



REPLY TO “COMMENTS ON RADIATION-DAMAGE RESISTANCE IN PHYLLOSILICATE MINERALS FROM FIRST PRINCIPLES AND IMPLICATIONS FOR RADIOCESIUM AND STRONTIUM RETENTION IN SOILS”

MICHEL SASSI¹, KEVIN M. ROSSO¹, MASAHIKO OKUMURA², AND MASAHIKO MACHIDA²

¹ Physical Sciences Division, Pacific Northwest National Laboratory, Richland, WA 99354, USA

² CCSE, Japan Atomic Energy Agency, Kashiwa, Chiba 277-8587, Japan

INTRODUCTION

In this reply the authors address comments in Wampler (2017) regarding Sassi *et al.* (2016), the focus of which is on *ab initio* calculation of threshold displacement energies (TDEs) for atoms in vermiculite, and the relative probabilities for Frenkel-defect formation among atom types arising from radioisotopes of the kind in the contaminated soils at Fukushima. Wampler (2017) offers suggestions attacking the context and importance, from a knowledge base that appears deficient. Specifically, with regards to the concentration of fallout radioactivity in soils, the present authors show that for radiocesium at Fukushima, Wampler's (2017) homogeneous dilution model fails to stand up against direct experimental measurements, and further provide references showing that the local concentrations of these ions at the sub-micrometer level may be much higher than would be predicted from homogenous assumptions. No cognizance of this readily available data is demonstrated in Wampler (2017). With regards to the more peripheral topic of absolute Frenkel-defect formation probabilities, Wampler (2017) argues against damage accumulation within any individual phyllosilicate grain from self-contained radiocesium – an agreeable concept. Based on these data, however, the present authors suggest that the radiation volumes of radiocesium-bearing particles as dispersed in Fukushima soils are likely to be strongly overlapping and thus the question of their mutual interaction persists. The durability of radiocesium-phyllosilicate interactions over the long term, even in fallout scenarios, remains as a research frontier worthy of exploration.

DISCUSSION

Concentration of fallout radioactivity in soils

In an attempt to paint a picture of an homogeneous dilution of fallout Cs in Fukushima soils, Wampler (2017)

adopts a view of soil that ignores its basic heterogeneity in terms of mineralogy, chemistry, and physical structure properties such as porosity. Neither does Wampler (2017) show any cognizance of readily available data that gives a direct measure of selective Cs sorption and local enrichment in a relatively minor phase of the overall makeup of Fukushima soils, namely weathered biotites, preferring instead to rely on a crude homogeneous box model of soils. For example, to justify his argument, he gives several concentrations of ¹³⁷Cs, ranging from about 8×10^{10} to 6.7×10^{12} radiocesium atoms g⁻¹ of soil, and evidently for comparison, he further states that “there are $\sim 7 \times 10^{20}$ unit cells g⁻¹ of vermiculite” (Wampler, 2017). The apparent inference is that the juxtaposition of these orders of magnitude should mean that there would be no chance for radiocesium to become concentrated locally. The estimated 7×10^{20} unit cells g⁻¹ of vermiculite has been obtained, however, by assuming that the structure and composition of soil can be represented by a 1 g vermiculite crystal alone, with no other phases, or any attendant soil pore volume, organics, plant matter, fungi, *etc.*

Note that the Sassi *et al.* (2016) study has no issue whatsoever with the concept that, at the macroscopic scale, radiocesium is dilute in Fukushima soils or in fallout-contamination situations generally. This is pointed out by Wampler (2017), who then goes on to suggest that the present authors have misled the reader by stating “Sassi *et al.* (2016) were aware that radionuclides are dilute at the scale of whole particles, but they asserted that radionuclides could become concentrated locally in clay structures.”. In Sassi *et al.* (2016), the present authors show clear cognizance of the dilution of radiocesium in Fukushima soils, and also rely on a vast and diverse body of previous work which shows that highly dispersed radiocesium can become concentrated locally at a fine scale in a relatively minor singular fraction of soil constituents – phyllosilicates. Data which are readily available show that local Cs concentrations in Fukushima phyllosilicates can reach larger values than those estimated by Wampler (2017).

Although Fukushima soil contains the usual complexity of diverse organic and inorganic components, studies

* E-mail address of corresponding author:

michel.sassi@pnnl.gov

DOI: 10.1346/CCMN.2017.064078

have shown that weathered biotite is the primary sorbent of radiocesium (Mukai *et al.*, 2014, 2016a, 2016b; Yamada, 2014). For example, Mukai *et al.* (2014) analyzed 50 radioactive particles taken from a soil sample originating from the Fukushima contaminated area and demonstrated clearly that radiocesium is not distributed homogeneously among soil constituents because they were able to differentiate radioactive from non-radioactive particles (Mukai *et al.*, 2014, SI figure S2). This distinction would not have been possible if the concentration of radiocesium was homogeneously dilute among soil components. The 50 extracted radioactive particles were classified into three types: Type 1 (14 particles) was identified as particle aggregates of clay minerals; Type 2 (20 particles) was identified as particles containing organic matter and clay mineral particulates; and Type 3 (16 particles) was of weathered biotite. For each particle type here, the amount of radioactive ^{137}Cs and ^{134}Cs atoms in the particle aggregates is estimated based on their γ -ray emission spectra as measured by Mukai *et al.* (2014, figure 10, and SI figure S4a and S4b). Note that the γ -ray emission spectra have been obtained for only one radioactive particle of Type 1, one of Type 2, and approximately three of Type 3 (T. Kogure, pers. comm., 2017). The total number of radiocesium (*i.e.* $^{137}\text{Cs}+^{134}\text{Cs}$) atoms per particle of Type 1, 2, and 3 is 640,976, 344,157, and 188,133, respectively, with the last one assuming that each of the three particles of Type 3 contains an identical number. The data do not allow for insight into radiocesium distributions at finer scales within these aggregate particles. Nevertheless, it is interesting to view the aggregates of clay minerals (Type 1) as local 'hot spots' from which >640,000 decays of radiocesium can occur. While this is but one example, taken from one experimental study, for which the authors do not make any claims regarding its representation of Cs concentrations in clay minerals across the entire contaminated Fukushima area, it is nonetheless a counter argument to the 'homogeneous dilution' view of Wampler (2017).

An argument is made by Wampler (2017) about the importance of natural background ^{133}Cs as a more highly concentrated competitive cation for radiocesium that would work against its uptake *via* cation exchange in phyllosilicates. The data above show clearly that Fukushima fallout radiocesium has indeed already found its way to what are undoubtedly the strong selective binding sites in certain phyllosilicates. Wampler (2017) further claims "As far as the present author is concerned, there is no basis for the assertion that radioisotopes appear to be concentrated locally in clay structures." . While true that, at the typical scale of single phyllosilicate crystallites, mapping the distribution of radiocesium held within a Fukushima particle in three dimensions continues to challenge the sensitivity of most present-day analytical tools, there is a substantial body of theoretical work, not mentioned by

Wampler (2017), showing that at the atomic scale there is a thermodynamic driving force for cesium replacements in interlayer spaces to be cooperative – and from this, given its very similar chemical behavior (*vis à vis* Wampler's stated competition), it is safe to infer the same should also be true for radiocesium. For example, on the basis of density functional theory (DFT) calculations on a model mica, Okumura *et al.* (2014a) showed that cesium exchange with potassium is energetically favored when the neighboring exchange sites are preoccupied by cesium. More recently, using molecular dynamics simulations and DFT, Pestana *et al.* (2017) illustrated more completely the strength of this positive feedback mechanism for multiple cesium replacements in a single interlayer. In short, such work suggests that once radiocesium exchange into phyllosilicates begins to occur, as it clearly has at Fukushima, there is a small but ever-present thermodynamic driving force for zones of segregation in interlayers to form. The potential impact of radiocesium transmutations occurring in such segregated interlayers on its long-term retention in phyllosilicates has been investigated recently and discussed by Sassi *et al.* (2017). Furthermore, while Wampler (2017) points out correctly that laboratory experiments performed with high aqueous concentrations of cesium, which through atomic-scale imaging have given clear and direct evidence for this cesium segregation in interlayers (Kogure, 2012; Okumura, 2014b; Tamura, 2014), do not represent the aqueous concentrations to which Fukushima phyllosilicates were exposed, the collective theoretical and experimental evidence that cesium thermodynamically prefers to exchange close to other cesium atoms in phyllosilicate interlayers is compelling enough to warrant further consideration. For radiocesium-bearing Fukushima phyllosilicate minerals specifically, the aforementioned research has even provided some initial evidence that the radiocesium has penetrated deep into particle interiors, residing not just at edge sites (Mukai *et al.*, 2016b). This is, conceptually, fully consistent with the model just described. The present authors make no claims that the radiocesium in Fukushima phyllosilicates has yet had the time to reach this equilibrium thermodynamic expectation, but with certainty refute the claim that "there is no basis."

Probability of Frenkel-pair formation

The primary focus of Sassi *et al.* (2016) was on computation of the threshold displacement energies (TDEs) to form various Frenkel defects among atom types in vermiculite. The TDE values themselves are not in dispute. Instead, Wampler (2017) specifically calls into question the usefulness of the probability estimates that β radiation can cause these defects, because the Rutherford scattering probability was not included. Nowhere in Sassi *et al.* (2016) do the authors claim that the given probabilities are absolute. Instead, they

are used primarily to discuss the probabilities of one Frenkel-defect type vs. another, in a relative sense, among atom types in the crystal structure of vermiculite. Specifically, in the description of the computational method the authors stated clearly that these absolute values are upper limits and not the complete picture of electron–atom interaction: “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 (ET) to an atom is given by the following relativistic equation...”

As correctly stated by Wampler (2017), the authors agree that the beta particle emitted from the radioactive decay of radiocesium typically travels up to 1 mm away from the decay event and is thus unlikely to create Frenkel defects within the same particle that held the radioisotope. The emitted beta particle can create Frenkel defects in neighboring clay particles located within a 1 mm radius from the decay event, however. In particular, with respect to damage accumulation in any given radiocesium-bearing soil particle, the relevant question is the extent to which the irradiation volumes of all such particles are overlapping. To show how this is relevant to Fukushima specifically, here a rough estimate of this overlap is given by calculating the total irradiation volume accessible by beta particles emitted from radioactive particles at the approximate density with which they occur in Fukushima soil, and comparing it to actual typical soil volume. If one

assumes a typical soil density of 2.3 g/cm^3 , then 1 g of soil occupies a volume of $\sim 0.43 \text{ cm}^3$. From Table 1, five radioactive particles can contain ~ 1.17 million radiocesium (*i.e.* ^{137}Cs and ^{134}Cs) atoms. In their work, Mukai *et al.* (2014) initially measured an activity of 1400 Bq g^{-1} and 727 Bq g^{-1} from ^{137}Cs and ^{134}Cs , respectively. By taking a half-life of 30 y for ^{137}Cs and 2 y for ^{134}Cs , one can calculate the initial number of radiocesium atoms contained in 1 g of soil sample to be $\sim 1.91 \times 10^{12}$ for ^{137}Cs and 6.62×10^{10} for ^{134}Cs . The estimated total number of radioactive particles contained in 1 g of such soil is ~ 8.4 million. If each radioactive particle has a radiative volume of $3.142 \times 10^{-3} \text{ cm}^3$ ($=\pi \times 0.1^3$), then the total volume accessible for beta particle radiation is $26,393 \text{ cm}^3$ ($=8.4 \times 10^6 \times 3.142 \times 10^{-3}$). This volume is $\sim 61,000$ times larger than the actual soil volume per gram, meaning that the density of soil would have to decrease by this many times for the radiative volumes of radiocesium-bearing particles to be approximately non-interacting. Therefore, this implies that a random radiocesium-bearing particle in Fukushima soil, each loaded with hundreds of thousands of radiocesium atoms, will be bombarded by beta particles originating from tens of other such radioactive particles nearby. The actual local exposure to beta particles will obviously depend on the actual distribution of radiocesium-bearing particles, and the picture is most certainly incomplete. While only approximate, the model does, however, make the point that radiocesium-bearing particles at Fukushima are probably exposed to beta radiation from other such particles.

The present authors suggest that Wampler (2017) disproportionately emphasizes aspects of the work by

Table 1. Estimate of the number of ^{137}Cs and ^{134}Cs atoms present in radioactive particles extracted from the contaminated soil of the Fukushima area. Number of counts and duration time of the measurements were taken from γ -ray emission spectra as measured by Mukai *et al.* (2014, figure 10, and SI figures S4a and S4b). The numbers of particles used for the measurements are from T. Kogure (pers. comm., 2017).

Particle group	Number of particles used	Number of counts	Duration time (s)	Activity ($\times 10^{-4}$ Bq)	Number of Cs atoms	Number of Cs per particle
Radioactivity from ^{137}Cs						
Type 1 (clay minerals)	1	158	346,000	4.555	621,672	62,1672
Type 2 (organic matter + clay minerals)	1	189	776,000	2.436	332,501	33,2501
Type 3 (weathered biotite)	3	80	200,000	3.994	545,174	18,1725
Radioactivity from ^{134}Cs						
Type 1 (clay minerals)	1	73	346,000	2.121	19,304	19,304
Type 2 (organic matter + clay minerals)	1	99	776,000	1.281	11,656	11,656
Type 3 (weathered biotite)	3	42	200,000	2.113	19,226	6409

Sassi *et al.* (2016) that the latter paper did not specifically compute or elaborate upon in detail, with respect to absolute radiation-induced defect-formation probabilities. Instead, Wampler (2017) overlooks selectively the explicit statements included in Sassi *et al.* (2016) to maintain a balanced presentation of the results. Examples in the Introduction alone include: “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.”; “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.”; and “A key element of the dose rate is the local concentration of emitters that accumulate in the structure by means of exchange.” The authors of Sassi *et al.* (2016) are, thus, well aware of the fact that the absolute magnitude of the damage caused by radioisotope decay on clay minerals is a complex function beyond just the amount of radioactive isotopes dispersed and their local concentration.

Some minor problems

(1) The present authors thank Dr Wampler for having noticed an error of calculation in our probabilities (not the TDEs) of table 1 (Sassi *et al.*, 2016). Those probabilities were recalculated using the correct mass for each species and listed in Table 2 below. The difference is insignificant for Mg, and values for Si and Al show a small decrease. The probabilities for O and H increase substantially. The changes are inconsequential in terms of the trends discussed in the paper. The present authors emphasize again that these probabilities are a “limiting case scenario, not representative of a typical electron–atom interaction within the solid” (Sassi *et al.*, 2016).

(2) The “misconception” raised by Wampler (2017) is simply a result of a poor choice of wording. A more precise way to state what was intended is that a beta

particle colliding with a Mg atom with an incident direction perpendicular to the basal plane is more likely to create a defect than if the beta particle collides with a Mg atom with an incident direction parallel to the basal plane.

CONCLUSIONS

Experimental data are available for Fukushima soils that demonstrate clearly that the macroscopically dilute fallout radiocesium concentrates locally in the phyllosilicate mineral fraction and, furthermore, primarily within certain phases such as weathered biotites. The enrichment into these microscopic domains is probably much greater than estimated by Wampler (2017). Furthermore, thermodynamic data built from computational chemistry calculations generally suggest that the equilibrium configuration of cation-exchanged cesium residing in interlayer sites is in segregated domains. Until detailed analytical microscopy can quantify the spatial distribution of radiocesium within single phyllosilicate crystallites, the extent to which this segregation has manifested itself in Fukushima soil grains at the nanoscale will remain unknown. However, one may immediately begin to question the veracity of Wampler (2017) on the simple basis of why all critically relevant work in this regard was ignored. In contrast to Wampler (2017), the present authors reinforce here the underlying point made by Sassi *et al.* (2016) that further work on this important microscopic topic is scientifically valid and justified. Statements such as “the contribution of β -radiation damage to release of fallout radionuclides from soil and sediment is and will continue to be negligible” (Wampler, 2017) are dangerous because they are based on a simplistic view, ignoring the fact that the actual true complexity of radioisotope–clay association at a microscopic level remains poorly quantified. In contrast to Wampler (2017), the present authors presume nothing about the long-term behavior of this system apart from what the available data and computations suggest is possible. Sassi *et al.* (2016) simply explores a reasonable

Table 2. TDE values and corresponding corrected probabilities to permanently eject an atom from its structural site in vermiculite. The atom labels refer to those shown in figure 1 of Sassi *et al.* (2016).

Atom		TDE (eV)	¹³⁷ Cs (%)	⁹⁰ Sr (%)	⁹⁰ Y (%)
Mg1	// basal plane	52	9	10	80
	⊥ basal plane	33	25	29	86
Mg2	// basal plane	47	11	12	82
	⊥ basal plane	30	30	34	88
Si		33	14	16	85
Al		27	25	28	87
O1		23	53	57	93
O2		19	59	63	94
O3		17	62	66	94
H (hydroxyl)		8	99	99	100

scientific question at the nanoscale, consistent with the current set of available facts on the behavior of radiocesium contamination at the Fukushima site. In this context, the authors believe that Sassi *et al.* (2016) contributes to the general information database relevant not only to Fukushima but also to the many past and likely future accidental nuclear releases. This includes by aerial fallout, as well as liquid discharges of high-level radioactive wastes. Studies like that of Sassi *et al.* (2016) could prove relevant to the challenge of storing, processing, and/or repurposing the ~20 million m³ of contaminated waste soil collected from the Fukushima site (Ministry of the Environment, Japan, 2017) for the long term. In particular, with respect to storage, the 2016 study specifically provides scientific information useful for risk assessment of waste-soil classification methods. Classification of the waste soil is one of the current candidates for waste-volume reduction prior to storage, which separates the waste soil into high- and low-level wastes (Ministry of the Environment, Japan, 2017). If classification is performed, the densities of clay minerals and their radiocesium inventories will increase significantly. Possible consequences of their artificial enrichment include those covered by Sassi *et al.* (2016).

REFERENCES

- Kogure, T., Morimoto, K., Tamura, K., Sato H., and Yamagishi, A. (2012) XRD and HRTEM evidence for fixation of cesium ion in vermiculite clay. *Chemistry Letters*, **41**, 380-382.
- Ministry of the Environment, Japan (2017) Progress on off-site cleanup and interim storage in Japan October 2017, http://josen.env.go.jp/en/pdf/progressseet_progress_on_cleanup_efforts.pdf (accessed on Nov. 21, 2107).
- Mukai, H., Hatta, T., Kitazawa, H., Yamada, H., Yaita, T., and Kogure, T. (2014) Speciation of radioactive soil particles in the Fukushima contaminated area by IP autoradiography and microanalyses. *Environmental Science & Technology*, **48**, 13053–13059.
- Mukai, H., Hirose, A., Motai, S., Kikuchi, R., Tanoi, K., Nakanishi, T.M., Yaita, T., and Kogure, T. (2016a) Cesium adsorption/desorption behavior of clay minerals considering actual contamination conditions in Fukushima. *Scientific Reports*, **6**, 21543.
- Mukai, H., Motai, S., Yaita, T., and Kogure, T. (2016b) Identification of the actual cesium-adsorbing materials in the contaminated Fukushima soil. *Applied Clay Science*, **121–122**, 188–193.
- Okumura, M., Nakamura, H., and Machida, M. (2014) Energetics of atomic level serial ion exchange for cesium in micaceous clay minerals. *Clay Science*, **18**, 53–61.
- Okumura, T., Tamura, K., Fujii, E., Yamada, H., and Kogure, T. (2014) Direct observation of cesium at the interlayer region in phlogopite mica. *Microscopy*, **63**, 65–72.
- Pestana, L.R., Kolluri, K., Head-Gordon, T., and Lammers, L.N. (2017) Direct exchange mechanism for interlayer ions in non-swelling clays. *Environmental Science & Technology*, **51**, 393–400.
- Sassi, M., Rosso, K.M., Okumura, M., and Machida, M. (2016) Radiation-damage resistance in phyllosilicate minerals from first principles and implications for radiocesium and strontium retention in soils. *Clays and Clay Minerals*, **64**, 108–114.
- Sassi, M., Okumura, M., Machida, M., and Rosso, K.M. (2017) Transmutation effects on long-term Cs retention in phyllosilicate minerals from first principles. *Physical Chemistry Chemical Physics*, **19**, 27007–27014.
- Tamura, K., Kogure, T., Watanabe, Y., Nagai, C., and Yamada, H. (2014) Uptake of cesium and strontium ions by artificially altered phlogopite. *Environmental Science & Technology*, **48**, 5808–5815.
- Wampler, J.M. (2017) Comments on radiation-damage resistance in phyllosilicate minerals from first principles and implications for radiocesium and strontium retention in soils. *Clays and Clay Minerals*, **65**, 367–370.
- Yamada, H., Yokoyama, S., Watanabe, Y., Suzuki, M., Suzuki, S., and Hatta, T., (2014) Cesium-adsorption behavior of the weathered biotite from Fukushima prefecture depends on the degree of vermiculization. *Journal of Ion Exchange*, **25**, 207–211.

(Received 22 November 2017; revised 29 November 2017; AE: J.W. Stucki)