural analogues of actinide HLW matrices are minerals where U, Th, and REE are contained as major elements or isomorphic admixtures. The study of these minerals is helpful for synthesis of durable artificial forms of wastes that ensure reliable insulation of HLW up to the complete decay of actinides independently of such engineering barriers of underground repositories as containers and bentonite buffers. The main requirements on confinement matrices include a high isomorphic capacity with respect to actinides and other HLW components, chemical and radiation stability, and technological feasibility of their industrial production. The natural and artificial minerals—uraninite, monazite, zirconolite, pyrochlore, britholite, garnet, and murataite—characterized in this paper may serve as a basis for efficient matrices for immobilization of actinide wastes.

DOI: 10.1134/S1075701507030014

INTRODUCTION

The development of nuclear power industry is accompanied by increasing accumulation of radwastes, which require considerable resources for their safe disposal. After more than 40 years of investigations, specialists from different countries came to agreement that the insulation of radwastes in underground repositories is the only acceptable way to remove these wastes from the sphere of the vital interests of humankind. The disposal of high-level radioactive wastes (HLW) with long-lived actinides faces the greatest difficulties because the required time of actinide isolation from the biosphere is virtually unlimited. The problem may be simplified by separation of HLW into Cs–Sr and actinide fractions. The isotopes of the Cs–Sr fraction will decay almost entirely in 500 years. Therefore, they may be vitrified and disposed of in clayey or crystalline rocks. Engineering barriers of repositories—corrosion-resistant containers, bentonite buffers, and concrete reservoirs or encasings—will provide the necessary insulation.

The safe disposal of long-lived nuclides of the actinide fraction may be ensured only by their conversion into a stable solid and disposal in deep underground repositories. Unfortunately, some doubts remain regarding the ability of these structures to ensure actinide insulation for many millennia. The removal of dissolved radionuclides into the biosphere along with subsurface water is the main hazard. Insulating radwastes from subsurface water by placing them

into containers or enclosing them in a buffer is possible only for a limited time interval that covers a few millennia. In this regard, the best method of insulation is conversion of wastes to a form that is able to retain radionuclides for a long time despite interaction with subsurface water. We attempted to solve this problem on the basis of our data and those of other authors on the properties of some actinide- and REE-bearing minerals and their artificial analogues.

NATURAL MINERAL CONCENTRATORS OF U, Th, AND REE

In concentration of radioactive and rare earth elements, four groups of minerals are recognized: (1) minerals with extremely low contents of U, Th, and REE, which occur as sporadic dispersed atoms (quartz, feldspars, light micas, nepheline, olivine, etc.); (2) minerals with low contents of U, Th, and REE, which occur largely in absorbed forms (Fe- and Ti-bearing minerals: biotite, amphibole, and pyroxene and products of their secondary alteration—hematite, limonite, leucoxene, etc.); (3) minerals with high contents of U, Th, and REE, which are incorporated into the crystalline lattice (zircon, zirconolite, pyrochlore, fergusonite, betafite, britholite, etc.); and (4) minerals where U, Th, and REE are major elements (uraninite, thorianite, thorite, cerianite, monazite, etc.). It is evident that minerals of groups (3) and (4) are of the greatest interest as potential matrices capable of retaining actinides under the conditions of the geologic medium. Hereafter, we consider some of

these minerals, whose capacity with respect to actinides and REE and radiation stability indicate the possibility of using them for immobilization of actinide HLW. Let us start with uraninite as an analogue of spent nuclear fuel (SNF).

Uraninite

Uraninite, with the theoretical formula UO_2 , has a fluorite-type structure. Each U^{4+} ion is surrounded by eight O^{2-} ions making up cubic polyhedrons connected by common edges. Natural uraninite occurs in granitic and alkaline pegmatites, leucogranites, and rocks affected by contact metamorphism. In vein and stringer-disseminated uranium ores, uraninite is observed as a fine-grained or cryptocrystalline variety known as nasuran, or pitchblende. No natural uraninite samples that would fit the theoretical formula in composition are known to date. Uraninite always contains an admixture of U(VI), and its composition corresponds to UO_{2+x} , where x may attain 0.6. As indicated by the increase in the degree of oxidation of uraninite grains from the inner parts outward, a considerable percentage of hexavalent uranium is related to oxidation after extraction of the mineral from the subsurface. High-temperature uraninite contains isomorphic admixtures of Th, REE, Zr, and other elements.

At some uranium deposits, uraninite has been preserved over hundreds of millions of years owing to reducing and near-neutral properties that have been acquired by subsurface water as a result of long-term interaction with host rocks under conditions of sluggish water exchange at a depth below 500 m (Laverov et al., 2001a). Under oxidizing conditions, uraninite is replaced by secondary minerals. This process is often accompanied by removal of uranium and its dispersion in host rocks in absorbed form. In the course of SNF alteration under the effect of oxygen-bearing water, the newly formed U(VI) phases are able to contain neptunium owing to the close dimensions of uranyl (UO_2^{2+}) and neptunyl (NpO_2^+) groups (Burns et al., 1997). Below the zone of chemical weathering, uraninite is commonly stable.

The study of natural uraninite provides extraordinarily deep insights into the conditions of safe underground disposal of SNF, which consists of more than 95% uranium dioxide, with the remainder being the products of nuclear reactions. Pu, Am, Cm, Np, Th, REE, Nb, and Zr may be incorporated into the uraninite lattice. Therefore, while UO_2 is stable, the leakage of these elements into subsurface water is ruled out. Other elements (Cs, Sr, Tc, I, Sn, Se) occur as nonstructural admixtures. They tend to escape from the uraninite matrix by diffusion toward microfractures and intergranular boundaries and accumulate in the intergranular space. When SNF shells are damaged, gaseous radionuclides (^{85}Kr , ^3H , ^{14}C) will enter the environment first of all. If subsurface water penetrates an under-

ground repository, the nonstructural, readily soluble radionuclides will spread as well. During the first few hundred years after SNF disposal, ^{137}Cs and ^{90}Sr are the most hazardous radioisotopes.

Thus, the insulating properties of uraninite are different for specific elements and a uraninite matrix may serve as a reliable barrier only for the elements incorporated into the UO_2 structure. Although a uraninite matrix theoretically may be applied for immobilization of the actinide HLW fraction, it is not able to ensure insulation of all radionuclides that occur in SNF. If uraninite is used for this purpose, disposal under conditions of its stability (a reducing or near-neutral character of groundwater) should be combined with engineering barriers (corrosion-resistant containers and a bentonite buffer) that prevent leakage of nonstructural radionuclides from SNF.

Monazite

Monazite, LREE phosphate, has the theoretical formula APO_4 ($A = \text{LREE, Th, U, Ca}$). Its structure consists of chains in which each LREEO_6 polyhedron is connected by bridging oxygen atoms with five PO_4 tetrahedrons. REE may be replaced by tri- and tetravalent actinides. In this case, the electrical neutrality of the lattice is provided by incorporation of Ca^{2+} into the structure ($2\text{REE}^{3+} = \text{Ca}^{2+} + \text{Th}^{4+}$). Brabantite $[(\text{Ca}_{0.5}\text{Th}_{0.5})\text{PO}_4]$ is the end member of this isomorphic series of solid solutions. In nature, monazite occurs as an accessory mineral in granites, gneisses, and pegmatites. The highest monazite contents are noted in placers, which are mined to recover Th and REE. Monazite mostly occurs as small monoclinic grains; large crystals are observed in pegmatites. Natural monazite consists of up to 60 wt % REE_2O_3 , 25–30 wt % P_2O_5 , 4–20 wt % ThO_2 , and up to 15 wt % UO_2 ; CaO and ZrO_2 are noted. In terms of immobilization of actinide HLW, the ability of monazite to incorporate a great amount of actinides and its high radiation stability are the most important features.

Most natural monazites have been affected by radiation owing to α decay of actinides during the long time of existence of minerals. The radiation doses received are comparable with those that will be achieved in artificial HLW matrices. Such doses lead to metamict damage to the crystal lattices of minerals and to an increase in their solubility. In contrast to most radioactive minerals, monazite retains its crystalline structure even at great cumulative doses (Boatner and Sales, 1988; Seydoux-Guillaume et al., 2004) because of its ability to heal radiation damage. It should be taken into account that, in nature, monazite receives a high dose of radiation over a very long time (millions of years) at a relatively low intensity of radiation and thus is able to recover its structure. The rate of radiation of artificial HLW matrices is much higher than in natural minerals. As a result, high radiation doses will be accumulated over a short time (thousands of years) and prevent the repair of radiation damage.

One more specific feature of monazite is its good preservation in geologic processes, which allows its application for isotopic age determination (Seydoux-Guillaume et al., 2004). Monazite grains mostly behave as a closed isotopic system, and even the high-temperature granulite facies metamorphism does not disturb the U/Pb ratio (De Wolf et al., 1993). Monazite is retained in the course of physical weathering, accumulating in quartz sand and making up placer deposits. Chemical weathering leads to disintegration of monazite grains and their dissolution. Here, REE and especially readily oxidized uranium are partly removed, whereas thorium is fixed in the newly formed phases and virtually does not migrate in the process of monazite dissolution (Read et al., 2002). In general, monazite is resistant to hydrothermal alteration, and, in contrast to other HLW matrices, the solubility of monazite decreases with increasing temperature.

The aforementioned features of monazite led to the suggestion of its potential use as an HLW matrix (Boatner et al., 1980). This idea has been developed in regard to particular types of wastes in dozens of publications, including patents for inventions (Strel'nikov et al., 1996; Fiquet and Croixmarie, 2000). Techniques of synthesis of such matrices have been elaborated and artificial monazites of various compositions produced with hot compaction or cold compaction combined with sintering at 1000–1300°C. Like natural monazite, its artificial counterpart is characterized by a high chemical stability. The rate of U, Cs, and Sr leaching with water at 90°C from monazite containing 20% HLW imitators is 20 times lower than from borosilicate glass, and the rate of dissolution of the matrix itself is 1000 times lower (Boatner and Sales, 1988). According to Aloy et al. (2002), the rate of ^{241}Am leaching from LaPO_4 -based ceramics is 10^{-4} g/m^2 per day, i.e., an order of magnitude lower than from borosilicate glass.

The study of artificial monazites containing radioisotopes corroborated their radiation stability. For example, the structure of monazite LuPO_4 doped with 1% ^{244}Cm was not damaged after 18 years of monitoring (Liu et al., 1998). The $1.5 \times 10^{19} \alpha$ decays/g that occurred over this time are equal to 2300 years of disposal of artificial monazite containing 10 wt % ^{239}Pu . Burakov et al. (2004) used ^{238}Pu -doped $[\text{PuPO}_4]$ and $[(\text{La},\text{Pu})\text{PO}_4]$ to demonstrate a relationship of monazite radiation stability to its composition. Monazite $[(\text{La},\text{Pu})\text{PO}_4]$ retains its crystalline structure at a dose of $1.19 \times 10^{19} \alpha$ decays/cm³, whereas the $[\text{PuPO}_4]$ phase becomes amorphous at a lower dose of $4.2 \times 10^{18} \alpha$ decays/cm³. Amorphization is accompanied by expansion and cracking of grains and leads to an increase in the area contacting solution and thus promotes an increase in the solubility of monazite in water.

The properties of monazite indicate that a ceramic based on this mineral is promising for immobilization of actinides and REE. This possibility was supported by

a patent on its use as a matrix (Strel'nikov et al., 1996) and by plans for immobilization of the actinide-REE fraction of radwastes at the Mayak Production Association (Rovnyi et al., 2004). However, the results of investigations of natural and artificial monazites do not allow us to count on the possibility of incorporation of the entire range of components contained in HLW into a monazite matrix, e.g., Cs, Sr, corrosion products, etc. Because of this selectivity, when monazite is applied for immobilization of unfractionated HLW, additional phases that appear in the matrix diminish its chemical stability in solutions.

Zirconolite

Zirconolite has been found as an accessory mineral in kimberlites and carbonatites, alkaline mafic and ultramafic rocks and related products of metasomatic alteration, placers, lunar soil, and even meteorites. Its structure consists of networks made up of three- and six-membered rings of Ti–O polyhedrons. Three of four Ti atoms are surrounded by six and the fourth atom by five oxygen atoms (Mazzi and Munno, 1983). Layers of Ca cations with a coordination number of 8 and Zr cations with a coordination number of 7 are sandwiched between networks of Ti–O polyhedrons.

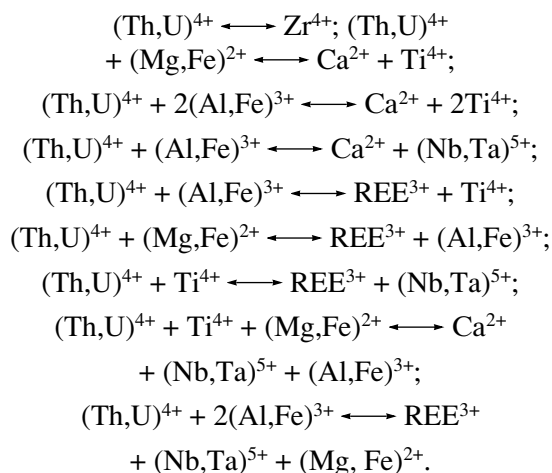
Depending on the character of arrangement of adjacent networks of Ti–O polyhedrons, monoclinic (zirconolite-2M), orthorhombic (-3O), and trigonal (-3T) varieties are formed (Bayliss et al., 1989). This nomenclature has been approved by the Commission on New Minerals of the International Mineralogical Association, and thus the previously used terms *polymignite* (zirconolite-3O) and *zirkelite* (zirconolite-3T) have lost their significance. The modern understanding of the term *zirconolite* was discussed in detail by Laverov et al. (1996).

Owing to isomorphic replacements, the compositions of natural zirconolites appreciably differ from the theoretical formula $[\text{CaZrTi}_2\text{O}_7]$. Elements with ionic radii varying from 0.40 to 1.14 Å and charges from 1+ to 6+ have been detected therein. The ability to incorporate various elements makes zirconolite a peculiar indicator of the composition of the mineral-forming medium. For example, zirconolite from lunar basalt is depleted in Nb, Ta, U, and Th but enriched in Fe, Zr, Hf, and REE (the REE_2O_3 total attains 32 wt %). Zirconolite from metasomatized carbonate rocks is characterized by a wide range of U, Th, and REE contents and, as a rule, low Nb and Ta contents; zirconolite from carbonatite is poor in Al, Mg, etc. A change in formation conditions is a cause of growth of zonal crystals. Analytical data indicate that more than 30 elements may occur in zirconolites from different rocks; the main compositional variations are expressed in the proportions of Ca, Zr, Ti, Nb + Ta, Al + Fe^{3+} , Mg + Fe^{2+} , REE, U, and Th (Giere et al., 1998). Correlation analysis allows the recognition of 24 variants of possible exchanges. In the light of the problem under discussion,

Table 1. Chemical composition of zirconolites of generations I and II, wt %

Oxide	CaO	Gd ₂ O ₃	ZrO ₂	TiO ₂	Al ₂ O ₃	FeO
Zirconolite I	4.7	30.3	32.0	26.7	6.1	<0.1
Zirconolite II	4.4	35.1	10.5	41.8	7.9	0.3

the replacements with participation of Th, U, and REE attract the most interest:



Proceeding from the theoretical formula $[\text{CaZrTi}_2\text{O}_7]$, the major oxide concentrations in zirconolite must be (wt %) 16.5 CaO, 36.3 ZrO₂, and 47.2 TiO₂. However, natural samples contain (wt %) 2.6–16.5 CaO, 24.3–45.4 ZrO₂, and 13.6–45.9 TiO₂. Such wide variations are caused by a great isomorphic capacity of zirconolite with respect to Th, U, and REE, which reaches (wt %) 24 UO₂, 22 ThO₂, and 32 REE₂O₃ (Lumpkin, 2001). Si, Mn, Hf, W, Y, Cr, Zn, Sr, Ba, K, Na, and Pb are trace elements (<1 wt %).

Zirconolite is highly stable chemically. Microscopic examination and isotopic analysis have shown that low-temperature processes do not alter this mineral (Lumpkin, 2001; Lumpkin et al., 2001). The removal of Th and U from zirconolite and its replacement by zircon, titanite, and rutile were observed only as a result of high-temperature effects (Giere and Williams, 1992). The U and Pb isotopic compositions of natural zirconolites show that uranium commonly is not removed, including from samples amorphized under the effect of α decay. The solubility of even metamict minerals in water and brine at 200°C is 1000 times lower than that of borosilicate glass (Oversby and Ringwood, 1981).

In contrast to monazite, most natural zirconolites are metamict due to the high dose of radiation and the inability of the zirconolite lattice to quickly recover from radiation damage, particularly at a low temperature. Nevertheless, it must be recognized that zirconolite is characterized by a rather high radiation stability. The critical dose of radiation resulting in amorphization (D_c) depends on the age of mineral. If the age is <100 Ma, $D_c = 10^{19}$ α decays/g, whereas, at an age

>1 Ga, $D_c = 10^{20}$ α decays/g (Giere, 1999). This implies that the structure of the mineral is recovered with time.

Artificial zirconolite has been prepared by sintering of an oxide blend at 1450°C (Pudovkina and Pyatenko, 1964) for the study of the structure. However, most important is the application of zirconolite as an actinide matrix. In the 1970s, a ceramic with zirconolite as one of its phases was prepared at Sandia National Laboratories in the United States (Harker, 1988). Most such ceramics, named Synroc, were elaborated in Australia (Ringwood, 1978; Ringwood et al., 1981, 1988). The first variety, Synroc-A, based on titanates (perovskite, zirconolite, and hollandite) and silicates (barium feldspar and leucite), was obtained by melting at 1300°C and crystallization of the melt. Further, to enhance the strength of actinide bonding in matrices, silicates were eliminated and pressure sintering at 1200°C and 20–40 MPa was used. The most well-known matrix, Synroc-C, consists of 30% zirconolite, 30% hollandite, 20% perovskite, 15% rutile, and 5% metals and calcium phosphate. Since the grain size of this ceramic is limited to fractions of a micrometer, the examination of particular phases meets serious difficulties.

In Russia, zirconolite ceramics have been obtained by induction melting in a cold crucible (IMCC) and by cold compaction combined with sintering (Stefanovsky et al., 1996, 2003; Laverov et al., 1998b, 2002). The investigation of such ceramics was stimulated by the high isomorphic capacity of zirconolite with respect to actinides and REE; its resistance to radiation and hydrothermal impacts; and, hence, the possibility of its use for immobilization of the actinide HLW fraction.

A melted sample was prepared from a mixture of Ti, Ca, Al, and Zr oxides, and Gd was used as an imitator of actinides. The ceramic composition was as follows (wt %): 30.0 Gd₂O₃, 26.3 TiO₂, 25.4 ZrO₂, 7.5 Al₂O₃, 4.9 CaO, 5.6 SiO₂, 0.2 FeO, 0.2 Na₂O, and 0.2 K₂O. The presence of the latter four oxides is caused by the dissolution of the refractory lining of the crucible in the melt. In addition to 80–85% zirconolite, oxide $[(\text{Zr,Gd})\text{O}_{2-x}]$ and a glass (up to 10%) were detected in the sample. The sample contained two generations of zirconolite distinct in composition and formed at different stages of crystallization (Table 1).

Zirconolite I occurs as relatively large (up to 1 mm) prismatic crystals and their star-shaped aggregates (Fig. 1). Small crystals of zirconolite II up to 5 μm in length grow over lateral facets of zirconolite I grains at an angle of 45°. The zirconolite I/II ratio is 1/4. The composition of the mineral is recalculated to a formula with seven oxygen atoms and a total number of cations equal to four. In zirconolite I, the Zr content decreases from the core of grains to their margins, whereas the Ti and Gd contents increase in the same direction. It is evident that the melt is depleted in Zr and enriched in Ti and Gd during crystallization. The determination of the zirconolite composition confirmed its high capacity with respect to REE and actinides. The maximum REE

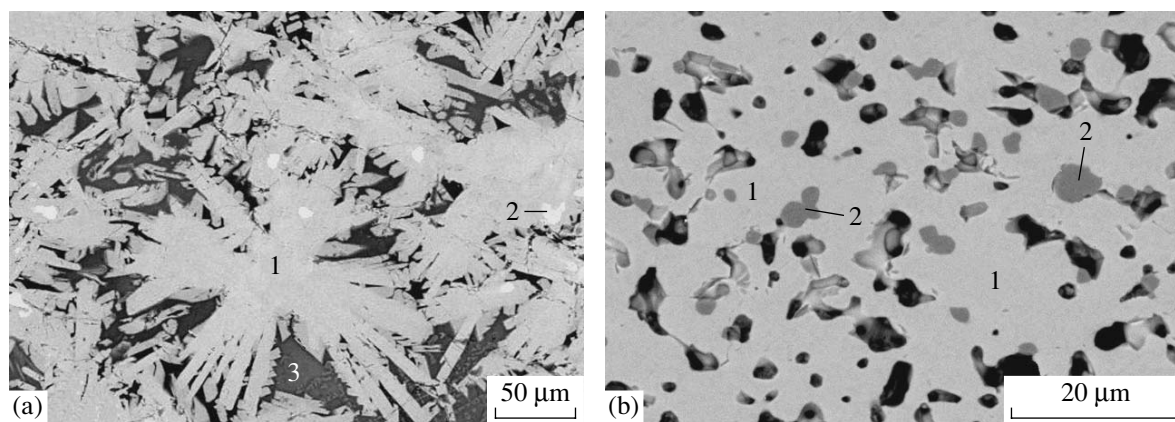


Fig. 1. Zirconolite-based matrices prepared (a) by IMCC: (1) zirconolite, (2) Zr and Gd oxides, (3) glass; (b) by cold compaction combined with sintering: (1) zirconolite, (2) perovskite; pores are black.

concentration in zirconolite from hot-compacted ceramics is 30 wt % (Kesson et al., 1983; Vance et al., 1995). In zirconolite from melted ceramics, the REE content is higher, probably, due to the higher temperature of synthesis. Two zirconolite varieties that contain 18.4 and 36.1 wt % PuO_2 were revealed in hot-compacted ceramics (Jostons et al., 1996). These data testify to a similar distribution of Gd and Pu in ceramics and corroborate the validity of application of REE as actinide imitators. The main difference of the ceramics prepared by IMCC from those produced by pressing and sintering is a larger size of zirconolite crystals.

Depending on valence, actinides and REE occupy the sites of Zr^{4+} or Ca^{2+} . In the latter case, charge stabilizers, e.g., Al^{3+} and/or Fe^{3+} , are required. The degree of replacement of Ca by REE (with accompanying replacement of Ti^{4+} by Al^{3+} or Fe^{3+}) increases with decreasing ionic radius. For HREE, zirconolite REEZrTiAlO_7 (REE = Y, Gd, or Tb) has been obtained (Stefanovsky et al., 2003a, 2003b). The lattice capacity for tetravalent actinides is lower; when more than 0.2–0.3 atoms of these actinides are incorporated into the formula, a phase with pyrochlore structure is formed instead of zirconolite (Kesson et al., 1983). Zirconolite where Zr is replaced by Hf has been synthesized (Strachan et al., 2004).

The phase formation during synthesis of zirconolite by pressing and sintering was considered by Laverov et al. (2002). Experiments with an oxide charge $[\text{CaZrTi}_2\text{O}_7]$ were performed within a temperature range of 800–1500°C during 1–48 h. The percentage of zirconolite in run products increases with increasing temperature and/or duration of sintering. In samples prepared at 1200°C over 20 h, zirconolite becomes the prevalent phase. Nevertheless, rutile, baddeleyite, and perovskite contents still remain high, indicating that the system is out of equilibrium. An increase in the sintering temperature to 1300°C at the same duration of 20 h results in the disappearance of rutile and baddeleyite and depletion of perovskite. With a further increase in

temperature or run duration, the phase composition of samples does not change, indicating that equilibrium has been achieved. At 1300°C, the attainment of equilibrium requires 20 h, while, at 1450–1500°C, equilibrium is reached in 5 h. The zirconolite composition differs from the theoretical formula and fits $[\text{Ca}_{1.12}\text{Zr}_{1.04}\text{Ti}_{1.90}\text{O}_7]$. In addition to zirconolite, about 5% perovskite $[\text{Ca}_{1.08}\text{Zr}_{0.04}\text{Ti}_{0.94}\text{O}_3]$ was detected in the products of runs carried out at the highest temperature and the greatest duration.

A zirconolite-based matrix has been prepared from a charge of (wt %) 2.6 Al_2O_3 , 2.4 BaO , 10.0 CaO , 6.6 Nd_2O_3 , 48.4 TiO_2 , 19.6 ZrO_2 , and 10.4 UO_2 by cold compaction combined with sintering at 1500°C (Vance et al., 1995). The matrix consists of 80% zirconolite and additionally contains perovskite, hollandite, and rutile. The following rates of leaching with water heated to 90°C have been reported (g/m^2 per day): 10^{-1} – 10^{-2} for Ca, 10^{-2} – 10^{-3} for Ba, 10^{-3} – 10^{-4} for Nd, 10^{-4} – 10^{-5} for U, 10^{-6} for Ti, and 10^{-7} for Zr. The rate of Pu leaching is 10^{-4} – 10^{-5} g/m^2 per day (Hart et al., 1998). Zirconolite is the most stable phase of Synroc (Lumpkin et al., 1995). Titanium oxides and hydroxides (anatase and brookite) appear at the surface of hollandite and perovskite as soon as after 1–7 days of interaction with water at 150°C, whereas the zirconolite surface remains clean. Zirconolite is stable in the presence of water up to 250°C and 50 MPa pressure, i.e., under conditions of deep-seated repositories (Malmstrom et al., 1999). Above 250°C, zirconolite is replaced by calzirtite $[\text{Ca}_2\text{Zr}_5\text{Ti}_2\text{O}_{16}]$ and perovskite $[\text{CaTiO}_3]$ at 50 MPa or perovskite, titanium oxides, and baddeleyite $[\text{ZrO}_2]$ at 200 MPa. Thereby, REE, Zr, Hf, and Ti enter into the newly formed phases, whereas Al and Ca pass into solution.

The effect of short-lived actinides (^{244}Cm , ^{238}Pu) on the stability of artificial zirconolite has been studied by Ringwood et al. (1998) and Strachan et al. (2004). A dose of 2×10^{18} α decays/g results in the appearance of

disordered sites along with retention of the monoclinic structure as a whole. Complete amorphization is reached at a dose of 3×10^{18} α decays/g, which corresponds to 0.5 displacements/atom. This is a few times less than is established for natural zirconolites, which are characterized by an amorphization dose of 1–6 displacements/atom. Such a difference is likely related to the recovery of radiation damage to the lattice during geologic history. Amorphization raises zirconolite solubility by ten times (Weber and Ewing, 2002). Strachan et al. (2004) noted that the increase in solubility does not affect Pu leaching; in our view, this statement is dubious.

In general, it should be recognized that, owing to the high capacity of zirconolite with respect to various elements of radwastes, including actinides and REE, as well as its radiation and chemical stability and the feasibility of artificial zirconolite synthesis, this mineral is a promising matrix for immobilization of actinide HLW after extraction of Cs and Sr.

Pyrochlore

This group is composed of Ti, Nb, and Ta minerals that have pyrochlore structure either in the natural state or after annealing (*Minerals...*, 1967). Pyrochlore occurs in nepheline syenite and products of its metasomatic alteration, e.g., in albitite; alkaline ultrabasic rocks; albitized granite and pegmatite; and high-temperature hydrothermal basic veins hosted in dolomite near contacts with granitoids. In the literature on confinement matrices, the term *pyrochlore* is used in regard to natural minerals and artificial phases with pyrochlore structure irrespective of their chemical composition. Pyrochlore pertains to a cubic system with a unit cell varying from 0.9 to 1.2 nm in size. The elementary motif of its lattice may be expressed as a fluorite cell doubled along the edge where half of the cubes are transformed into octahedrons due to the removal of two diagonal anions. The theoretical pyrochlore formula is $[^{VIII}A_2^{VI}B_2^{IV}O_6^{IV}Y]$, where VIII, VI, and IV are coordination numbers; *A* and *B* are cations; and *Y* is anions (O^{2-} , OH^- , and F^-). Site *A* is occupied by cations with charges from 1+ to 6+ and ionic radii from 0.086 to 0.155 nm; the major cations are Na^+ , Ca^{2+} , REE^{3+} , Th^{4+} , U^{4+} , and U^{6+} ; the auxiliary cations are K^+ , Sr^{2+} , Sb^{3+} , Sn^{4+} , Cs^+ , Ba^{2+} , Pb^{2+} , Bi^{3+} , Mn^{2+} , and Fe^{2+} . Site *B* is occupied by cations with charges from 3+ to 6+ and ionic radii from 0.06 to 0.083 nm (Lumpkin, 2001); the major cations are Nb^{5+} , Ta^{5+} , and Ti^{4+} ; the auxiliary cations are Mg^{2+} , Al^{3+} , Si^{4+} , Mn^{3+} , Fe^{3+} , Sb^{3+} , and W^{6+} . The pyrochlore structure is commonly distinguished by a deficiency of atoms at sites *A* and *Y*, and therefore, the real composition of minerals corresponds to the formula

$$A_{2-m}B_2O_{6-w}Y_{1-n}pH_2O \\ (m = 0-1.7, w = 0-0.7, n = 0-1.0, p = 0-2).$$

The number of elements in natural samples reaches 25 or even more, and their contents vary widely. The compositional diversity of minerals belonging to the pyrochlore group gave rise to the appearance of many mineral names and controversies in their application. In terms of proportions of Nb, Ta, and Ti, pyrochlore proper ($Nb > Ti, Ta$), microlite ($Ta > Nb, Ti$), and betafite ($Ti > Nb, Ta$) are recognized. Wide variations in element contents at site *A* are noted. Pyrochlores enriched in uranium are termed uranpyrochlore and uranmicrolite; a pyrochlore variety enriched in U and Y is named obruchevite; marignacite and pandaite are pyrochlores enriched in Ce and Ba, respectively; etc. The UO_2 , ThO_2 , and REE_2O_3 contents in minerals of the pyrochlore group reach 30, 9, and 16 wt %, respectively. In U-rich betafite, the $[CaUTi_2O_7]$ mole fraction is 50% (Lumpkin et al., 1999), and this mineral may be regarded as a matrix with a high capacity with respect to actinides. In general, the composition of minerals belonging to the pyrochlore group testifies to the possible incorporation of many elements into their structure, first of all, actinides and REE.

In the process of physical weathering, pyrochlore grains are fragmented owing to their brittleness. The hydrothermal alteration of pyrochlore results in its replacement by columbite $[(Fe, Mn)(Nb, Ta)_2O_6]$, fersmite $[(Ca, REE)(Nb, Ti)_2(O, OH)_6]$, natroniobite $[NaNb_2O_5(OH)]$, and calcite. The alteration of pyrochlore is expressed in the removal of Na, Ca, and U and gain of Mn and Fe. In the course of chemical weathering, pyrochlore is hydrated with removal of Na, Ca, and F along with insignificant enrichment in Mn and Fe. Thus, pyrochlore undergoes alteration under both hydrothermal and supergene conditions. In unaltered or only slightly altered rocks, pyrochlore occurs as octahedral crystals; their age may be many hundred million years.

To study the radiation stability of minerals from the pyrochlore group, 19 samples varying in age from 280 to 2600 Ma were examined. The studied minerals contained 0.5–8.2 wt % UO_2 and 0.5–6.1 wt % ThO_2 . The wide range of these contents predetermined various doses of radiation and degrees of radiation damage to the crystalline lattice. The formulas of minerals calculated from SEM/EDS data are presented in Table 2; calculations were performed based on the hypothesis that the number of atoms in the octahedral position of the lattice is equal to two. The unit cell dimensions determined from XRD are given in Table 2 as well. Note that most of the studied minerals turned out to be X-ray amorphous. The totals in analyses decrease from almost 100% for crystalline varieties to 85% for metamict samples due to their hydration. The metamict samples are characterized by a wide scatter of the cation sum at site *A*. The radiation doses received by minerals differ by almost three orders of magnitude, from $<0.1 \times 10^{19}$ to 4.6×10^{20} α decays/g (Table 3). The degree of sample heterogeneity increases with the radi-

Table 2. Calculated formulas of minerals from the pyrochlore group and parameters of their unit cells

Sample	Calculated crystallochemical formula	<i>a</i> , Å	ΣA ⁿ⁺
1	(Ca _{1.22} Na _{0.71})(Nb _{1.75} Ti _{0.25})O _{5.85} F _{1.2}	10.43	1.93
2	(Ca _{1.17} Na _{0.68} Sr _{0.07} Ce _{0.02})(Nb _{1.76} Ti _{0.24})O _{5.65} F _{1.67}	10.46	1.94
3	(Ca _{1.17} Na _{0.73})(Nb _{1.82} Ti _{0.15} Si _{0.04})O _{5.57} F _{1.74}	10.39	1.90
81/2	(Ca _{1.16} Na _{0.7} Ce _{0.02})(Nb _{1.77} Ti _{0.23})O _{6.41}	10.43	1.88
81/3	(Ca _{1.07} Na _{0.64} Ce _{0.02})(Nb _{1.72} Ti _{0.2} Si _{0.08})O _{5.48} F _{1.61}	10.39	1.73
81/6	(Ca _{1.01} Na _{0.98})(Nb _{1.85} Ti _{0.15})O _{5.71} F _{1.43}	10.43	1.99
81/7	(Ca _{1.06} Na _{0.74})(Nb _{1.79} Ti _{0.17} Ta _{0.04})O _{5.63} F _{1.44}	10.39	1.80
4	(Ca _{1.24} Na _{0.57} Th _{0.03} U _{0.01})(Nb _{1.58} Ti _{0.33} Si _{0.05} Ta _{0.04})O _{5.36} F _{2.11}	Am	1.86
5	(Ca _{1.18} Na _{0.65} Th _{0.06} Ce _{0.02})(Nb _{1.7} Ti _{0.3})O _{5.55} F _{1.9}	The same	1.91
6	(Pb _{1.3} Ca _{0.28} Fe _{0.3} U _{0.08} Mn _{0.04})(Nb _{0.94} Ta _{0.58} Si _{0.38} Ti _{0.09})O _{6.82}	"	1.98
7	(Ca _{0.88} Na _{0.75} Ce _{0.08} U _{0.02} Th _{0.02})(Nb _{1.58} Ti _{0.31} Si _{0.06} Ta _{0.05})O _{5.65} F _{1.2}	"	1.74
105/7	(Ca _{1.04} Na _{0.61} Th _{0.09} Ce _{0.08} Nd _{0.03})(Nb _{1.45} Ti _{0.44} Si _{0.06} Ta _{0.05})O _{5.65} F _{1.59}	"	1.85
1-c	(Ca _{1.02} Na _{0.82})(Nb _{1.86} Ti _{0.14})O _{5.53} F _{1.67}	"	1.84
2-c	(Ca _{1.05} Na _{0.8})(Nb _{1.83} Ti _{0.17})O _{5.46} F _{1.79}	"	1.84
4-c	(Y _{0.4} Ca _{0.16} U _{0.09} Fe _{0.09} Pb _{0.06})(Nb _{1.35} Si _{0.36} Ti _{0.18} Ta _{0.11})O _{6.05}	"	0.96
5-c	(Y _{0.22} Ca _{0.18} U _{0.11} Fe _{0.11} Pb _{0.06})(Nb _{1.29} Si _{0.49} Ti _{0.11} Ta _{0.11})O _{5.33} F _{0.86}	"	0.79
518	(Ca _{0.12} La _{0.12} Fe _{0.06} Mn _{0.05} Ce _{0.03} U _{0.03} Pb _{0.02})	"	0.48
	(Nb _{1.12} Si _{0.56} Ti _{0.28} Ta _{0.03})O _{4.54} F _{1.31}	"	
626	(Ca _{0.54} U _{0.07} Ce _{0.05})(Nb _{1.56} Ti _{0.41} Ta _{0.03})O _{4.86} F _{1.38}	"	0.66
644	(Ca _{0.86} Na _{0.85} U _{0.1} Ce _{0.05} Pb _{0.03})(Nb _{1.55} Ti _{0.39} Ta _{0.06})O _{5.34} F _{2.08}	"	1.89

Note: *a*, unit cell; ΣAⁿ⁺, sum of atoms in site A; Am, amorphous.

Table 3. Radiation doses of pyrochlores and degree of damage to their structure

Sample and its age (Ma)	Content, wt %		Dose × 10 ¹⁹ , α decays/g	Dose, displacements/atom	Degree of structure damage
	UO ₂	ThO ₂			
1-c (300)	–	<0.5	<0.1	<0.1	I
2 (300)	0.8 ¹ (0.7–1.2) ²	–	0.7 (0.6–1.0)	0.5 (0.6–0.9)	II
518 (400)	2.5 (0.8–2.6)	0.9 (0.8–1.3)	3.1 (1.1–3.4)	2.7 (0.9–2.9)	II
5 (280)	–	4.0 (3.4–4.6)	1.1 (0.5–1.3)	0.7 (0.5–1.0)	III
4 (280)	0.9 (0.8–1.3)	2.0 (1.7–2.5)	1.1 (1.0–1.4)	0.9 (0.8–1.1)	III
105/7 (280)	–	6.1 (5.0–7.5)	1.17 (1.0–1.4)	1.0 (0.8–1.2)	III
7 (400)	1.1 (0.9–1.5)	0.9 (0.7–1.0)	1.5 (1.2–2.0)	1.3 (1.0–1.7)	III
4-c (280)	7.3 (3.0–9.5)	–	5.8 (2.4–7.5)	5.6 (2.3–7.2)	III
644 (400)	6.3 (5.8–6.7)	–	7.2 (6.6–7.6)	6.2 (5.7–6.5)	III
5-c (280)	9 (4.9–12)	–	7.1 (3.9–9.5)	6.8 (3.7–9.2)	III
6 (2600)	5.0 (3.4–6.6)	–	46.4 (31.5–61.2)	59.9 (53.7–60.8)	III

Note: I, initial stage of radiation damage to the structure; II, intermediate stage of damage; III, complete amorphization. See text for explanations.

¹ Average.

² Range over different measurement points.

ation dose and is expressed in variable composition with respect to radioactive elements and even in the appearance of uraninite (Fig. 2).

Using XRD and TEM, three levels of lattice damage have been distinguished: (I) a distinct X-ray diffraction pattern and a dotted electron diffraction pattern for the

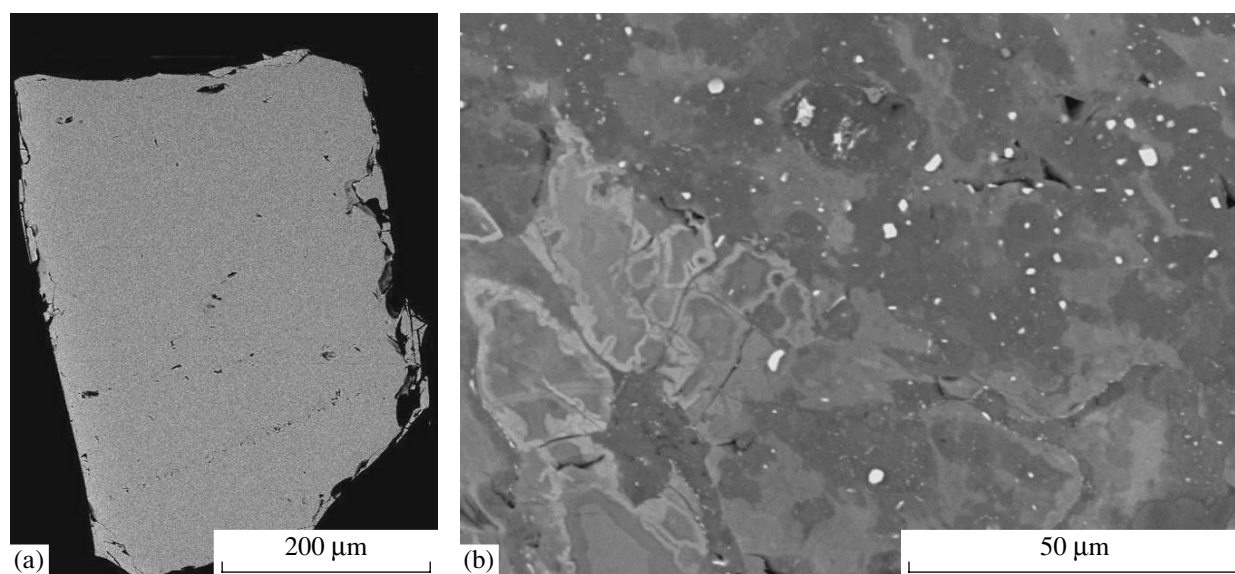


Fig. 2. SEM images of pyrochlore with (a) minimal (sample 1-c) and (b) maximal (sample 6) radiation doses and ages. White inclusions in (b) are uraninite grains.

samples affected by low doses and retaining an undestroyed structure; (II) diffuse peaks in the X-ray diffraction pattern and an electron diffraction pattern with elements of a ring structure, which indicate a predominance of damaged domains, although amorphization has not been reached; and (III) amorphous samples without peaks in the X-ray diffraction pattern and a wide ring around the central reflection in the electron diffraction pattern (Fig. 3). The complete destruction of the lattice occurs after 1.1×10^{19} α decays/g, although sample 518, which received a dose three times higher, retained its crystallinity. These data are close to the results reported by Lumpkin et al. (1999), who studied betafite 40 Ma in age that contained 30 wt % U and 1 wt % Th. The dose of amorphization for this mineral is 10^{19} α decays/g, and the time of its accumulation is estimated at 22–29 Ma. The highest dose of amorphization for natural pyrochlores corresponds to 4×10^{20} α decays/g (Lumpkin et al., 2001), i.e., is 40 times higher than the estimates given above. These differences allow us to suggest that the damage to the lattice is combined with its recovery. The lower the content of radioactive elements in the mineral, the more slowly destruction proceeds and the more completely the tendency to recovery is realized. Therefore, a higher dose of radiation is required to amorphize pyrochlore with low U and Th contents. Temperature also exerts an effect on the degree of structure recovery; however, it is commonly impossible to evaluate the temperature regime of the mineral residence in the crust. The radiation dose necessary for amorphization also depends on the mineral composition. All the aforementioned factors are responsible for the revealed variations in critical radiation doses required for amorphization of pyrochlores.

In the context of the problem of HLW immobilization, some artificial pyrochlore-type phases, including actinide-bearing ones, have been synthesized (Laverov et al., 2001a; Ewing et al., 2004). Pyrochlore-based samples with waste imitators (Ce, U, Th) and Pu obtained by cold compaction combined with sintering were characterized by Ebbinghaus et al. (1998) and Strachan et al. (2004, 2005). A Ce-bearing matrix consists of pyrochlore (70%), zirconolite, and perovskite. In a Pu-bearing ceramic containing (wt %) 10.0 Ca, 35.8 TiO₂, 10.6 HfO₂, 23.7 UO₂, 8.0 Gd₂O₃, and 11.9 PUO₂, pyrochlore is associated with brannerite, rutile, and a small amount of U–Pu oxide (Ebbinghaus et al., 1998). In contrast to the Ce-bearing sample, this ceramic is devoid of perovskite, probably due to the different valence of Pu⁴⁺ and Ce (up to 30% as Ce³⁺), which stabilizes the perovskite phase (Teterin et al., 2004).

The matrix elaborated in the United States for immobilization of plutonium consists of pyrochlore [(Ca, Gd, Pu, U, Hf)₂Ti₂O₇], Hf-zirconolite [(Ca, Gd)(Gd, Pu, U, Hf)Ti₂O₇], brannerite [(U, Pu, Gd)₂Ti₂O₆], and rutile [(Ti, Hf)O₂]. The PUO₂ content in this matrix is 10 wt %. The rate of Gd and Pu leaching at 90°C is $(1\text{--}4) \times 10^{-5}$ g/m² per day; this value is close to the stability of zirconolite in water (Strachan et al., 2005). In an acid medium, the rate is somewhat higher than that in a zirconolite ceramic, while, in a slightly alkaline medium (pH 8), the rate is virtually the same and does not exceed 10^{-5} g/m² per day at 75°C. It should be noted that the rate of Pu leaching from the currently used glassy HLW matrices is $10^{-1}\text{--}10^{-2}$ g/m² per day.

In pyrochlore ceramics prepared by melting and crystallization, the grain size is tens of times larger than in solid-phase matrices. Pyrochlore dominates in their

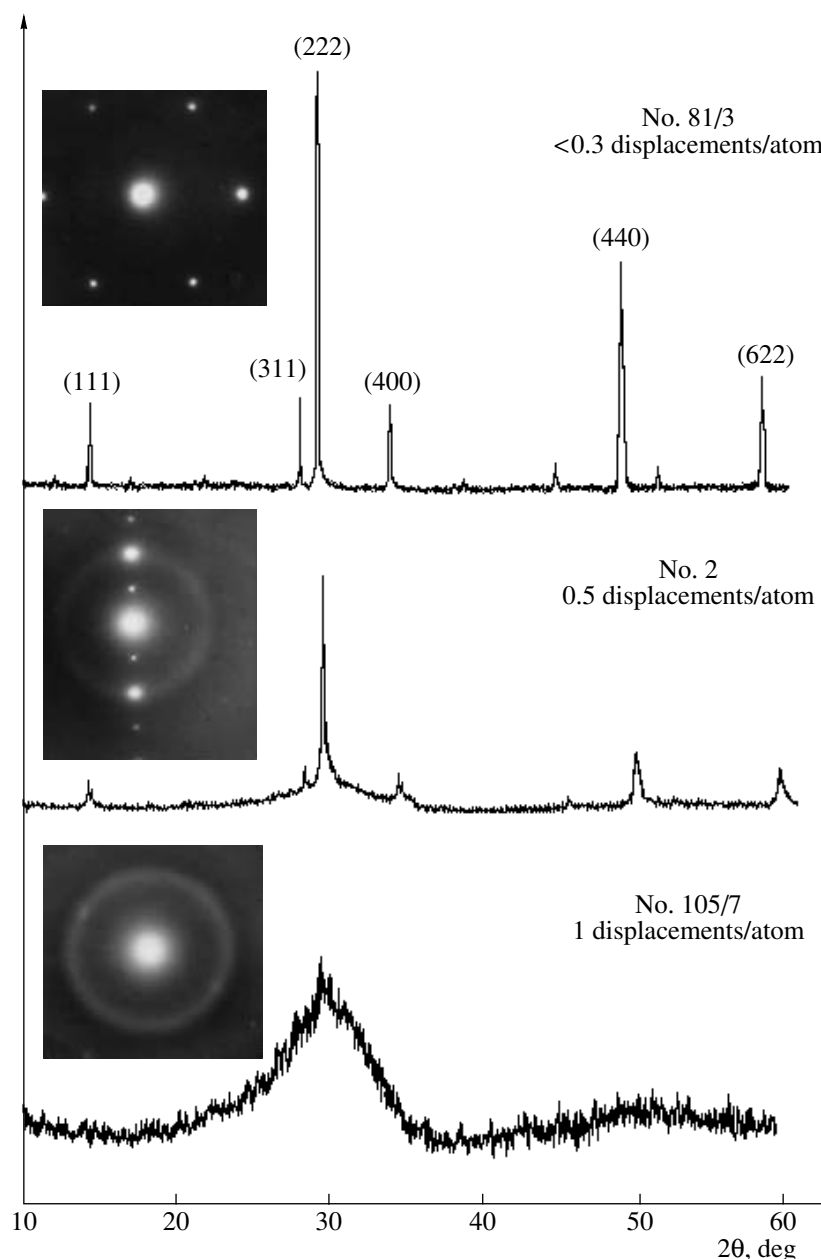


Fig. 3. Damage to pyrochlore crystalline structure under the effect of radiation.

composition in association with brannerite $[\text{UTi}_2\text{O}_6]$ and rutile. The rates of Ti, Zr, and U leaching on interaction of matrices with water heated to 95°C are $(2-6) \times 10^{-5} \text{ g/m}^2$ per day (Stefanovsky et al., 2001).

The radiation stability of artificial phases depends on their composition. Titanate pyrochlore is damaged by radiation relatively easily. Amorphization of pyrochlore $[(\text{Ca}, \text{Gd}, \text{Pu})_2(\text{Ti}, \text{Hf})_2\text{O}_7]$ and $[(\text{Gd}, \text{Cm})_2\text{Ti}_2\text{O}_7]$ doped with ^{238}Pu or ^{244}Cm (the half-life periods are 88 and 18.1 yr, respectively) occurs at a dose of $(2-4) \times 10^{18} \alpha$ decays/g or 0.2–0.3 displacements/atom (Volkov et al., 2004; Matzke and van Geel, 1996; Weber and

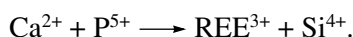
Ewing, 2002). Amorphization is accompanied by 5% expansion and an increase in solubility by 20–50 times in comparison with pyrochlore that does not contain ^{244}Cm . At the same time, zirconate pyrochlores $[\text{Gd}_2\text{Zr}_2\text{O}_7]$ and $[\text{Er}_2\text{Zr}_2\text{O}_7]$ retain their structure even at very high doses of more than 100 displacements/atom, or $5 \times 10^{21} \alpha$ decays/g (Ewing et al., 2004).

The study of radiation effects on natural and artificial pyrochlores makes it possible to forecast the behavior of actinide-bearing phases in geologic repositories. Titanate-based matrices will become amorphous within a few hundred years after disposal, and, as a result, the

rate of radionuclide leaching will increase. The insulating properties of pyrochlore-based matrices may be markedly enhanced by replacing titanium with zirconium. At the same time, such a change will complicate their industrial production because the rate of pyrochlore formation depends on its composition. The varieties enriched in Ti are synthesized rapidly, whereas Zr-rich pyrochlores are synthesized slowly. To form a $[\text{Gd}_2\text{Zr}_2\text{O}_7]$ matrix even at 1600°C , the sintering should last for 50 h, while the synthesis of $[\text{Gd}_2\text{Ti}_2\text{O}_7]$ pyrochlore takes 1 h at 1500°C and 3 h at 1300°C (Laverov et al., 2002).

Britholite

The britholite group embraces REE and Ca silicates with an apatite-type structure and the formula $A^{\text{IX}}_4B^{\text{VII}}_6(\text{XO}_4)_6Y_2$, where A, B, and X are cations and Y is O^{2-} , OH^- , or F^- . Tetrahedrons XO_4 ($X = \text{Si}^{4+}$, P^{5+} , and rarely Al^{3+} and B^{3+}) make up the framework of the structure; they are connected by polyhedrons having seven and nine apices with a large cation in the center and oxygen atoms at the apices. Taking into account the structure and composition of britholite, this mineral may be regarded as a variety of apatite with the replacement

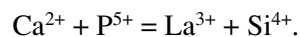


The study of natural minerals has shown the absence of a continuous series Ca phosphate (apatite)–REE–Ca silicate (britholite), although complete miscibility between the end members has been proved for artificial compounds (Boyer et al., 1997; Ito, 1968). Site $[A]^{\text{IX}}$ of britholite is largely occupied by calcium; $[B]^{\text{VII}}$, by REE; and $[X]^{\text{IV}}$, by silicon. The Ca/REE ratio in the formula commonly varies from 4/6 to 2/8; however, Ca-free varieties are known as well. Numerous series of solid solutions with britholite structure and the general formula $[(M^+, M^{2+}, Y^{3+}, \text{REE}^{3+}, \text{Th}^{4+})_{10}(\text{Si}^{4+}, \text{P}^{5+}, \text{B}^{3+})_6\text{O}_{26}]$, where $M^+ = \text{Li}$ and Na and $M^{2+} = \text{Ca}$, Pb , Sr , Ba , Mn , and Mg , have been prepared by sintering at $T = 950\text{--}1280^\circ\text{C}$ in air (Ito, 1968). REE are predominant in their composition; however, compounds with high contents of tetravalent actinides, in particular, Th, have been obtained as well.

The necessary and sufficient attributes for classing a mineral with the britholite group are an apatite-type structure (space group $P6_3/m$) and high REE, Si, and Ca contents. Natural britholite occurs as hexagonal prismatic crystals up to 1 cm in size or intergrowths of grains in nepheline syenites, related pegmatites, and contact zones. The number of elements in natural samples attains 25 or more, and their concentrations vary widely. The maximum REE, Th, and U contents reach 60, 20, and 4 wt %, respectively. In addition to britholite proper, such minerals as lessingite, fenghuanglite, abukumalite, melanocerite, caryocerite, tritomite, etc., are identified based on variable proportions of LREE and HREE, as well as contents of ThO_2 , P_2O_5 , and B_2O_3 .

Varieties with elevated Al content are named Al-britholite, Al-melanocerite, etc. (Kupriyanova et al., 1966).

The high contents of radioactive elements and REE stimulated the examination of britholite as a matrix for the actinide–REE fraction of HLW. Using a method of solid-state synthesis at $1200\text{--}1400^\circ\text{C}$ and varying the proportions between $(\text{La}^{3+}, \text{SiO}_4^{4-})$ and $(\text{Ca}^{2+}, \text{PO}_4^{3-})$, Boyer et al. (1997) managed to obtain samples making up several series between britholite and apatite. The first series is described by the formula $[\text{Ca}_{10-x}\text{La}_x(\text{SiO}_4)_x(\text{PO}_4)_{6-x}\text{F}_2]$, where $0 \leq x \leq 6$. In this case, the variation in composition is determined by the isomorphic exchange



In the next series, oxygen replaces fluorine according to the reaction $2\text{F}^- = \text{O}^{2-} + \square$. Lanthanum appears here as an imitator of trivalent actinides, Am and Cm. Britholites with tetravalent actinides have been synthesized likewise. The isomorphic capacity of a transitional member of the apatite–britholite series having a composition $[\text{Ca}_9\text{Nd}_{1-x}(\text{Th}, \text{U})_x(\text{SiO}_4)_{1+x}(\text{PO}_4)_{5-x}\text{F}_2]$ and synthesized at 1400°C by sintering was 20% for Th and 5–8% for U (Terra et al., 2006). This discrepancy is likely caused by preferential incorporation of the relatively large Th cation into the britholite structure instead of the smaller U cation and LREE in comparison with HREE. Varieties much richer in Th, up to $[\text{Ca}_6\text{Th}_4(\text{SiO}_4)_6\text{O}_2]$, are known among silicate members (britholite proper). The britholite capacity with respect to plutonium depends on the valence of this element: the capacity for Pu(III) is an order of magnitude higher than for Pu(IV), as follows from the formulas of the respective phases: $[\text{Ca}_2\text{Pu}_8^{3+}(\text{SiO}_4)_6\text{O}_2]$

and $[\text{Ca}_{2.1}\text{Gd}_{7.3}\text{Pu}_{0.6}^{4+}(\text{SiO}_4)_6\text{O}_2]$. The isomorphism of Np, Am, and Cm in britholite is apparently similar to that of actinide (U) and REE (Nd) ions close to the former in charge and dimensions.

The radiation stability of natural britholites has been studied by Livshits (2006). On the basis of the U and Th contents in minerals and the isotopic age of samples, the radiation doses were calculated, and the degree of structure damage was determined with XRD and TEM (Table 4). Sample Bt-8, with a radiation dose of 0.9×10^{19} α decays/g (0.8 displacements/atom), is amorphous, whereas sample 1769, which received a dose of 1.4×10^{19} α decays/g (1.2 displacements/atom), still retains relics of the crystalline structure. The critical dose necessary for complete amorphization of britholite may be estimated at 10^{19} α decays/g (1.0 displacements/atom). This value corresponds to the dose that an artificial ceramic containing 10 wt % ^{239}Pu accumulates over 2000 years of disposal. The alteration of britholite is accompanied by the redistribution of actinides and the formation of zones enriched in these elements in their axial portions (Fig. 4).

Table 4. Th and U contents, wt %, in britholites and their radiation doses

Sample and its age (Ma)	UO ₂	ThO ₂	$D \times 10^{19}$, α decays/g	D , displacements/atom	Degree of structure damage
65863 (320)	0.2	2.0 ¹ (1.5–2.7) ²	0.6 (0.3–1.5)	0.5 (0.3–1.3)	II
1769 (1500)	0.6	1.3 (0.9–2.1)	1.4 (1.0–2.2)	1.2 (0.8–1.9)	II
Bt-8 (320)	0.3	4.1 (3.0–5.3)	0.9 (0.6–1.0)	0.8 (0.5–0.9)	III
89510 (260)	–	1.2 (0.8–2.3)	2.3 (1.5–4.3)	1.8 (1.2–3.5)	III
1775 (320)	0.8 (0.2–1.2)	11.1 (9.8–12.1)	3.2 (2.3–3.7)	2.8 (2.1–3.4)	III
62388 (300)	–	13.8 (11.5–14.2)	2.8 (2.4–2.9)	2.4 (2.0–2.5)	III
1771 (260)	0.6	4.3 (3.8–4.6)	8.1 (7.2–8.7)	6.9 (6.1–7.4)	III

Note: II, III, stages of structure damage. See text for explanations.

¹ Average.

² Range over different measurement points.

Gong et al. (1997) examined britholite with a non-uniform distribution of radioactive elements. Domains with a partially, substantially, or completely disordered (amorphized) crystalline lattice were selected. Domains with a retained structure correspond to radiation doses of less than 0.3 displacements/atom ($\sim 4 \times 10^{18}$ α decays/g); domains with a partially damaged structure, to 0.5 displacements/atom ($\sim 6 \times 10^{18}$ α decays/g); and amorphous domains, to about 1 displacement/atom ($> 10^{19}$ α decays/g).

The behavior of artificial britholites under irradiation was studied using the effect of accelerated ions

(Laverov et al., 2003; Ewing et al., 1995; Utsunomiya et al., 2003) or doping with short-lived ²⁴⁴Cm and ²³⁸Pu (Weber and Ewing, 2002). The critical doses that induce amorphization are 0.15 (ionic irradiation) and 0.5 displacements/atom (²⁴⁴Cm or ²³⁸Pu decay). As for other minerals, radiation doses giving rise to amorphization of natural britholites are much higher than those for artificial phases. This difference is apparently caused by recovery of the crystalline structure of radioactive minerals during their long geologic history.

The examples given above show that some natural radioactive minerals firmly retain U, Th, and REE for a

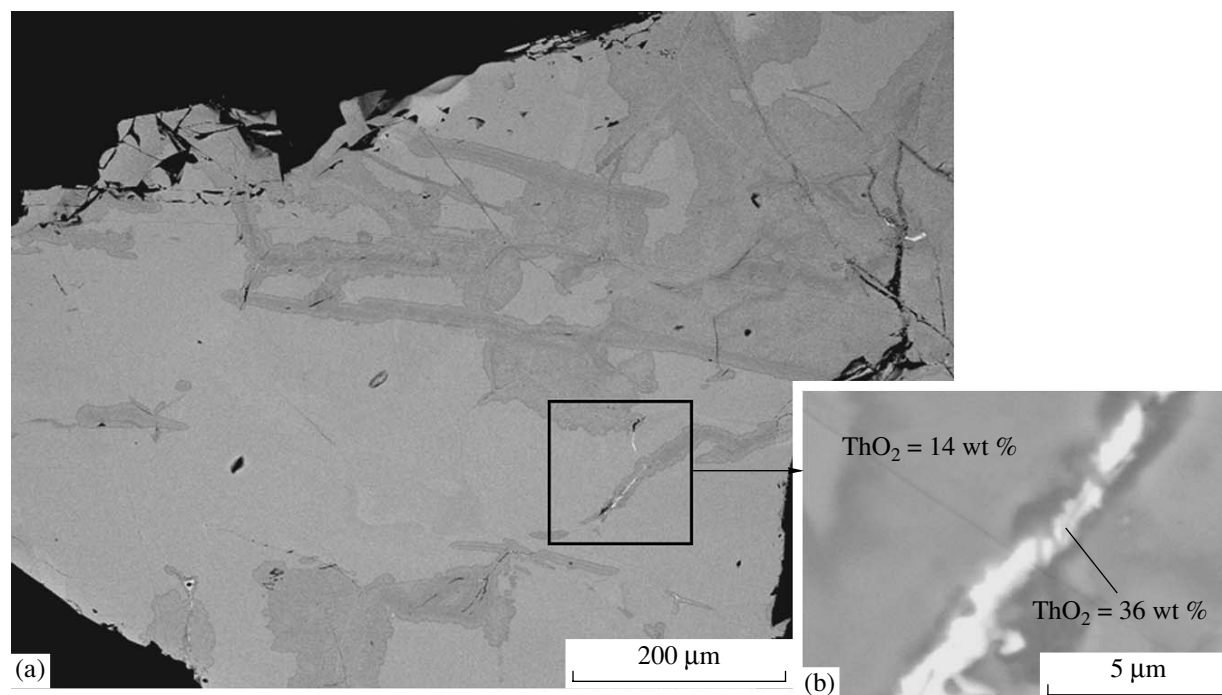


Fig. 4. SEM image of britholite, sample 62388: (a) general view; (b) structure of an altered zone with the highest Th content in its central part.

Table 5. Chemical composition of natural murataite, wt %

No.	Na ₂ O	CaO	TiO ₂	MnO	FeO	ZnO	Y ₂ O ₃	Ln ₂ O ₃	Nb ₂ O ₅	F
1	5.8	0.9	37.9	0.6	4.4	12.5	12.1	9.7	10.0	6.5
2	5.9	6.7	48.2	–	2.3	16.2	20.5	0.7	–	–

Note: (1) Adams et al., 1974; (2) Portnov et al., 1981. Ln₂O₃ is the total REE, mainly HREE; a dash denotes that an element was not detected.

practically infinite time, despite the fact that they are affected by subsurface water. Irrespective of differences in radiation stability, many minerals show partial or complete damage to the crystalline lattice. However, radioactive elements are reliably fixed therein even after amorphization and virtually do not pass into solution. The critical radiation dose resulting in amorphization fits the value of the radiation impact of actinide wastes over many thousands of years, thus indicating that artificial matrices that will provide for safe long-term disposal of the actinide fraction of HLW may be synthesized on the basis of these minerals.

ARTIFICIAL MINERALS AS CONCENTRATORS OF ACTINIDES AND REE

The diversity of natural conditions predetermines the existence of a wide range of minerals markedly enriched in actinides and REE. At the same time, it has to be recognized that only certain combinations of chemical settings are realized in nature. Under laboratory conditions, one can choose any combination with participation of actinides, including those unrealized in the geologic medium, and thus synthesize phases unknown in nature. The question arises of whether it would be possible to create highly resistant artificial minerals that are able to incorporate various HLW components, first of all, actinides. Compounds with unknown natural radioactive counterparts attract special interest. Such artificial mineral carriers of actinides expand the range of search for optimal matrices confining actinide wastes. In our opinion, murataite and garnet, characterized below, are the most promising materials for immobilization of actinide HLW.

Murataite

Twenty-five years ago, Morgan and Ryerson (1982) published information on an unknown phase found in a matrix with HLW imitators at the Savannah River Plant in the United States. This phase contained (wt %) 0.7 Na₂O, 9.3 Al₂O₃, 7.8 CaO, 32.1 TiO₂, 7.8 MnO, 23.4 FeO, 1.0 Ln₂O₃, 13.2 ZrO₂, and 3.3 UO₂; the X-ray diffraction pattern was close to murataite, a rare natural mineral. It was suggested that the structure of this phase can be expressed via an oxide motif of fluorite type with a threefold unit cell. According to microprobe results, the formula was written as [(Ca, Mn)₂Zr(Fe, Al)₄Ti₃O₁₆]. In contrast to the natural mineral, the synthetic phase is

devoid of Zn but contains Mn, Zr, Al, and U (Table 1). The U content turned out to be four times lower than in zirconolite from the same sample. Therefore, at that time, murataite did not attract interest as a possible actinide matrix.

Later, Laverov et al. (1997) published data on the discovery of a murataite-like phase in a ceramic with imitators of wastes from the Mayak Production Association. This phase was characterized by heterogeneous composition in different portions of grains. From the core to the margins, the concentrations (wt %) of the following oxides decreased: UO₂ from 11.9 to 0.8, ZrO₂ from 5.7 to 3.8, Ce₂O₃ from 6.0 to 2.7, and CaO from 15 to 13; at the same time, the amounts of TiO₂, MnO, and Al₂O₃ increased from 54.8 to 65.9, from 3.6 to 5.7, and from 0.8 to 5.7, respectively. In a sample containing 5 vol % of this mineral, it accumulated about 40% of the total uranium, regardless of the occurrence in the sample of zirconolite and perovskite in great amounts. The high content of uranium in the center of grains as compared to the periphery was of special interest. The periphery is enriched with low-solubility titanium and serves as a protective shell against leaching of actinides from the center of the grain. These data initiated the investigation of the possible use of murataite as a matrix for immobilization of actinides (Laverov et al., 1998a, 1998b, 1998c, 1999, 2003, 2006; Yudin et al., 2001). The main features of natural and artificial murataites are summarized below.

Natural murataite is Na, Ca, REE, Zn, and Nb titanate with a structure derived from the fluorite lattice. This very rare mineral has been found in alkaline pegmatites from Colorado in the United States (Adams et al., 1974) and the Baikal region in Russia (Portnov et al., 1981). Natural murataite is characterized by elevated Ti, Zn, Y, and Na contents (Table 5). Murataite from Colorado is distinguished by high Nb and F contents, while that from the Baikal region is devoid of these elements but contains calcium. Some differences have been established in REE. While the total REE contents are similar, murataite from Colorado contains Y and HREE in equal amounts, whereas Y is sharply prevalent in the mineral from the Baikal region. The structural study of the sample from Colorado (Ercit and Hawthorne, 1995) confirmed the cubic lattice of the mineral (space group $F\bar{4}3m$, $a = 14.89 \text{ \AA}$, $Z = 4$) and allowed an idealized formula $[A_6B_{12}C_4TX_{40-x}]$ ($A = Y, Na$; $B = Ti$; $C = Fe$; $T = Zn$; $X = O, F$) to be proposed. Four cation sites are distinguished: distorted cube (A^{18}),

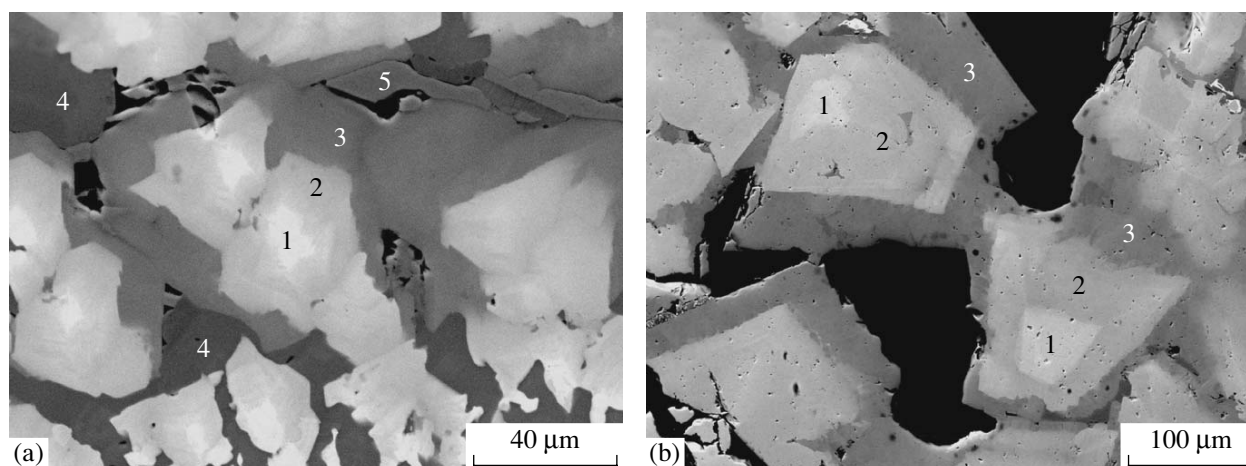


Fig. 5. SEM image of murataite ceramics containing 10 wt % (a) U and (b) Th. (1) Murataite M5, (2) murataite M8, (3) murataite M3; (4, 5) titanates with (4) crichtonite–loveringite and (5) pyrophanite–ilmenite structure. Chemical compositions of murataite phases are given in Table 6.

octahedron ($B^{[6]}$), pentatope ($C^{[5]}$), and tetrahedron ($T^{[4]}$). No radioactive elements are contained in natural murataite, and, therefore, in contrast to zirconolite, pyrochlore, monazite, and other U- and Th-bearing minerals, murataite did not attract attention as a matrix for actinides.

In comparison with natural murataite, its artificial analogues contain Mn, actinides, and Zr instead of Zn, Na, and Nb. To choose optimal compositions of matrices for immobilization of actinides, more than 100 samples of murataite ceramics have been prepared. It has been established that the highest murataite contents are typical of samples that contain (wt %) 55 TiO_2 , 10 MnO , 10 CaO , 5 Al_2O_3 , 5 Fe_2O_3 , 5 ZrO_2 , and 10 HLW components (Laverov et al., 1999). Most investigations were performed with this basic charge composition. Actinide oxides (UO_2 , ThO_2 , NpO_2 , PuO_2) and REE oxides (La_2O_3 , CeO_2 , Pr_6O_{11} , Nd_2O_3 ,

Sm_2O_3 , Eu_2O_3 , Gd_2O_3 , Tb_2O_3 , Dy_2O_3 , Y_2O_3) or their mixtures corresponding to the compositions of actinide or actinide–REE fractions served as imitators of HLW. A comprehensive consideration of murataite ceramics containing REE, actinides, and imitators of the actinide–REE fraction of HLW is presented in a special paper (Laverov et al., 2006).

Natural murataites are characterized by a threefold motif of the lattice with respect to the fluorite-type cell, while varieties M3, M5, and M8 with three-, five-, and eightfold repetition of the lattice have been detected among synthetic phases. Their crystals are regular zonal octahedrons (Fig. 5). The inner zone commonly consists of variety M5; the intermediate zone, of variety M8; and the outer zone, of M3. The highest actinide concentrations are detected in the inner zone and the lowest, in the outermost zone. The U, Th, and Pu contents differ by three to five times (Table 6). Such a struc-

Table 6. Chemical compositions of artificial murataite phases in actinide-bearing ceramics

Oxide, wt %	U-bearing sample			Th-bearing sample		
	M5	M8	M3	M5	M8	M3
Al_2O_3	2.1	4.4	8.9	2.7	4.3	8.0
CaO	7.9	8.9	8.6	11.2	10.9	9.5
TiO_2	47.1	51.6	54.6	52.2	54.8	55.6
MnO	9.6	10.6	12.9	8.5	9.2	10.9
Fe_2O_3	3.1	4.0	7.7	3.0	3.6	7.2
ZrO_2	10.1	6.0	2.1	9.7	6.5	2.1
UO_2	17.8	13.1	5.1	–	–	–
ThO_2	–	–	–	12.6	10.9	5.1
Total	97.7	98.6	99.9	99.9	100.2	98.4

Note: M5, M8, and M3 are murataite phases with five-, eight-, and threefold fluorite motifs. A dash denotes that an element was not detected.

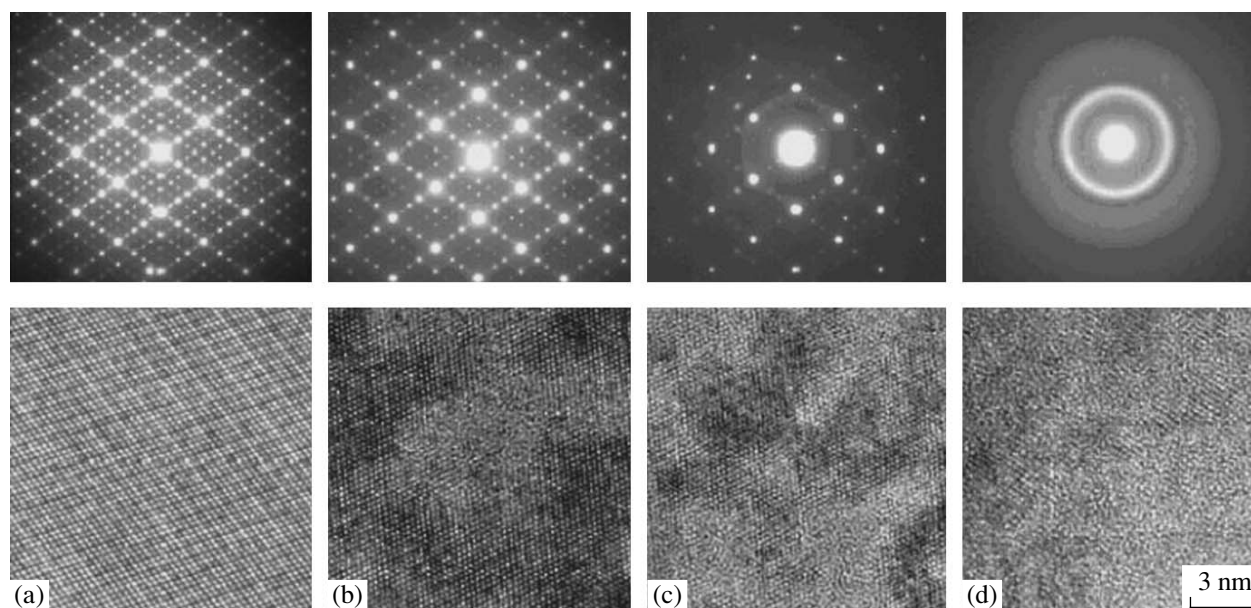


Fig. 6. Variation of electron diffraction patterns caused by irradiation of murataite M5 and the respective HRTEM images. (a) Before irradiation; (b) 4.38×10^{13} (0.04), (c) 9.39×10^{13} (0.08), and (d) 15.6×10^{13} $\text{Kr}^{2+}/\text{cm}^2$ (0.13 displacements/atom), after Laverov et al. (2006).

ture of murataite grains provides an additional protective barrier because the inner zone enriched in actinides is enclosed in a shell with low concentrations of these elements. The outer shell prevents their removal from the matrix interacting with solution. Experiments on the interaction of murataite ceramics with water at 90°C under static and dynamic conditions have shown that the rate of U, Th, and Pu leaching is only 10^{-5} – 10^{-6} g/m² per day, i.e., is two to three orders of magnitude lower than for other actinide matrices based on zirconolite or titanate pyrochlore.

Murataite ceramics with complete phase formation were synthesized by cold compaction combined with sintering at 1300°C for 4 h or by melting at 1500 – 1600°C for 1 h and subsequent crystallization of the melt. The maximum murataite content reaches 95%. Despite variations in the charge composition and synthesis conditions, we failed to obtain a single-phase murataite ceramic. In addition to murataite, some other titanates—crichtonite, rutile, Fe–Mn titanate, and perovskite—occur as well (Table 6). Various wastes, including the actinide and actinide–REE fractions, Am–Ga residues left behind after plutonium conversion to nuclear fuel, or separate actinides (Np, Pu), may be incorporated into murataite ceramics.

Because natural murataite does not contain radioactive elements, radiation damage to this artificial mineral cannot be estimated on the basis of study of its natural analogues. To determine the radiation stability of artificial murataites, samples were irradiated with a 1-MeV Kr^{2+} ion beam (Fig. 6) or by doping with 2 wt % ^{244}Cm (Lian et al., 2005; Laverov et al., 2006). In chemical and radiation resistance, murataite is comparable with

or exceeds other titanate phases, being at the same time a more universal matrix because it includes corrosion products (Mn, Fe, Al, Ga) together with actinides.

The variation in composition and structure of artificial murataites may be interpreted in terms of participation of modification M3 and pyrochlore blocks in their structure (Urusov et al., 2005). With consideration of this interpretation, the formulas of the murataite phases have been calculated. They may be written for pyrochlore and murataite M3 as $[\text{R}_2\text{N}_2\text{O}_{7-x}]$ and $[\text{R}_3\text{N}(1)_6\text{N}(2)_2\text{O}_{20-x}]$, where sites *R* are occupied by Ca, Mn, REE, and actinide ions; sites *N*(1) and *N*(2), by Ti, Zr, Fe, Al, and Ga; and $x = 0$ –1. In this case, formula M5 corresponds to $[\text{R}_5\text{N}(1)_8\text{N}(2)_2\text{O}_{27-x}]$, and M8, to $[\text{R}_8\text{N}(1)_{14}\text{N}(2)_4\text{O}_{47-x}]$. These formulas are consistent with the observable differences in phase compositions. As follows from this model, actinide and REE contents decrease in the series pyrochlore > M5 > M8 > M3, whereas Ti, Al, and Fe contents markedly increase in the same direction.

Ferrigarnet

The garnet structure (space group $Ia3d$ and formula $\text{A}_3\text{B}_2\text{X}_3\text{O}_{12}$) is a three-dimensional framework that consists of alternating $[\text{XO}_4]$ tetrahedrons and $[\text{BO}_6]$ octahedrons connected by common apices. The cavities of this framework are filled with large anions. The presence of sites *A*, *B*, and *X* with coordination numbers 8, 6, and 4 permits incorporation of various elements into the lattice. Site $[\text{A}]^{\text{VIII}}$ is occupied by bivalent (Ca, Mn, Mg, Fe, and Co) and trivalent (Y and REE) cations. Site $[\text{B}]^{\text{VI}}$ is occupied by trivalent (Fe, Al, Ga, Cr, Mn, In,

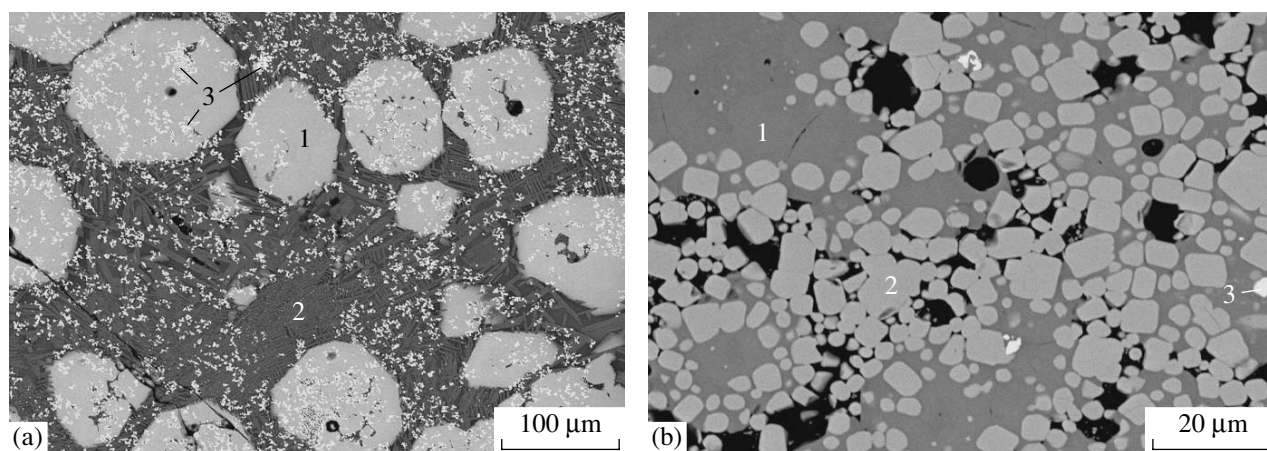


Fig. 7. SEM images: (a) sample 10-Th: (1) garnet, (2) hibonite and glass, and (3) thorianite; (b) sample 12-Th: (1) garnet I and (2) garnet II. Chemical compositions of ferrigarnet are given in Table 7.

Sc, and Ni) and tetravalent (Zr, Ti, and Sn) cations, while trivalent (Al, Ga, and Fe), tetravalent (Si and Ge), and pentavalent (V and As) cations reside in a tetrahedron (Geller, 1968).

Most natural garnets are silicates with Si^{4+} ions that occupy site $[\text{X}]^{\text{IV}}$. However, some minerals are low-silicic, with 1–2 formula units of silicon and the other tetrahedral positions filled with Fe^{3+} or Ti^{4+} . Nonsilicate minerals with a garnet-type structure are also known: berzeilite $[(\text{Na}, \text{Ca}_2)\text{Mn}_2\text{As}_3\text{O}_{12}]$ and cryolithionite $[\text{Na}_3\text{Al}_2\text{Li}_3\text{F}_{12}]$. Despite the diversity of natural garnets, the U and Th contents in these minerals do not exceed fractions of a percent and the REE contents, a few percent (Schingaro et al., 2001). However, in some cases, garnet is associated with minerals rich in these elements: monazite, xenotime, thorite, etc. Thus, the lattice of natural garnets is not favorable for incorporation of actinides and REE.

The possible synthesis of artificial phases with a garnet-type structure was considered by Yudinsev (2003). It has been shown that ferric garnets, where Si^{4+} ions are replaced by Fe^{3+} , should have a high capacity with respect to these elements. To verify this suggestion, more than 50 matrix samples containing REE and actinides were synthesized and examined (Yudinseva, 2005; Yudinsev et al., 2004). Oxide mixtures with garnet stoichiometry were compacted at a pressure of 200–400 MPa into pellets and sintered at 1300–1500°C. Kinetic runs show that equilibrium is reached at 5 and 2 h at temperatures of 1300 and 1400°C, respectively, while, at a temperature above 1400°C, the charge is melted. The percentage of garnet in samples varied from 30–40 to 100 vol %; some samples contained two phases with a garnet-type structure (Fig. 7; Table 7). Samples in which garnet is associated with independent phases of UO_2 , ThO_2 , and PuO_2 are most important for estimation of the ability of garnet to incorporate actinides into its lattice. In this case, the actinide con-

Table 7. Chemical composition of garnet from SEM/EDS results recalculated to 100%

Sample	CaO	Al_2O_3	SiO_2	Fe_2O_3	ZrO_2	Gd_2O_3	ThO_2	Other phases
1-Th	18.1	7.3	–	20.3	33.4	–	20.9	Hib, Thor
4-Th	17.7	–	–	29.1	33.1	–	20.1	Thor
5-Th I	5.5	0.7	–	29.7	–	33.3	30.8	The same
5-Th II	4.9	2.4	–	38.1	–	29.1	25.5	
10-Th	5.5	13.8	3.9	23.3	–	46.3	7.2	Hib, Thor, Gl
11-Th	8.7	8.8	4.8	27.5	8.3	37.2	4.7	The same
12-Th I	4.1	–	<0.2	31.3	–	43.6	20.8	Thor
12-Th II	5.5	–	5.2	41.2	–	42.6	5.5	
13-Th I	4.3	–	0.6	30.9	2.9	45.3	16.0	–
13-Th II	7.6	–	4.2	37.4	7.7	39.9	3.2	

Note: Samples 5-Th, 12-Th, and 13-Th contain two phases (I, II) with a garnet-type structure. A dash denotes that an element was not detected. Hib, hibonite $[\text{Ca}(\text{Fe}, \text{Al})_{12}\text{O}_{19}]$; Thor, thorianite (ThO_2); Gl, interstitial glass (Fig. 7).

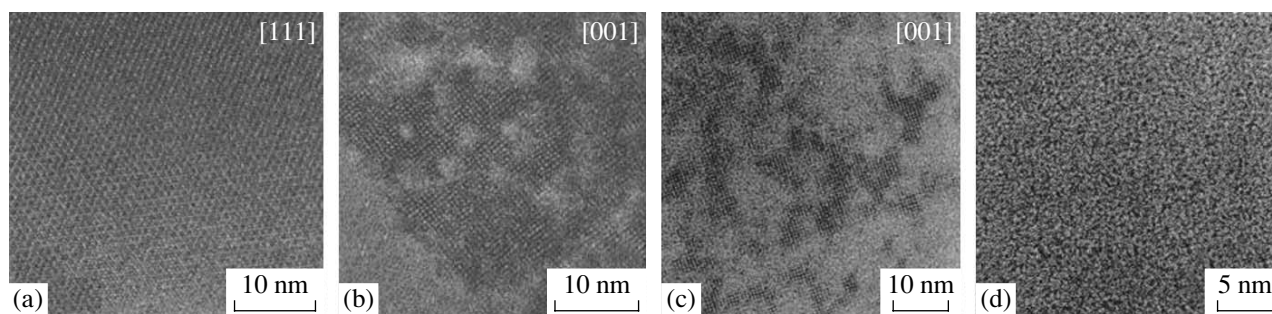


Fig. 8. HRTEM images of ferrigarnet. (a) Initial garnet and (b–d) garnet irradiated by 1 MeV Kr^{2+} ions up to receiving a dose of (b) 0.09, (c) 0.14, and (d) 0.22 displacements/atom. [111] and [001] are lattice indexes, after Laverov et al. (2003).

tents in garnet attain a maximum that corresponds to the isomorphic capacity of this mineral. The highest actinide content in ferrigarnet has been established to be 30 wt % and to drop with addition of Al and especially Si (Table 7), as is clearly seen when two garnets of different composition occur in the same sample. The lowered maximum actinide concentration in garnet is probably related to the decrease in size of structural sites on replacement of Fe^{3+} by smaller Al^{3+} in the octahedron or Si^{4+} and Al^{3+} in the tetrahedron.

The radiation stability of garnet has been studied using irradiation with accelerated ions (Laverov et al., 2003; Utsunomiya et al., 2005) and doping with 1.8 wt % ^{244}Cm . In both cases, the critical dose was about 0.2 displacements/atom at 25°C (Fig. 8); this value is close to those for artificial pyrochlore and britholite. According to the standard procedures of the MCC-1 and MCC-2 (MCC, Materials Characterization Center) tests, the solubility of ferrigarnet matrices has been investigated in water, 0.01 M HCl, or 0.01 M NaOH (90–150°C, $S/V = 10 \text{ m}^{-1}$). The composition of ferrigarnets corresponds to the formulas $[\text{Ca}_{1.5}\text{GdCe}_{0.5}\text{ZrFeFe}_3\text{O}_{12}]$, $[\text{Ca}_{2.5}\text{Ce}_{0.5}\text{Zr}_2\text{Fe}_3\text{O}_{12}]$, and $[\text{Ca}_{1.5}\text{GdTh}_{0.5}\text{ZrFeFe}_3\text{O}_{12}]$. The rate of leaching of Ce, Gd, and Th as imitators of HLW with water and the alkaline solution is very low: $3 \times 10^{-5} \text{ g/m}^2$ per day for Gd and 10^{-6} g/m^2 per day for Ce and Th (Yudintsev et al., 2004; Livshits and Yudintsev, 2006). In the acid solution, the rate increases up to 10^{-3} g/m^2 per day for Gd and Th and up to 0.2 g/m^2 per day for Ce. Being affected by the bentonite buffer, the subsurface water in an HLW repository will be slightly alkaline (pH 8–9). Under these conditions, the ferrigarnet matrix is characterized by very high stability. Hence, in chemical and radiation stability, ferrigarnet is not inferior to other matrices for actinide HLW, while, in capacity for waste components and efficiency of synthesis, it surpasses them. In conclusion, we note that the absence of natural ferrigarnets is explained by the fact that a high activity of the Fe^{3+} ion and low activities of Si^{4+} and Al^{3+} are necessary for their crystallization. Such conditions can be set artificially but are not realized in nature.

DISCUSSION

The data presented above indicate that some radioactive minerals firmly retain U, Th, and REE. All these minerals were formed under high-temperature conditions of magmatic or postmagmatic hydrothermal processes. For many millions of years after their origin, they were affected by low-temperature subsurface water, which was far from equilibrium with high-temperature minerals. Nevertheless, except for cases of intense hydrothermal or supergene alteration, these minerals commonly retain their initial composition and structure and appear in routine petrographic descriptions as unaltered. The minerals that reside in blocks of poorly permeable rocks only slightly affected by tectonic processes are distinguished by the best preservation. The results of isotopic studies indicate that often they have remained closed systems and may be used for isotopic dating. It is evident that the interaction of minerals with water proceeds extremely slowly and, as a rule, does not lead to appreciable alteration, particularly in zones of low permeability. At the same time, while defining a mineral as unaltered, we have to admit the conditional nature of this definition. As a matter of fact, no absolutely unaltered minerals occur in nature, even in poorly permeable zones. Minerals are subject to the constant effect of solutions that occur as fine films in microfractures, intergranular sutures, and pores. This interaction is directed toward the establishment of equilibrium between minerals and subsurface water. Local studies (electron microscopy, fission track radiography) show that such interaction results in the formation of micro- and nanoparticles of secondary minerals and diffusive redistribution of elements within the host mineral, which retains its bulk composition. The leached elements, including U, Th, and REE, either are fixed in the newly formed minerals or pass into absorbed forms (especially uranium). Thereby, it is precisely the secondary minerals (Fe and Ti oxides and hydroxides, chlorite, etc.) that behave as the most active sorbents.

The above reasoning allows us to suggest that confinement matrices prepared on the basis of such radioactive minerals as zirconolite, monazite, pyrochlore, and britholite will be in underground repositories under

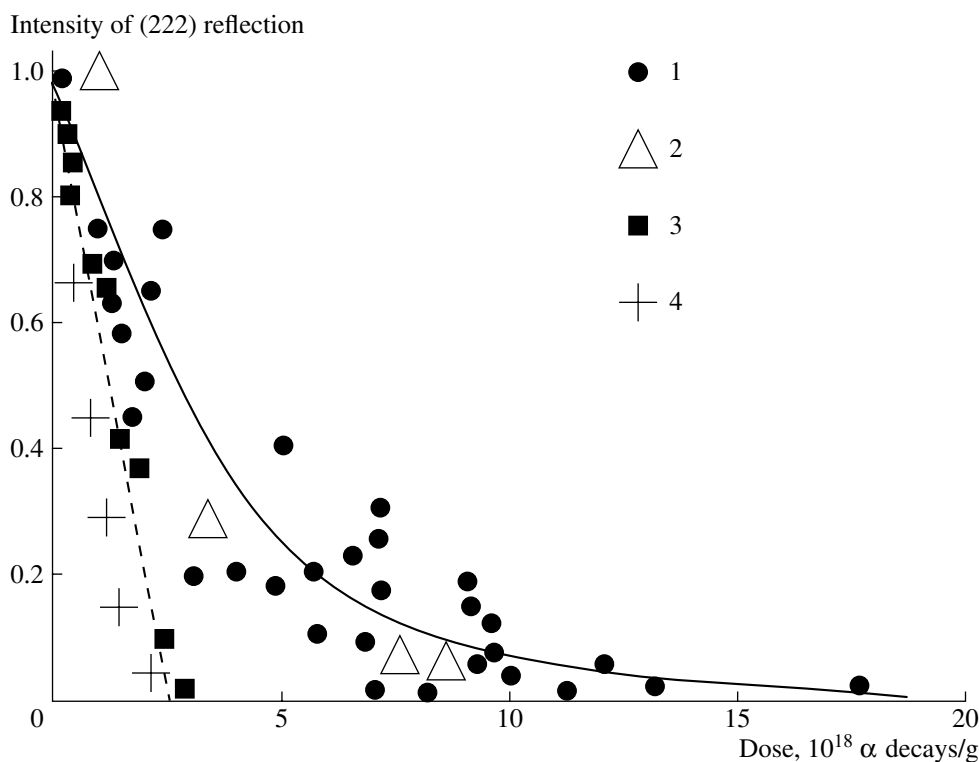


Fig. 9. Radiation doses that induce amorphization of (1, 2) natural pyrochlores and (3, 4) their artificial analogues, after Laverov et al. (2003).

conditions far from equilibrium, which will provoke their transformation. However, in poorly permeable rocks, the alterations will proceed so slowly and their results will be so insignificant that they will not exert an appreciable effect on the insulating properties of matrices. Thus, the safety of HLW repositories may be ensured if actinide-bearing ceramics consisting of artificial analogues of stable natural U, Th, and REE minerals are disposed of in poorly permeable rocks that rule out hydrothermal activity or chemical weathering.

The question of the reliability of mineral stability estimates based on results of natural observations and laboratory experiments merits discussion. The results of sluggish processes proceeding at a low temperature over millions of years may be judged only from natural observations and commonly cannot be simulated in short-term (tens of days; in exceptional cases, a few years) laboratory experiments. To compare the chemical stability of different matrices, leaching experiments are performed. The conditions of these experiments (temperature, pH and Eh of solutions, mineral/solution ratio, rate of surface interaction, etc.) differ from the conditions in underground repositories. However, the results of testing make it possible to compare the relative stability of various minerals or the same minerals of varying composition. The implications of such results are especially important for materials that do not have natural radioactive analogues, e.g., murataite or garnet. In solving the problem of the chemical stability

of confinement matrices in the geologic medium, preference should be given to observations on natural radioactive counterparts.

The results of natural observations and laboratory experiments are used for estimation of the radiation stability of minerals. A dose of irradiation is determined from the isotopic age of a mineral and the U and Th contents therein. Comparing received doses and the degree of lattice damage, one can estimate the critical dose of amorphization. Such estimates are not accurate because the damage to the mineral structure is combined with its recovery. The higher the temperature, the more intense the recovery. At a certain temperature, a mineral does not become amorphous at all owing to a higher rate of the competitive process of recovery. Unfortunately, in most cases, it is impossible to estimate the temperature regime of minerals during a particular interval of geologic time. Therefore, the critical doses for the same mineral may differ by tens of times. It is also important to keep in mind that, at the same temperature, the rate of radiation damage recovery is not equal for different minerals. Minerals that readily recover their structures, e.g., monazite, retain crystallinity throughout their life irrespective of the received dose. In examining such a mineral, it is not easy to determine what is the cause of lattice retention: a high radiation stability or an ability to heal damage.

Experimental results give much more definite information on radiation stability. For this purpose, minerals

are doped with a highly radioactive isotope (^{244}Cm or ^{238}Pu) and undergo subsequent XRD monitoring. In this way, it is possible not only to determine the critical irradiation dose that induces amorphization of the structure but also to trace the progressive stages of structure damage. Another technique is based on bombardment of a mineral by ions of inert gases, Cs, Pb, Au, etc. In this case, the material does not acquire induced activity, which simplifies the experimental procedure. The critical radiation doses obtained with this technique are lower than the estimates obtained from data on the isotopic age and the U and Th contents in natural minerals (Fig. 9). For example, the critical dose for zirconolite based on the data on natural minerals is estimated at 1–6 displacements/atom, whereas the experimental results yield 0.5 displacements/atom and 0.8–1.0 and 0.15–0.25 displacements/atom for pyrochlore and britholite. It is evident that the critical dose of amorphization established in this way characterizes the true radiation stability of minerals without consideration of the inverse process of recovery of radiation defects.

The time that an actinide-bearing mineral occurs in the crystalline state depends on the concentrations of radioisotopes, temperature, the resistance of the mineral to radiation effects, and its ability to recover its structure. If experimental results are taken into account, then 10 wt % ^{239}Pu contained in any minerals except zirconate pyrochlore and monazite will ensure their amorphization over 1000 yr (a dose of 7×10^{18} α decays/g). Taking into account that, in addition to ^{239}Pu , HLW contain other radioactive isotopes with shorter half-lives, such a radiation dose is quite realistic for HLW matrices.

Therefore, in assessing the safety of repositories, one should assume complete amorphization of radwaste matrices 1000 yr after disposal. Amorphization must be regarded as an unwanted phenomenon since it gives rise to the increasing solubility of phases. For some minerals, this increase is insignificant, but for others it may reach 1.0–1.5 orders of magnitude. The expansion of amorphous minerals, mostly by 5–6%, is another negative factor. The expansion of zircon reaches 18%. The increase in volume is accompanied by cracking of minerals and an increase in the area contacting subsurface water, which stimulates dissolution. Nonetheless, the insulating properties of even amorphous minerals are rather high. For example, samples of metamict zirconolite from Sri Lanka have remained closed systems with respect to U and Th and products of their decay; their solubility in water and brines at 200°C is 1000 times lower than that of borosilicate glass (Oversby and Ringwood, 1981). Therefore, the radiation stability is not a crucial factor in the choice of HLW matrices. The capacity with respect to actinides, ability to include a wide range of elements contained in radwastes, stability in solutions, feasibility of industrial production, and physical properties (strength, thermal conductivity) are of greater importance.

CONCLUSIONS

(1) Some natural minerals firmly retain U, Th, and REE analogues of transuranic actinides for millions of years despite the effects of subsurface water. These minerals may serve as a basis for synthesis of artificial HLW matrices that ensure reliable insulation of long-lived actinides in underground repositories for a virtually infinite time. This shows the real possibility of solving the problem of disposal of actinide wastes of nuclear energy and weapons production.

(2) The aforementioned minerals were formed at a high temperature and are not in equilibrium with subsurface waters that occur as films in microfractures, intergranular sutures, and pores. Their effect on minerals is expressed in the formation of micro- and nanoparticles of secondary phases and in diffusive redistribution of elements within mineral grains. The rate of this interaction is low and its results are so minor that natural minerals remain virtually unaltered for many millions of years. The safety of actinide HLW repositories will be ensured by disposal of actinide ceramics based on high-strength minerals in poorly permeable rocks under conditions that rule out hydrothermal activity or chemical weathering.

(3) The natural radioactive minerals—uraninite, monazite, zirconolite, pyrochlore, and britholite—have been characterized. It has been shown that, in most cases, their artificial analogues will be considerably or completely amorphized in a few hundred years. The results of laboratory testing and examination of natural minerals show that, although amorphization gives rise to some increase in solubility, crystalline matrices remain many times more stable than glassy materials even after damage to their structure. Crystalline matrices show the highest stability when they are disposed of in rocks that contain reducing and slightly alkaline subsurface waters. Irrespective of engineering barriers (containers, a clay buffer), such conditions will ensure insulation of actinide wastes from the biosphere during the time of their potential hazard.

(4) The list of potential phases suitable for immobilization of actinides is not limited only to those that have natural analogues of similar structure and composition. The results of investigations of ferrigarnet and titanate murataite ceramics have shown that artificial compounds without full natural analogues also may be promising matrices for actinide wastes. To characterize such matrices, laboratory studies of samples containing components of radwastes, including transuranic actinides, are necessary.

(5) In general, the choice of an HLW matrix should take into account its chemical stability in water solutions, isomorphic capacity with respect to actinides, and ability to include a wide range of other chemical elements, as well as the technological feasibility of production of a radioactive ceramic. To immobilize actinide wastes of extremely complex chemical composition, matrices consisting of several phases may be used.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research, project nos. 05-05-64005 and 05-05-64094.

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