COMMENTS ON "RADIATION-DAMAGE RESISTANCE IN PHYLLOSILICATE MINERALS FROM FIRST PRINCIPLES AND IMPLICATIONS FOR RADIOCESIUM AND STRONTIUM RETENTION IN SOILS" BY M. SASSI, K.M. ROSSO, M. OKUMURA, AND M. MACHIDA

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INTRODUCTION

Sassi *et al.* (2016) used *ab initio* molecular dynamics calculations to obtain threshold displacement energy (TDE) values for Mg, Si, Al, O, and H atoms within vermiculite. Then they used the TDE values "to estimate the probability of Frenkel-pair creation by direct electron−ion collision" upon β decay of ^{137}Cs, ^{90}Sr, and ^{90}Y. In a context of concern about the long-term effects of fallout radionuclides, they used these probability values to imply substantial radiation damage to phyllosilicates in fallout-contaminated soils and sediments: "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."

The TDE values may be useful for understanding the effects of radiation in vermiculite contaminated by high-level nuclear waste, but in soils and sediments contaminated by radioactive fallout the expected radiation damage owing to Frenkel-pair formation will be so little and so well dispersed that it will have no appreciable effect on retention of fallout radionuclides. That such radiation damage will be little is evident from comparison of the number density of radioactive atoms in fallout-contaminated soil ($<2 \times 10^{13}$ cm^{-3}) with the typical number density of unit cells (~1×10^{21} cm^{-3}) in the 2:1 phyllosilicate minerals that hold most of the fallout radioactivity. That such radiation damage will be well dispersed is evident from the typical range in common silicates of β^{-} particles having sufficient energy to displace most kinds of atoms in the minerals (from ~0.1 mm to ~1 mm), which is much greater than the dimensions of clay particles.

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DISCUSSION

Concentration of fallout radioactivity in soils

The most heavily contaminated soil sample examined by Steinhauser *et al.* (2013, table S1), from a radio-activity hot spot 1.5 km from the damaged Fukushima I power plant, contained 6.7×10^{12} radioactive atoms of Cs and Sr (predominantly ^{137}Cs, 4.6×10^3 Bq g^{-1}) per g of dried soil. The radioactivity was much less in 16 soil samples representative of typical (not extreme) radio-activity in a belt of high fallout that runs to the northwest of the Fukushima accident site, corresponding to 1.6×10^{11} atoms g^{-1} for the most contaminated sample and to 8×10^{10} atoms g^{-1} on average (Sahoo *et al.*, 2016). For comparison, there are ~7×10^{20} unit cells g^{-1} of vermiculite. Because, on average, only about one atomic displacement should occur per ^{137}Cs decay event (Hess *et al.*, 2000), Frenkel-pair formation owing to β radiation should affect only a minute fraction of the unit cells of the clay minerals that hold most fallout radioactivity.

Most important for this discussion is that Kaneko *et al.* (2015) found ~3×10^3 Bq g^{-1}, ~4×10^{12} atoms g^{-1}, of ^{137}Cs in a <1 μm fraction separated from severely contaminated soil in which the clay held at least 78% of the ^{137}Cs. Because particle volume in this fraction must have ranged downward from ~1 μm^3, the number of particles was >4×10^{11} g^{-1}. Fewer than 10 radioactive atoms per clay particle were in this severely contaminated soil clay.

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: "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."

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. The cited reports were of distribution of stable Cs, not radiocesium, after phyllosilicates had been in contact with aqueous stable Cs at concentrations which were orders of magnitude greater than the concentration of either stable Cs or radiocesium in fallout-contaminated soil solutions. Cs in high concentrations interacts with phyllosilicate interlayers in ways not possible at the low Cs concentrations typical of natural soil solution (Grütter *et al.*, 1986), so the results of experiments at high Cs concentration are not directly useful for understanding the behavior of fallout radiocesium.

No evidence was presented by Sassi *et al.* (2016) for local concentration of radionuclides in selective regions of clay structures. Such concentration of radioactive Cs or Sr atoms from fallout is very unlikely, because the radioactive atoms must compete with much more abundant stable atoms of Cs and Sr for any sites highly selective for these elements. Kondo *et al.* (2015) reported values of ammonium acetate-exchangeable ^{133}Cs that average 0.9 µmol kg^{-1} for four paddy soils from Fukushima Prefecture. In the sample with the least exchangeable ^{133}Cs (0.12 µmol kg^{-1}), the exchangeable ^{133}Cs was 2.6×10^4 times more abundant than ^{137}Cs (and 11 times more abundant than the ^{137}Cs in the most highly contaminated sample of Steinhauser *et al.*, 2013).

Probability of Frenkel-pair formation

The tabulated probability estimates of Sassi *et al.* (2016, table 1) for displacement of octahedral Mg by a β particle from ^{137}Cs decay range from 9% for in-plane displacement of "Mg1" ions to 30% for out-of-plane displacement of "Mg2" ions. Although these estimates are described in the table title as "probabilities to permanently eject an atom from its structure site in vermiculite," each is simply the fraction of ^{137}Cs β particles initially having enough kinetic energy to transfer a specified TDE to a Mg atom. Alone, such probability values are not useful because they do not include a complementary probability factor – the probability that a β particle with sufficient energy to cause an atomic displacement will experience a direct collision with an atom before the β particle's kinetic energy falls too low to cause the displacement. The 'direct collision' process is Rutherford scattering of a β particle that approaches the nucleus of an atom closely enough to be backscattered at a high angle (Fultz and Howe, 2013, §5.6.1). The probability of such scattering by a particular atom is extremely small. For electrons having sufficient kinetic energy (>100 keV) to displace

atoms of Si, Al, Mg, and O in vermiculite, the integral cross sections for backscattering (all scattering by $\geqslant 90°$) are $<1 \times 10^{-22}$ cm^2 (Figure 1). Backscattering from an H atom is extremely improbable except for a narrow range of energy well below 100 keV.

Although the probability estimates of Sassi *et al.* (2016) are much larger than the actual probabilities of Frenkel-pair creation by direct electron−ion collision, the inflated values are of no consequence to the question of how many Frenkel pairs are created by β decay because Sassi *et al.* (2016) failed to consider Frenkel pairs caused by secondary atomic collisions. Considering secondary atomic collisions, Hess *et al.* (2000) suggested, on average, about one atomic displacement per ^{137}Cs decay event (in pollucite). Consequently, the low probability of Rutherford backscattering is more important to the present discussion for what it tells about the spatial distribution of β decay-induced Frenkel defects than for what it tells about the number of such defects. The number density of atoms in vermiculite is $\sim 1 \times 10^{23}$ cm^{-3}, so the probability that a β particle will displace an atom of Si, Al, Mg, or O while traversing vermiculite is less than $(1 \times 10^{23}$ cm$^{-3})(1 \times 10^{-22}$ cm$^2)(1 \times 10^{-4}$ cm µm$^{-1}) = 1 \times 10^{-3}$ µm^{-1}. The typical dimensions of clay particles in soil and sediment are ~ 1 µm, so the β particle from a disintegrating fallout atom causing an atomic displacement in the same clay particle that held that atom is very unlikely. A β decay-induced Frenkel defect in fallout-contaminated soil or sediment could be anywhere within hundreds of micrometers from the atom that emitted the β particle.
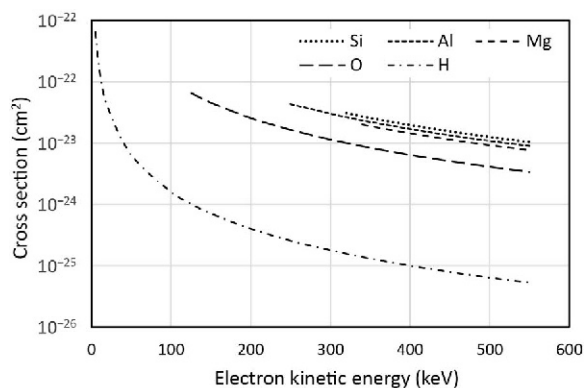

Figure 1. Cross section for Rutherford backscattering ($\geqslant 90°$) of electrons from various atomic nuclei as a function of electron kinetic energy, calculated by integration from $\Omega = 2\pi$ to $\Omega = 4\pi$ of differential cross section values (Ω) from equation 5.56 of Fultz and Howe (2013). Curves terminate leftward where electron energy is insufficient, according to the threshold displacement energies of Sassi *et al.* (2016), to displace an atom of the specified element in vermiculite by direct collision (180° scattering).

Mobility of radiocesium

In the view of the present author, the suggestion made by Sassi *et al*. (2016) that fallout Cs and Sr sorbed by clay particles would be held irreversibly if no radiation damage occurred is incorrect. They stated, "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)."

Evidence was presented by Wampler *et al*. (2012) that stable Cs has been held with remarkable tenacity by Savannah River Site (South Carolina, USA) soils for thousands of years, but those authors made no claim that migration of Cs depends exclusively on physical transport of clay particles – such transport was not mentioned. Highly Cs-selective cation exchange sites in interlayer-wedge zones of 2:1 phyllosilicates are thought to be responsible for uptake and fixation of radiocesium (Wampler *et al*., 2012), but that such uptake of radiocesium is at least partially reversible is well known (Evans *et al*., 1983; de Koning and Comans, 2004). Sr has been shown (Zaunbrecher *et al*., 2015) to be the most mobile of the large-ion alkali and alkaline-earth elements in Savannah River Site soils – very little Sr remains in these soils.

Exchangeable Cs in trace amounts is retained tenaciously by 2:1 phyllosilicates because of the great ion-exchange selectivity for Cs over other cations at interlayer-wedge sites. In fallout-contaminated soils and sediments, not all radiocesium becomes fixed; some remains exchangeable, and the amount of exchangeable radiocesium will not be affected appreciably by widely dispersed Frenkel defects caused by β radiation.

Some minor problems

(1) The probability values for Si, Al, O, and H in table 1 of Sassi *et al*. (2106) were determined incorrectly. The values are those one would obtain by using the atomic mass of Mg for each of these elements in their equation 1. The consequences of the miscalculation are most pronounced for H. Using the correct mass value for H shows, for example, that 99%, not 75%, of the β particles from ^{137}Cs have enough energy to transfer the TDE (8 eV) to a hydroxyl H atom.

(2) A surprising assertion that β radiation would not be isotropic in vermiculite appears to have arisen from a misconception that a β particle is likely to be back-scattered from atoms that are very close to its source (Sassi *et al*., 2106): "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 ^{137}Cs and ^{90}Sr 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." Atoms close to the source are the most likely to be *traversed* by a β particle, but the probability of backscattering from one of those neighbors is extremely small.

CONCLUSION

The contribution of β-radiation damage to the release of fallout radionuclides from soil and sediment is and will continue to be negligible because (1) radioactive atoms are extremely dilute (in comparison with stable atoms) in fallout-contaminated soil and sediment, (2) no evidence exists that such radioactive atoms become concentrated in specific clay interlayers, (3) the damage caused by β radiation extends hundreds of micrometers from the source, and (4) some radioactive Cs and most radioactive Sr already occur as exchangeable cations. The concluding assertions by Sassi *et al*. (2016) "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." are troubling.

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