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Assessment of the potential ability of phyllosilicates to accumulate and retain tritium in structural OH-groups

A complex of hierarchical criteria is proposed by which OH-bearing phyllosilicates can be divided into different classes according to their ability to accumulate and retain tritium in structural OH-groups during interaction with heavy water. The criteria are based on the distinctions of phyllosilicates mineral structure and its crystal-chemistry. Besides, we were taking into account the structural and energy state of OH-groups and water molecules in the minerals, potential mechanisms of tritium transfer from the water phase into the mineral structure and hydrogen isotope exchange with protons of OH-groups. Phyllosilicates with interlayer or channel spaces containing either mobile water molecules or continuous hydroxyl nets are the most promising ones. In the first case, the water molecules increase the capacity for tritium interaction with protons of structural OH-groups by means of O-lattice ions; in the second, tritium can be incorporated into hydroxyls through interaction of free mineral matrix protons with tritium ions of dissociated HTO or T_2O molecules.

1. Introduction

In recent years our research group's work has been directed to the evaluation of the properties of clay minerals as a barrier for tritium contamination, establishing that some phyllosilicates are able to accumulate and retain tritium in their structures [11–14, 16, 18–20]. It was determined that tritium is accumulated by clay minerals in various forms and structural positions. A considerable amount of tritium is easily adsorbed on the surface of particles in the form of water films and conformably washed away with infiltration flow. Somewhat smaller amount of tritium accumulate in the interlayer space, but are not strongly bound either. The strongest fixation results from isotope-hydrogen exchange in structural OH-group positions. Hence, from the standpoint of assessment of barrier properties, the minerals with enough OH-groups in their structure are of particular interest.

According to DANA's mineral classification [4] and the mineralogy database [1], the group of phyllosilicates includes 226 species. Naturally, to study so many minerals regarding their suitability as barriers is time consuming. Thus the aim of this study was to select a group of phyllosilicates whose structure can accumulate and retain tritium. Promising minerals were selected among this group accordance to criteria based on experimental data and suggested exchange mechanisms for heavy hydrogen isotopes in the "heavy water-mineral" system.

2. State of the art

Phyllosilicates can be found in a multitude of geological context. Many are formed by hydrolysis of primary silicates, in both supergenic alterations and under low-grade metamorphism [5, 10]. They also appear in association with hydrothermal veins, in amygdales found in volcanic rocks and as interaction products of Al and Fe hydroxides with SiO_2 gel and sea water. Although some of these minerals are formed in large amounts as a result of surface processes, they occasionally form large deposits in marine and lacustrine basins.

Variations in formation conditions in the weathered surf3ace result in considerable variety of phyllosilicate species, which are determined both by the specific features of structural bonding of silicon-oxygen radicals and by the isovalent and heterovalent isomorphism of cations and anions [3]. The large group of phyllosilicates is made up of minerals in which silicon may be substituted by aluminium in tetrahedron coordination, with Si-Al ratios from 4 :

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0 to 1 : 3. Besides, in some cases Si is substituted by B (boron-muscovite).

In most of phyllosilicates, the hexagonal mesh arrangement of Si–O (or Al–Si–O) tetrahedron is associated with gibbsite or brucite octahedral sheets and forms two main types of layers, the so-called 2 : 1 (or T.O.T.) and 1 : 1 (or T.O.) layers. Minerals with a 2 : 1 structure are formed at earlier and higher-temperature stages of hydrolysis than minerals with 1 : 1 layer. The structure of chlorites is typically hybrid, consisting of alternating 2 : 1 and brucite (or gibbsite) layers. Alteration of these minerals generally gives rise to the appearance of mixed-layer minerals [2], whose structures alternate layers of mica, smectites, kaolinite, chlorite, etc. according to their composition.

Regarding their chemistry, the phyllosilicates are characterized by a great compositional variability. Apart from Si and Al, the most common cations are Mg, Fe, K, Na, Ca, and, to a lesser extent, Mn, Ti, Ba, Li, as well as Ni, Pb, Cu, Zn. The main anions are O and (OH), although it is very common to find isomorphic substitutions of hydroxyl by F and Cl; sometimes sulphate and carbonate anionic groups are also found [3, 5].

3. Proposal of classification criteria

Phyllosilicates can be classified according to different principles, depending on the aim of view. Regarding their potential ability to accumulate and retain tritium, we propose, besides the structure and crystal-chemistry, a hierarchical succession of criteria taking into account the structural and energy state of OH-groups and water molecules, the potential mechanisms of tritium transfer from water into the mineral structure and the hydrogen isotope exchange with protons of OH-groups.

3.1. *First criterion: presence of* OH-*groups, with potential exchange capacities for tritium fixation in the mineral structure.* Of the 226 species, 174 minerals have OH-groups in their structure (Table 1). This group is further arranged according to crystal-chemical and structural features [1].

3.2. *Second criterion*: *presence of* H_2O *molecules in the structure of phyllosilicates.* As in liquid phase tritium migrates mostly in the form of tritium water molecules (HTO, T_2O), the main transport agent providing delivery of this isotope into the mineral structure is water molecules. On the base of this criterion, the 174 mineral having OH-groups were divided into two groups: 69 mineral species containing H_2O molecules in their crystalline-chemical formulae and 105 mineral species not containing H_2O molecules.

3.3. *Third criterion*: *structural positions of* OH-*groups and water molecules.* This criterion is based on distinctive exchange mechanisms of protium by tritium, depending on whether

Table 1. **Phyllosilicates with OH-groups**

Index	**Phyllosilicates**	Number of species
VIII-71	*Phyllosilicate with Six-Membered Rings*	
71.0	Minerals Without Dana Classification	4
71.1	Phyllosilicate Sheets of Six-Membered Rings with 1:1 layers	27
71.2	Phyllosilicate Sheets of Six-Membered Rings with 2:1 Layers	53
71.3	Phyllosilicate Sheets of Six-Membered Rings with 2 : 1 clays	14
71.4	Phyllosilicate Sheets of Six-Membered Rings interlayered 1 : 1, 2 : 1, and octahedra	21
71.5	Phyllosilicate Sheets of Six-Membered Rings with other anions	1
VIII-72	*Phyllosilicate Two-Dimensional Infinite Sheets with Other Than Six-Membered Rings*	
72.1	Phyllosilicate with 4-membered Rings	3
72.2	Phyllosilicate with 4-, 6-, and 8-membered Rings	1
72.3	Phyllosilicate with 3-, 4-, or 5-membered rings and 8-membered rings	7
72.4	Phyllosilicate with 4-, 6-, and 12-membered rings	6
72.5	Phyllosilicate with corrugated and complex layers	5
VIII-73	*Phyllosilicate Condensed Tetrahedronl Sheets*	
73.1	Phyllosilicate with double layers	4
73.2	Phyllosilicate with double and single layers	7
VIII-74	*Phyllosilicate Modulated Layers*	
74.1	Phyllosilicate with joined islands	10
74.3	Phyllosilicate with joined strips	11
	TOTAL	174

there are OH-groups or H_2O molecules [7, 15].

A number of H_2O-bearing phyllosilicates (Table 2) have various energetic states of water molecules (parameters of diffusion in the interlayer space, exchangeability with liquid phase molecules, hydratability of exchange cations, etc.). H_2O molecules can hydrate exchangeable cations such as K, Ca and others (hydration water), form part of the mineral's structure (crystallization water) or can be found in the so-called "zeolitic channel" of some minerals as fibrous clays, for instance (zeolitic water). A contribution of these structural types of water molecules in tritium accumulation process depend on mineral's structure type.

Montmorillonite (dioctahedral smectite group) is a typical representative of hydrous phyllosilicates. The well-known models of sp^3-hybridization of oxygen ions [6] allow us to assume an exchange mechanism of H_2O protons with (OH) protons in the structure of this mineral. Of the four orbitals of lattice-oxygen of the Si–O tetrahedron, two are combined with two Si ions and the other two are oriented towards the interlayer space, where they are weakly bounded with the hydrogen of the water molecules. In the case of structural OH-groups, two of four orbitals are connected with two octahedrally co-ordinated cations (Al, $Fe^{+3,+2}$, Mg, etc.); the third one, which is directed at a 16° angle to the basal plane, is connected with the (H^+) proton and the fourth orbital, directed along the *c'* axis, is free. In the absence of water molecules in the interlayer space, interchangeable ions (Na, K, Ca, Li and others) shift towards the hydroxyls, sealing the hexagonal ring up. The entrance of water into the interlayer space causes rehydration of ions and their extraction from hexagonal rings and, consequently, a shift towards the interlayer space. As a result, water molecules protons increase the capacity for interaction with structural OH-group protons by means of O-lattice ions. Thus, the availability of free orbitals in both lattice-oxygen and in the hydroxyls makes exchange of hydrogen isotopes possible between water molecules and OH-groups.

Validity of the proposed model of tritium accumulation process in the montmorillonite structure was confirmed by experimental study of the "montmorillonite-deuterium water" system [15]. It should be mentioned that in this smectite, the exchange mechanism of heavy hydrogen isotopes with OH-group protons is a two-stage process: the initial stage is water-molecule diffusion into the interlayer space of montmorillonite, as the coefficients of water-molecule diffusion are approximately equal in the liquid phase and in the inter-layer space of a damp

Table 2. **Ranking of H_2O-bearing Phyllosilicates by structural type of water and mineral structure type**

Sub-class	**Class 1.1**	**Class 1.2**				
	1.1.A *structure type 1 : 1*	**1.2.A** *structure type 1 : 1*	**1.2.B** *structure type 2 : 1*	**1.2.C** *interlayered 1 : 1, 2 : 1, & octahedra*	**1.2.D** *structure with inverted ribbons*	**1.2.E** *Sheets with Other Layers*
α	Endellite	Hisingerite	**Dioctahedral Smectites gr.** (Montmorillonite, Beidelite, Nontronite, etc.), **Trioctahedral Smectites gr.** (Saponite, etc.), **Hydromica subgr.** (Hydrobiotite, Illite, Vermiculite, Brammallite), **Surite gr.,** Amstallite, Eakerite, Vertumnite, Brinrobertsite, Ekmanite, Bariumbannisterite	**Chlorite-Smectite gr.** (Tosudite, Corrensite, Rectorite, Aliettite, Glagolevite)	**Palygorskite gr.,** **Sepiolite gr.,** Chrysocolla, Krauskopfite, Makatite, Intersilite	Amstallite, Eakerite **Tobermorite gr.** (Clinotobermorite, Riversideite), Macdonaldite, Hydrodelhayelite, Vertumnite **Reyerite gr.** **Stilpnomelane gr.,** **Ganophyllite gr.**
β			Swinefordite			Varennesite, Zeophyllite, Tuscanite, Fedorite

mineral; in the second stage, the transfer of tritium from dissociated water molecules to structural positions of minerals with free orbital compensation takes place due to proton-tritium exchange. This process may be accelerated by gamma-irradiation of the system [17].

Thus, the presence of mobile water molecules in phyllosilicate structure promotes tritium penetration inside the mineral to potential places of protium-tritium exchange. On the basis of this criterion, the group of water-containing phyllosilicates may be divided into 2 classes according to the state of water molecules in their structure: class *1.1*, containing only zeolitic water and class *1.2* with zeolitic and hydration water (Table 2).

In phyllosilicates not containing interlayer water molecules (Table 3), the exchange mechanism of heavy water hydrogen isotopes with protons of structural OH-groups is determined by the presence or absence of continuous hydroxyl nets in the mineral structure. The quantity of OH-ions in the structural formula is > 2 or ≤ 2 respectively. Distinctive features of this exchange mechanism are showed using kaolinite as a representative example of the minerals in this group of anhydrous phyllosilicates [3–5, 10].

Experimental studies of deuterium accumulation in kaolinite structure during its interaction with deuterium-rich water revealed that absence of water molecules, which carry deuterium into the interlayer space to OH-groups, does not inhibit the accumulation of the heavy hydrogen isotope in the mineral structure. The possibility of such process is conditioned by the fact that there are continuous net of hydroxyl groups in the structure of kaolinite-type minerals. The surplus protons arising in their structure can able to migrate from one OH-group to other by jump. According to G. Maiti and F. Freund [9] protons life-time in structural OH-group of a mineral do not exceed 10^{-12} sec., comparable with their life in liquid phase of water. The quantity of such protons may reach about 10^{13} moles.

In kaolinite, continuous OH-group nets are located in structural packs (hydroxides) on the interlayer space side. In these minerals, the freely migration protons are exchange with the heavy isotopes of the water molecules in the course of "vibrations" on crystalline edges close to the water phase. Exchange process intensifies in case when OH-groups are adsorption centers on the edges of mineral particles. Violation of isotope equilibrium (concentration) promotes diffusion of tritium (deuterium) along structural OH-groups and formation of OT-(OD)-groups [7, 15].

In anhydrous phyllosilicates containing two or less OH-groups, continuous hydroxide nets are absent and protons cannot transfer into them. As a result, accumulation of hydrogen heavy isotopes does not occur in structural-OH positions of such minerals.

Table 3. **Ranking of Anhydrous Phyllosilicates by type of hydroxyl nets and mineral structure type**

Sub-class	**Class 2.1**			**Class 2.2**	
	2.1.A *structure type 1 : 1*	**2.1.B** *structure type 2 : 1*	**2.1.E** *Sheets with Other Layers*	**2.2.A** *structure type 1 : 1*	**2.2.D** *interlayered 1 : 1, 2 : 1, & octahedra*
α	**Bismutoferrite gr.**	**Pyrophyllite-Talc gr., Biotite subgr**. (Eastonite, Hendricksite, Aspidolite etc.) **Margarite subgr.,** Macaulayite	Prenite, **Pyrosmalite gr.** (Schallerite, Nelenite), Kvanefjeldite, Parsettensite, Zussmanite, Coombsite, Searlesite, Pianlinite	**Kaolinite gr.** (Dickite, Nacrite, Odinite, Halloysite) **Lizardite subgr., Amesite subgr., Chrysotile subgr.,** Imogolite	**Chlorite gr.** (Clinochlore, Chamosite, Pennantite, etc.), **Chlorite-Smectite gr.** (Dozyite), Franklinfurnaceite**,** Gonyerite**,** Kegelite
β		**Muscovite subgr.** (Nanpingite, Chromphyllite, Boromuscovite, etc.), **Biotite subgr.** (Biotite, Phlogopite, Lepidolite etc.)	**Pyrosmalite gr., *Fridelite* gr.,** Semenovite	Caryophilite	

On the base of this criterion, anhydrous phyllosilicates may be divided into two classes, where processes of substitution of protons by hydrogen heavy isotopes in structural OH-groups positions is potentially possible (quantity of OH-ions in the structural formula is > 2, class *2.1*, Table 3) or impossible (respectively quantity of OH-ions ≤ 2, class *2.2*, Table 3).

Thus, availability of continuous nets of structural OH-groups or (and) water molecules in the interlayer space of phyllosilicates is a favourable condition for accumulating and retaining hydrogen heavy isotopes in their structure.

3.4. *Fourth criterion: structure type.* As a rule, minerals having a 1 : 1 structure (excluding bismuthoferrite group) are characterised by the presence of continuous nets of OH-groups. Therefore in anhydrous phyllosilicates with two sheets (groups of kaolinite and serpentine), incorporation of tritium into structural OH-groups can occur due to the interaction of free protons from the mineral matrix with tritium ions of dissociated HTO or T_2O molecules. In H_2O-bearing phyllosilicates of this structural type (hisingerite, endellite) additional access of tritium ions to structural OH-groups is favoured by the diffusion of HTO (or T_2O) molecules into the interlayer space.

In most of the cases, minerals with a 2 : 1 structure do not contain continuous nets of OH-groups. The main carrier of tritium into their structure must be, therefore, the water found in the interlayer space. Dioctahedral and trioctahedral smectite groups are made up of mineral accumulators of tritium, as well as those included in the hydromica group (vermiculite, hydrobiotite and illite) and surite group, etc. (Table 3). Under normal conditions protium-tritium exchange does not occur in other anhydrous phyllosilicates with this 2 : 1 structure, like muscovite, biotite, pyrophyllite-talc and margarite subgroups etc. Partial incorporation of deuterium into the matrix of some of these minerals was noted only during their irradiation up to 10^7 Gy [15, 17].

In minerals with a 2 : 1 : 1 structure (chlorite group), hydroxyl ions are partially combined in three-sheet packs, but mainly co-ordinated by Mg and Fe in octahedral (brucite or gibbsite) layers easily accessible for isotope exchange.

Minerals having a structure with inverted ribbons (palygorskite and sepiolite groups often known as fibrous clays or pseudo-layered clays) are rather important for absorption of tritium. Such structure provides an easy access of HTO and T_2O molecules to the hydroxyls and substitution of free protons by tritium ions.

3.5. *Fifth criterion: availability of other ions* (F, Cl, etc.) *competitive for a proton in* OH-*structural positions.* Substitution of a part of OH-groups by F, Cl or O ions, or by complex anions (CO_2, SO_3, etc.) breaks the continuity of the hydroxyl net. As a result, the efficiency of formation of surplus protons and their isotope-hydrogen exchange capacity decrease. Such minerals (with index β in Tables 2, 3) — swinefordite, varennesite, zeophyllite, tuscanite, fedorite, caryophilite etc. are less efficient for the accumulation of tritium then phyllosilicates containing only OH-groups without other ions and anions (minerals with index α in Tables 2, 3 — Dioctahedral Smectites gr., Chlorite–Smectite gr., Palygorskite gr. etc.) and therefore less promising for their use as barriers for tritium contamination of environment.

Table 4. **List of Phyllosilicates prospective for use as accumulators and retainers of tritium**

Class	Minerals
1.1.A α	Endellite
1.2.A α	Hisingerite
1.2.B α	**Dioctahedral Smectites gr.** (Montmorillonite, Beidelite, Nontronite, etc.), **Trioctahedral Smectites gr.** (Saponite, etc.), **Hydromica subgr.,** (Hydrobiotite, Illite, Vermiculite, Brammallite), **Surite gr.,** Amstallite, Eakerite, Vertumnite, Brinrobertsite, Ekmanite, Bariumbannisterite
1.2.C α	**Chlorite-Smectite gr.** (Tosudite, Corrensite, Rectorite, Aliettite, Glagolevite)
1.2.D α	**Palygorskite gr., Sepiolite gr.,** Chrysocolla, Krauskopfite, Makatite, Intersilite
1.2.E α	Amstallite, Eakerite**, Tobermorite gr.** (Clinotobermorite, Riversideite), Macdonaldite, Hydrodelhayelite, Vertumnite, **Reyerite gr., Stilpnomelane gr., Ganophyllite gr.**
2.2.A α	**Kaolinite gr.** (Dickite, Nacrite, Odinite, Halloysite) **Lizardite subgr., Amesite subgr., Chrysotile subgr.,** Imogolite
2.2.D α	**Chlorite gr.** (Clinochlore, Chamosite, Pennantite, etc.), **Chlorite-Smectite gr.** (Dozyite), Franklinfurnaceite**,** Gonyerite**,** Kegelite

In spite of such high polytypical variety, phyllosilicates exhibit noticeably small variations of the main structural patterns. The most wide-spread patterns are reticulate structures with 6-membered rings of $[SiO_4]^{4-}$ tetrahedron (class *VIII-71*) [1, 4]. Classes *VIII-72* (two-dimensional infinite sheets with other than 6-membered rings of silicon-oxygen tetrahedron), *VIII-73* (condensed tetrahedron sheet) and *VIII-74* (modulated layers and joined islands of silicon-oxygen tetrahedron) are less prevalent and variable. With the noticeable exception of prehnite (*VIII-72.1* group), apophyllite (*VIII-72.3*), pyrosmalite (*VIII-72.4*), stilpnomelane (*VIII-74.1*) and palygorskite-sepiolite (*VIII-74.3*), they are exotic minerals appearing, for instance, filling effusive rocks vesicles.

Concluding remarks

The application of the suggested criteria, based on the crystal-chemical and geochemical characteristics of phyllosilicates, allow their classification according to the potential ability for tritium accumulation and retention in structural hydroxyl groups, as well as to make an estimation of their perspective for use as barriers for tritium contamination of environment (Table 4). The availability of continuous nets of structural OH-groups and water molecules in the interlayer space of phyllosilicates is a favourable condition for this on principle. Further assessment for the possible use of the 111 selected minerals can be performed taking into account their abundance, accessibility, price, and other technological parameters.

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1. *Barthelmy*, 2004. Internet WEB-page http://webmineral.com/danaclass.shtml
2. *Chamley* Clay sedimentology. — Berlin: Springer-Verlag, 1989. — 623 p.
3. *Deer W. A., Howie R. A., Zussman J.* Rock forming minerals. — London: Longmans, 1962. — 318 p.
4. *Gaines R. V., Skinner H. C. W., Foord E. E. et al.* Dana's new mineralogy: the system of mineralogy of James Dwight Dana and Edward Salisbury Dana. — 8th ed. — John Wiley & Sons, Inc, 1997. — 1872 p.
5. *Godovikov A. A.* Mineralogy. — Moscow: Nedra Press, 1983. — 647 p.
6. *Ishutina O. D., Litovchenko A. S., Melnikov A. A., Proshko V. Ja.* The dehydroxilatin mehanism in micas // Rept. Acad. Sci. of USSR. **A.** — 1987. — No 4. — P. 81–84.
7. *Kalinichenko E. A., Lytovchenko A. S., Baker J. H. et al.* The mechanism of exchange of hydrogen isotopes in kaolinite structure // 9th Conf. of the Europ. Clay Groups Assoc. EUROCLAY-1999 (Sept., 5–9, 1999): Abstr. Book. — Krakow (Poland), 1999. — P. 108.
8. *Kalinichenko E. A., Pushkareva R. A., Fenoll Hach-Ali P., Lepez-Galindo A.* Tritium accumulation in the structure of some clay minerals // Clay Minerals. — 2002. — **37**. — P. 497–508.
9. *Maiti G., Freund F.* Dehydration-related proton conductivity in kaolinite // Ibid. — 1981. — **16**. — P. 395–413.
10. *Povarennyh A. S.* Crystal-chemical classification of mineral species. — Kiev: Nauk. dumka Press, 1966. — 547 p.
11. *Pushkarev A. V., Lytovchenko A. S., Pushkareva R. A., Hach-Ali P. F.* Clay rocks as geological barrier for tritium contamination in storages of a radioactive waste // Proc. of ICAM (13–21 July, 2000). — Goetingen (Germany), 2000. — P. 633–636.
12. *Pushkarev A. V., Lytovchenko A. S., Pushkareva R. A., Yakovlev Ye. A.* Dynamics of tritium accumulation in mineral medium // Mineral Resources of Ukraine. — 2003. — No 3. — P. 42–45.
13. *Pushkarev A. V., Pushkareva R. A., Lytovchenko A. S., Koltunov B. G.* Buffering properties of the geological environment in situ of the radioactive waste repositories containing tritium // Coll. papers of State Sci. Center of Environmental Radiogeochem. Ser. Environmental Technogenic-Ecological Safety. — 2000. — No 1. — P. 117–127.
14. *Pushkarev A. V., Yakovlev Ye. A., Pushkareva R. A. et al.* Tritium hydrogeomigration in Radioactive Waste Repositories sites // Mineral Resources of Ukraine. — 2003. — No 2. — P. 38–40.
15. *Pushkareva R. A.* Exchange of the hydrogen isotopes in the clay minerals: PhD diss. thesis. — Kiev, 1999. — 19 p.
16. *Pushkareva R. A., Hach-Ali P. F., Galindo L. A. et al.* Fractionation of the hydrogen isotopes in clay // 9th Conf. of the Europ. Clay Groups Assoc. EUROCLAY-1999 (Sept., 5–9, 1999): Abstr. Book. — Krakow (Poland), 1999. — P. 124.
17. *Pushkareva R., Kalinichenko E., Litovchenko A. et al.* Irradiation effect on physic-chemical properties of clay minerals // Appl. Clay Sci. — 2002. — No 21. — P. 117–123.
18. *Pushkareva R. A., Lytovchenko A. S., Pushkarev A. V.* Hydrogen isotopes sorption capacity of clay minerals // Acta Mineral.-Petrogr. (March, 9–10, 2000). — Miskolc (Hungary), 2000. — **XLI**. — P. 90.
19. *Samodurov V., Ratko A., Fenoll Hach-Ali P. et al.* Tritium absorption effects in phyllosilicates // 10th

Conf. of the Europ. Clay Groups Assoc. EUROCLAY-2003 (Modena, Italy, June, 22–26, 2003): Abstr. Book. — Modena, 2003. — P. 246–247.

20. *Yakovlev Ye. A., Pushkarev A. V., Pushkareva R. A., Priymachenko V. M.* Assessment of the tritium transfer in aeration zone and aquifer // Mineral Resources of Ukraine. — 2004. — No 3. — P. 39–41.

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РЕЗЮМЕ. Предложен иерархический комплекс критериев для разделения ОН-содержащих филлосиликатов на различные классы в соответствии с их способностью накапливать и удерживать тритий в структурных ОН-группах при взаимодействии с тяжелой водой. Критерии базируются на различиях минеральной структуры и кристаллохимических особенностей филлосиликатов. Вместе с тем, мы учитывали структурные и энергетические позиции ОН-групп и молекул воды в минералах, потенциальные механизмы переноса трития из водной фазы в структуру минерала и механизмы изотопного обмена трития с протонами ОН-групп. Наиболее перспективными являются филлосиликаты, содержащие мобильные молекулы воды в межслоевом или канальном пространстве минеральной структуры, а также содержащие сплошные сети гидроксильных групп. В первом случае молекулы воды повышают возможность взаимодействия трития с протонами структурных ОН-групп через кислородные ионы сетки, во втором — тритий может входить в гидроксильные группы посредством взаимодействия свободных протонов матрицы с ионами трития из диссоциированных молекул НТО или T_2O.

РЕЗЮМЕ. Запропоновано ієрархічний комплекс критеріїв для розділення ОН-вмісних філосилікатів на різні класи згідно з їх здатністю накопичувати і утримувати тритій в структурних ОН-групах при взаємодії з важкою водою. Критерії базуються на різниці мінеральної структури та кристалохімічних особливостей філосилікатів. Разом з тим, ми враховували структурні та енергетичні позиції ОН-груп і молекул води в мінералах, потенційні механізми переносу тритію із водної фази до структури мінералу та механізми ізотопного обміну тритію з протонами ОН-груп. Найбільш перспективними є філосилікати, які вміщують мобільні молекули води в міжшаровому чи канальному просторі мінеральної структури, а також ті, що мають суцільні сітки гідроксильних груп. У першому випадку молекули води підвищують здатність взаємодії тритію з протонами структурних ОН-груп через кисневі іони сітки, в другому — тритій може входити в гідроксильні групи завдяки взаємодії вільних протонів матриці з іонами тритію з дисоційованих молекул НТО чи T_2O.