

RADIATION-DAMAGE RESISTANCE IN PHYLLOSILICATE MINERALS FROM FIRST PRINCIPLES AND IMPLICATIONS FOR RADIOCESIUM AND STRONTIUM RETENTION IN SOILS

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Abstract—Accidental discharges of the hazardous nuclear fission products $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ into the environment, such as during the Fukushima Dai-ichi nuclear accident, have occurred repeatedly throughout the ‘nuclear age.’ Numerous studies of the fate and transport of $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ in soils and sediments have demonstrated their strong and selective binding to phyllosilicate clay minerals, primarily by means of cation exchange into interlayer sites. The locally concentrated amounts of these radioactive beta-emitters that can be found in these host minerals raise important questions regarding the long-term interplay and durability of radioisotope–clay associations, which is not well known. The present study goes beyond the usual short-term focus to address the permanence of radioisotope retention in clay minerals, by developing a general theoretical understanding of their resistance to the creation of defects. The present study reports *ab initio* molecular dynamics (AIMD) calculations of the threshold displacement energy (TDE) of each symmetry-unique atomic species comprising the unit cell of model vermiculite. The TDE values determined are material specific, radiation independent, and can be used to estimate the probability of Frenkel-pair creation by direct electron–ion collision, as could be induced by the passage of a high-energy electron emitted during the beta-decay of ^{137}Cs , ^{90}Sr , and daughter ^{90}Y . For ^{137}Cs and ^{90}Sr , the calculated probability is ~36%, while for ^{90}Y the probability is much greater at ~89%. The long-term retention picture that emerges is that decay will progressively alter the clay interlayer structure and charge, probably leading to delamination of the clay, and re-release of residual parent isotopes. Further work examining the effect of Frenkel defect accumulation on the binding energy of parent and daughter radionuclides in the interlayer is thus justified and potentially important for accurate long-term forecasting of radionuclide transport in the environment.

Key Words—*Ab Initio* Molecular Dynamics, Cesium, Beta Emission, Defect, Frenkel Pair, Fukushima, Nuclear Power, Phyllosilicate, Radioactive, Radioisotope, Threshold Displacement Energy, Vermiculite.

INTRODUCTION

Phyllosilicates are common soil minerals that are powerful sorbents of cations through their naturally high capacity for selective cation exchange into their interlayer spaces. Nuclear accidents over recent decades have motivated governments and others to expend substantial effort in attempts to understand and quantify the thermodynamics and kinetics of cation exchange into various phyllosilicate clay minerals because this process defines the chemical speciation and migration potential of certain radioactive contaminants dispersed into the environment. In particular, the migration of radiocesium and strontium is known to be strongly attenuated by selective cation exchange for K, Ca, and Mg naturally present in clay-mineral interlayers. After the nuclear accident at the Fukushima Dai-ichi Nuclear Power Plant (Japan) in March 2011, a large area of surrounding soils and rivers was exposed to an aerial dispersal of primarily

^{137}Cs and, to a lesser extent, ^{90}Sr . Cation exchange of these isotopes into the dominant clay minerals vermiculite, kaolinite, and illite is thought to be effective and complete, comprising the primary retardation mechanism in Fukushima soils. The remaining long-term migration potential is thus thought to depend exclusively on physical transport of contaminated clay particles through watersheds (Wampler *et al.*, 2012).

Although the ^{137}Cs and ^{90}Sr retention mechanism in clay minerals is relatively well understood, long-term retention ability is less well known. Though generally accepted to be chemically irreversible, the permanence of these isotopes in their host crystallites over time will depend on the local concentration of emitting radioisotopes and the resistance of the surrounding crystal structure to attendant radioactive decay processes. With a half-life of ~30 y, ^{137}Cs and ^{90}Sr are prototypical examples of radioisotopes that undergo beta-decay. While ^{137}Cs transmutes simply into a stable daughter ^{137}Ba species, ^{90}Sr first transmutes into an intermediate ^{90}Y radioisotope, which has a much shorter half-life (64 h), and subsequently beta-decays into a stable ^{90}Zr species. The high-energy electron emitted during the decay processes, especially in the case of ^{90}Y to ^{90}Zr

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decay, has the potential to produce structural damage in the host material in a variety of ways (Hobbs *et al.*, 1994; Weber *et al.*, 1998), including by ionization, localized heating, or Bremsstrahlung. Atom displacements yielding permanent point defects may also be produced either by a direct elastic electron-atom collision or by the conversion of a radiation-induced electronic excitation into atom motion. The creation and accumulation of Frenkel pairs (vacancies and their corresponding atomic interstitials) can ultimately convert the host crystallite, locally or globally, to metastable phases that have different retention capacity from the residual radioisotopes. This process is material specific and depends on the type and rate of damage production, as well as the rate of competitive recovery processes such as recombination and defect migration.

A key element of the dose rate is the local concentration of emitters that accumulate in the structure by means of exchange. Early models focused on edge sites of phyllosilicates, not only as key entry points for exchange but also because locally increased concentrations of interlayer cesium could be found spectro-microscopically, probably due to the increased degrees of structural freedom available in these locations (McKinley *et al.*, 2004). More recently, however, and at much higher spatial resolution, transmission electron microscopy studies have shown that cesium also easily replaces entire interlayer planes throughout the bulk of clay crystallites (Kogure *et al.*, 2012; Tamura *et al.*, 2014). Although dilute at the scale of whole particles, radioisotopes appear to be concentrated locally in selective regions of clay structures. Because of the importance of electrostatic charge distribution for net attraction across the interlayer space, if radiation damage in these regions ‘outcompetes’ recovery processes, then delamination of clay particles may result, leading to re-release of residual parent isotopes. The whole sediment transport model would thus be one of cyclic binding and release from the available cation-exchange fraction over time.

The present study addresses the long-term permanence of radioisotope retention in clay minerals by developing a theoretical understanding of their resistance to defect creation. Predictive modeling of recombination processes is reserved for future work because it requires methods such as kinetic Monte Carlo (Bortz *et al.*, 1975), adaptive kinetic Monte Carlo (Xu and Henkelman, 2008), and temperature-accelerated dynamics (Sorensen and Voter, 2000) that are not routinely applied to radiation-damage problems. The focus here was to evaluate the probability of a high-energy electron to create Frenkel pairs by direct electron-ion collision using vermiculite ($[\text{Al},\text{Si}]_4[\text{Mg},\text{Fe}]_3\text{O}_{10}[\text{OH}]_2 \cdot 4\text{H}_2\text{O}$) as a Fukushima-relevant model system. *Ab initio* molecular dynamics was employed to calculate the TDE for each symmetry-unique atomic species comprising the vermiculite unit

cell and to evaluate the effect of crystallographic direction of displacement. A TDE represents the minimum kinetic energy that has to be transferred to an atom of the structure to permanently displace it and create a stable Frenkel pair. The TDE is an important quantity which is material-specific, independent of the type of radiation, and underpins the accumulation of radiation damage in material. The TDEs are also a crucial input parameter for large-scale radiation-stopping power simulation packages such as *SRIM* and *TRIM* (Ziegler *et al.*, 2010). The AIMD methods are ideal for building up a rigorous information database for this problem. By comparison, experimental measurements of TDEs are extremely cost-ineffective because a single defect created during the experiments has to be identified and associated with a well-defined energy and direction of incident radiation.

COMPUTATIONAL METHOD

The determination of a TDE value from *ab initio* molecular dynamics is computationally expensive, especially when the material, such as vermiculite, is compositionally complex and has low structural symmetry. In the present study, the TDEs have been calculated along six to 12 different directions, chosen based on the environment local to the atomic species of interest, for each symmetry-unique atom. A series of kinetic energies, initially imparted to each atom studied, has been investigated for each direction. The TDE is found when the atom with an initial kinetic energy does not subsequently relax to its original position but instead is ejected permanently from its structure site, resulting in the creation of a stable interstitial atom and a vacancy (*i.e.* a ‘Frenkel pair’). In the calculation of the initial kinetic energy attributed to the displaced atom, the translation and angular momentum components of the velocity have been removed so that no energy is lost in rotation and translation of the whole system. For kinetic energies close to the TDE value, a minimal variation step of 1 eV was applied in order to determine accurately the TDE.

The choice of an *ab initio* method to perform these calculations was motivated by two observations. First, the empirical parameters used in force fields have been optimized to calculate the thermodynamic quantities of well defined crystal structures for which the atoms remain in their structural site and are located at the well minima of the energy surface. In contrast, the calculation of a TDE requires the location of an atom far from its energy-minimum site in order to create an interstitial site (*i.e.* Frenkel pair). In this context, the saddle states and energy barriers that need to be overcome to reach an interstitial site are expected to be better described with *ab initio* methods than with force fields (Lucas and Pizzagalli, 2005a, 2005b). Second, *ab initio* methods are able to treat explicitly and rigorously the electron

density, which increases the degree of freedom of the system, and eventually allows a change in the polarization of the atoms, in contrast to force fields which would instead generate a structural deformation. Subsequently, these deformations could also affect the type defects generated at the end of the simulation.

The calculation of the TDEs for vermiculite was performed by AIMD simulations using the *VASP* program (Kresse and Furthmuller, 1996a, 1996b). At the beginning of each simulation, only the atom for which the TDE needs to be calculated was given an initial kinetic energy, often called a ‘primary knock on atom’ (PKA), in a particular direction. All of the calculations used at least a supercell containing 158 atoms, obtained by a $2 \times 1 \times 0.5$ combination of the primitive cell. Cutting the primitive cell in half along the [001] direction is valid for this study because the interlayer cations in vermiculite are fully hydrated with water molecules and Frenkel pairs spanning the interlayer space are thus physically unrealistic. This simplification provided the computational efficiency needed to expand the supercell in the [100;010] plane in order to improve the description of distortions induced by atoms displaced within basal plane directions. Most of the simulations used a supercell containing 316 atoms, obtained by a $2 \times 2 \times 0.5$ or $2 \times 1 \times 1$ combination. Such supercells were generally built for determining TDEs with energy >40 eV and also for simulations in which the atoms were at risk of interacting across the periodic boundaries. Prior to any TDE simulation, the structure of each supercell was thermalized at 300 K for 2 ps to achieve a relaxed initial atomic configuration. Subsequently, TDE simulations were carried out in the microcanonical ensemble (NVE) with a step time of 0.03 fs for kinetic energies of <40 eV and of 0.01 fs for kinetic energies of >4 eV. A Frenkel pair has been assumed to be stable if the interstitial atom and vacancy did not combine after 2.1 ps.

Each simulation used a convergence criterion of 10^{-5} eV for the total energy. The generalized gradient approximation (GGA) and the Perdew-Burke-Ernzerhof functional (PBE) (Perdew *et al.*, 1996) parametrization of the exchange-correlation was used. The cutoff energy of the projector-augmented wave (Blochl, 1994) pseudo-potential was set to 400 eV. To describe bond-breaking events correctly, both spin-polarization and the Vosko-Wilk-Nusair local density approximation scheme (Voskod *et al.*, 1980) were used.

The determination of the TDE values in vermiculite was performed for the eight symmetrically non-equivalent atomic sites. Vermiculite is a prototypical trioctahedral phyllosilicate mineral consisting of 2:1 tetrahedral:octahedral sheet units stacked along the [001] direction and bound primarily by hydrated Mg^{2+} cations. Cation sites in the tetrahedral sheets are occupied by Al and Si cations, whereas the octahedral sheet is fully occupied by Mg cations. The structure of

the octahedral sheet (Figure 1) involves two symmetrically distinct octahedral Mg sites, labeled as Mg1 (in the prototypical M1 site) and Mg2 (in the prototypical M2 sites). For both Mg atoms, the TDEs were calculated for displacements within the plane of the octahedral sheet, defined by a combination of the [100] and [010] directions, and out of the plane, for which the directions investigated have a component along [001]. In the tetrahedral sheet, the TDEs for silicon and aluminum atoms were determined for directions taking into account the tetrahedral symmetry of the site. In vermiculite, in addition to water oxygen, three different oxygen sites can be found for which: (1) an oxygen atom bridges two tetrahedral sheets; (2) an oxygen atom bridges the tetrahedral and the octahedral sheets; and (3) an oxygen atom constitutes part of a hydroxyl group in the octahedral sheet. These oxygen sites have been labeled as O1, O2, and O3, respectively (Figure 1). The last atomic site investigated was the hydrogen atom of the hydroxyl group of the octahedral sheet.

RESULTS

The TDE values calculated for each site considered (Table 1) were obtained by averaging the TDEs of several directions (see supplementary material deposited with the Editor-in-Chief and available at <http://www.clays.org/JOURNAL/JournalDeposits.html>). The structural configurations of the most frequently encountered Frenkel defects, obtained at the end of the simulations for each atomic species, are discussed below. The TDE values determined for Mg atoms with in-plane displacements are ~ 18 eV greater than those

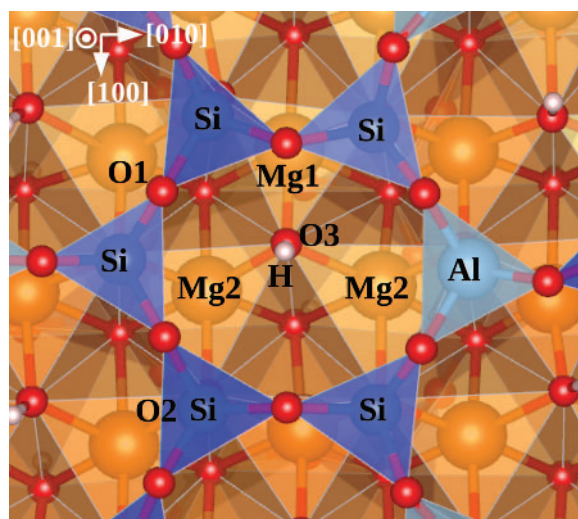


Figure 1. View along the [001] direction of a vermiculite 2:1 layer, made of Si/Al tetrahedral sheets above and the Mg octahedral sheet below. The interlayer Mg^{2+} cations and associated hydration waters have been removed for clarity.

Table 1. TDE values and corresponding calculated probabilities to permanently eject an atom from its structure site in vermiculite. The atom labels refer to those shown in Figure 1.

Atom		TDE (eV)	¹³⁷ Cs (%)	⁹⁰ Sr (%)	⁹⁰ Y (%)
Mg1	In-plane	52	9	10	80
	Out-of-plane	33	25	29	86
Mg2	In-plane	47	11	12	82
	Out-of-plane	30	30	34	88
Si		33	25	29	86
Al		27	34	38	90
O1		23	41	45	91
O2		19	49	53	93
O3		17	54	58	94
H (hydroxyl)		8	75	76	97

having out-of-plane displacements. This difference is due to a denser atomic distribution encountered for in-plane directions compared to that for out-of-plane directions where the Al/Si tetrahedral sheet provides lower-density pathways in the form of Al/Si siloxane rings. The TDE values calculated (Table 1) revealed that the atoms located in the Mg1 sites are slightly more difficult to eject in any direction than the atoms located in the Mg2 sites because the energy required to permanently displace an Mg atom is 3–5 eV greater. Although somewhat counterintuitive in light of the general preference for M2-site occupation implied by the existence of an entire family of M1-vacant dioctahedral phyllosilicates, the larger TDE value for Mg1 sites in vermiculite probably derives from fewer low-density escape pathways associated with the M1 site (Figure 1). In the tetrahedral sheet, the TDE value found for the Si site was 33 eV, while it was 27 eV for the Al site. The difference of 5 eV in favor of Si tetrahedra relative to Al tetrahedra may be the result of the greater positive charge of Si cations and resulting stronger net attraction to its four oxygen anions. The TDE values for the oxygen sites show that the oxygen atoms bridging two tetrahedra are the most difficult of the three O sites to eject permanently, followed by the oxygen atoms linking the tetrahedral and octahedral sheets, and then the oxygen atoms of the hydroxyl groups. The average of the three TDEs for O sites is 20 eV, which is less than TDEs of Si, Al, and the two Mg sites. The last site investigated was that of the hydrogen atom, from the hydroxyl group. The TDE value for this site is small, just 8 eV. Altogether, the calculated TDE values give an indication of the vulnerability of each atomic site in vermiculite, and the following sequence ranges from the most to the least resistant sites: Mg1 > Mg2 > Si > Al > O > H. The TDE values calculated here are comparable to those found in simple ceramics such as MgO, Al₂O₃, or zircon (ZrSiO₄), for which the TDEs for Mg, Al, Si and O are ~55, 20, 23, and 47–55 eV, respectively. In fact, the average TDE calculated for the three O atoms of

vermiculite (~20 eV) is more like that found in UO₂, which is 20 eV (Weber *et al.*, 1998).

The effect of the emitted beta-particle on the host material is difficult to quantify as it involves several physical processes. Nevertheless, one quantity that can be assessed easily is the energy transfer for a beta-particle with a kinetic energy, Q , colliding with an atom with a zero-degree angle at impact. For this limiting case scenario, not representative of a typical electron–atom interaction within the solid, the maximal energy transferred (E^T) to an atom is given by the following relativistic equation (Hess *et al.*, 2000):

$$E^T = \frac{2Q(Q + 2mc^2)}{Mc^2} \quad (1)$$

where Q is the kinetic energy of the emitted beta-particle, M is the mass of the target atom in the host material (*i.e.* Mg, Si, Al, O, or H), m is the mass of the beta-particle, and c is the speed of light. Using the calculated TDE values (Table 1), equation 1, and the beta-energy spectrum distribution for each radioisotope (Figure 2), one can calculate the probability of each radioisotope creating a defect at each site. These probabilities, listed in Table 1, show that a Mg atom is easier to displace and a Frenkel pair more easily created if the beta-particle travels perpendicular to the basal plane. Because cation-exchanged ¹³⁷Cs and ⁹⁰Sr radioisotopes substitute for interlayer Mg cations, beta emission along the [001] direction is more likely to occur, in contrast to beta-particles travelling parallel to the basal plane which would remain in the water interlayer, and such defects are thus highly likely. Lastly, even if the overall probability for ⁹⁰Sr to create a Frenkel pair at the Mg sites is only ~21%, the fact that ⁹⁰Sr unavoidably decays into ⁹⁰Y poses an important threat to the structure. Indeed, the beta-particle emitted by ⁹⁰Y has much more energy (see Figure 2) and hence is more likely (~85%) to create Mg Frenkel defects in the octahedral sheet.

An overall analysis of the data calculated (Table 1) suggests that ¹³⁷Cs and ⁹⁰Sr have similar probabilities of creating a defect in vermiculite despite their different beta-energy spectrum distribution. The probability of creating a defect at an Mg site ranged from 9 to 34%, depending on the direction of incidence of the beta-particle. For the Si and Al sites of the tetrahedral sheets, the probability ranges from 25 to 38%, while for an O site it ranges from 41 to 58%. The probability of ejecting a hydrogen atom is large, ~75%; however, due to the low concentration of hydroxyl groups in the overall structure of vermiculite, O–H bond breaking seems unlikely. Regardless of the atomic site, the probability of ⁹⁰Y creating a defect is high, >80%.

The atomistic simulations carried out in the present study gave new insight into the type of defects that can arise in the mineral upon electron–ion collision. When the initial kinetic energy attributed to an atom is greater

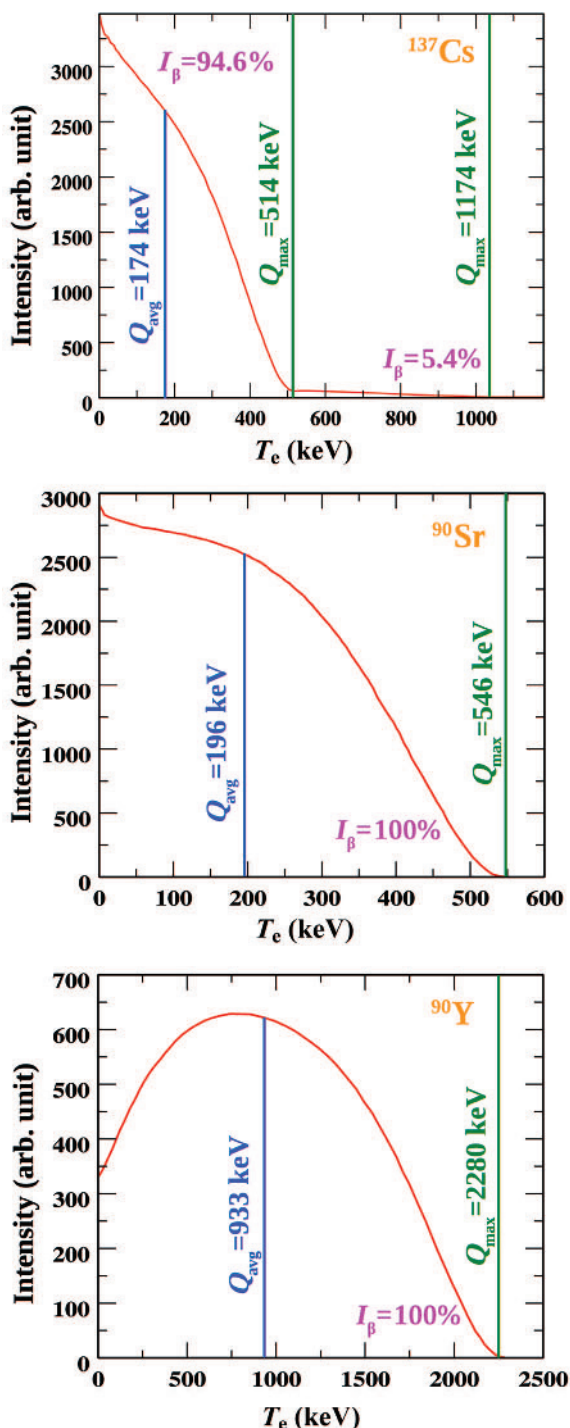


Figure 2. Beta-emission spectrum of ^{137}Cs , ^{90}Sr , and ^{90}Y . I_β is the probability of having a beta-particle with a kinetic energy between 0 eV and Q_{max} , and Q_{avg} is the average beta-particle kinetic energy for which $I_\beta = 50\%$. In the case of ^{137}Cs , Q_{avg} has been calculated assuming that 514 keV is the maximal kinetic energy, therefore ignoring the remaining 5.4% of particles with kinetic energy >514 keV.

than the TDE value of the corresponding site, certain types of defects are obtained frequently at the end of the simulations (Figure 3). Simulations involving the displacement of octahedral-sheet Mg atoms always lead to the same type of defect (Figure 3a), in which the Mg atom ejected leaves behind a vacancy and ends up at the center of an Al/Si siloxane ring at the interface with interlayer water. In this metastable location, the Mg atom is partially stabilized by capturing a water molecule from the interlayer region and by interacting simultaneously with the hydroxyl group of the octahedral sheet and the oxygen atoms of the siloxane ring, as shown by the magenta polyhedron (Figure 3a). In some simulations involving in-plane displacements of Mg atoms, an Mg split interstitial structure was observed but this configuration was metastable and one of the Mg atoms migrated away at the water interface.

The displacements of Si or Al atoms generally created two types of defects by breaking Si–O or Al–O bonds within the siloxane ring, and subsequently by reforming these bonds with oxygen atoms from the neighboring environment in order to restore tetrahedral coordination about these cations, in interstitial locations. New tetrahedra can be formed (Figure 3b), either by contact with the oxygen of the hydroxyl group on the Mg octahedral sheet (top panel) or by capturing hydroxyl groups from the water interlayer (bottom panel). In the former case, the newly restored tetrahedron is located below the tetrahedral sheet and is edge sharing with an octahedral Mg atom, while in the latter case, the new tetrahedron is located above the tetrahedral sheet. In the specific case of an Al atom ejected with a kinetic energy of >45 eV and directed toward the octahedral sheet (*i.e.* passing through the face of an Al tetrahedron), a Mg atom can subsequently be ejected and replaced by the incoming Al atom, which then resides in that octahedral environment. This case was never observed for a similarly displaced Si atom, which prefers instead to form an edge-sharing tetrahedron with a Mg octahedron (Figure 3b, upper).

The simulations of oxygen displacements generated different types of defects, depending on which oxygen atom was displaced. For oxygen atoms of the Al/Si siloxane ring (labeled O1 in Figure 1), two defect configurations were obtained. An oxygen vacancy (Figure 3c) forces two cations to either form a Si–Si or a Si–Al bond in order to keep the siloxane ring closed (top panel), or to create two separated tetrahedra each having an edge shared with the octahedral sheet (lower panel). The displacement of oxygen atoms linking the tetrahedral and octahedral sheets (labeled O2 in Figure 1) generally yielded a five-fold coordinated Si or Al atom, with the neighboring atom capturing the leaving oxygen, and a new tetrahedron, formed through the interaction of a water molecule, for the Si or Al atom that loses the oxygen. In the case of a displacement of the oxygen atom of the hydroxyl group on the octahedral

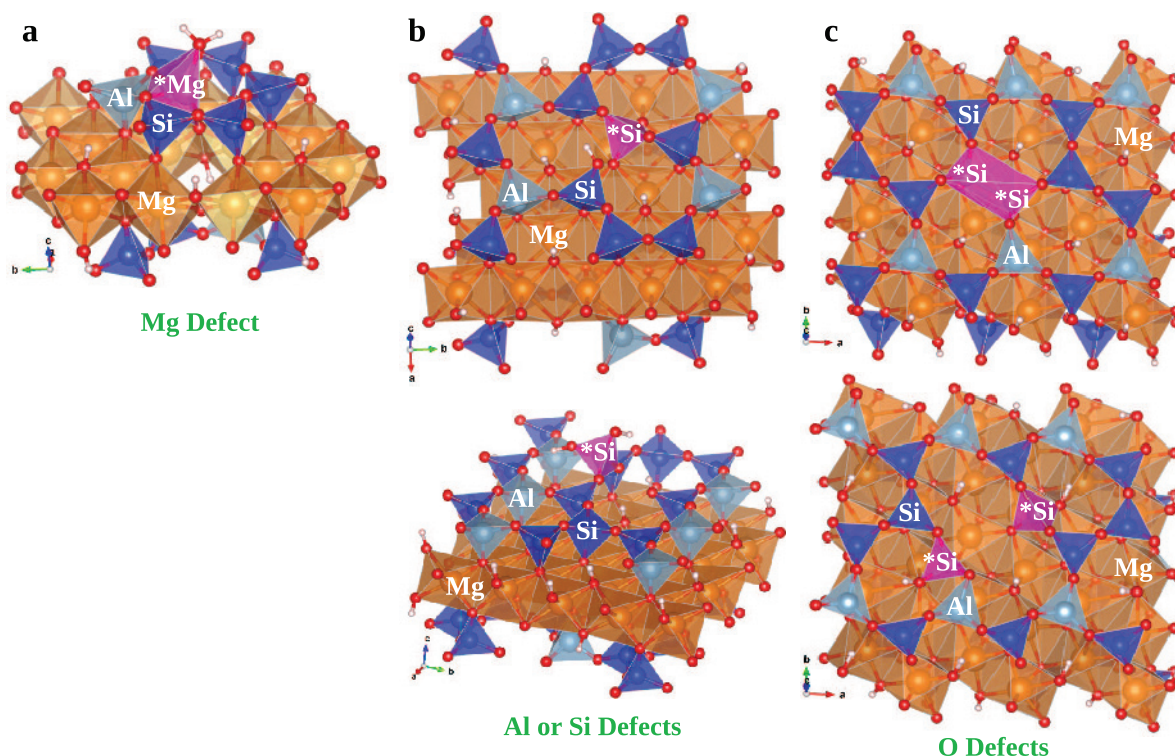


Figure 3. Structures of the most frequently encountered Frenkel defects, obtained at the end of the simulations after the displacement of: (a) Mg atoms, (b) Al or Si atoms, and (c) O atoms with kinetic energies above the TDE value. A star (*) symbol has been added to the label of each atom involved in the formation of a defect. Interlayer water molecules and Mg^{2+} cations have been removed for clarity.

sheet (labeled O3 in Figure 1), no specific defects were created in addition to the creation of three five-fold coordinated Mg atoms of the octahedral sheet resulting from the breaking of three Mg–O bonds.

In each simulation performed, the presence of interlayer water molecules was found to play an important role in stabilizing the final configuration of defects, especially through proton-transfer processes that quickly saturate the oxygen of broken Mg–O, Si–O, or Al–O bonds by forming hydroxyl groups. The water at the interlayer also offers a natural barrier for stopping or slowing the motion of atoms ejected with a high kinetic energy, therefore reducing the potential risk of these atoms to create secondary damage between adjacent layers of vermiculite.

CONCLUSIONS

The present study has contributed insights, at the atomic level, into energies, probabilities, and configurations of point defects that can be expected to occur with selective exchange of $^{137}\text{Cs}^+$ and $^{90}\text{Sr}^{2+}$ in vermiculite and related clay minerals, the octahedral sheets of which are occupied by Mg. The progressive accumulation of such defects over time is expected to destabilize the vermiculite structure, eventually leading to delamination

and re-release of residual parent isotopes in the interlayer space. Further simulations are required to quantify the accompanying increase in total free energy of the solid that contributes to clay-mineral destabilization and the amount of time until decomposition. The findings substantiate the prospect of a re-release model in the fate and transport of these hazardous fission product radionuclides, and justify future experimental and theoretical studies to examine the impact of accumulating radiation damage on the overall structural stability and interlayer cation exchange capacity. More such research is needed to build an information database that is useful for risk assessment, and to help guide management, disposal, and treatment of contaminated soils actively evolving in the Fukushima area.

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