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Reply to the comment on "Particle fluxes in groundwater change subsurface shale rock chemistry over geologic time"

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1. Zr immobility

The core argument of the Bern and Yesavage comment is that our inference of chemical immobility of Zr is incorrect. They pointed out that the Zr flux is a few orders of magnitude smaller than those of other elements because Zr is a trace element (150-300 ppm) in the soil and bedrock; therefore, they argue that the low Zr solute flux alone cannot be evidence of Zr immobility. In addition, they re-emphasized their previous study conducted at the Susquehanna Shale Hills Critical Zone Observatory (SSHCZO; Bern and Yesavage, 2018). In their study, Bern and Yesavage argued that about 40% of Zr in soil is mobilized as colloids as compared to the parent material.

The research question of our study (Kim et al., 2018) was whether particle losses can affect the soil and rock chemistry within a catchment. As we explained in the introduction of our paper, Zr is considered "chemically" immobile but is "physically" mobile. Zr in minerals is nearly insoluble and thus Zr does not mobilize significantly as solutes (i.e., chemical immobility). On the other hand, physical weathering processes such as erosion can remove particles, including particles containing Zr, from a system. These processes, however, are assumed to remove particles that have the same chemistry as the soil or rock; consequently, the soil and rock chemistry will not change (i.e., physical mobility). Most models of soil formation over a geological time scale rely on this argument and assume an element such as Zr is (chemically) immobile (e.g., Brimhall and Dietrich, 1987; Riebe et al., 2003). In our study, however, we documented that the mobile particles do not always show the same chemistry as the source material. During the wet season (winter), for example, at low discharge, the stream particle chemistry was similar to that of mobile particles in groundwater while at high discharge it was similar to that of the water dispersible colloids (WDCs) reported in Bern and Yesavage (2018).

To investigate our question, the evaluation of Zr immobility was important. We now realize, however, that our statement about Zr immobility in the original paper may be ambiguous because we did not explicitly discuss the physical and chemical immobility of Zr. Here we emphasize a discussion of the immobility of Zr with respect to both solutes and particles. First, Table 2 in our original paper shows that the flux of dissolved Zr is six orders of magnitude smaller than the total solute flux out of the Shale Hills catchment. This difference in the solute fluxes is also about two orders of magnitude lower than the fraction of Zr in the soil ($2.5-3\times10^{-4}$ g/g) or parent bedrock ($1.5-2\times10^{-4}$ g/g). Therefore, we conclude that it is reasonable to argue that Zr is chemically immobile as solutes. This is consistent with the extremely low solubility of Zr-containing phases, including the source mineral, zircon, observed in the catchment.

Second, we analyze the effect of loss of Zr as particles. If only physical erosion occurs, the chemistry of mobile particles will be the same as the source material; therefore, the ratios of other elements (e.g., Al, Fe) to Zr in the mobile particles and in the source material will be the same. However, if some degree of particle selection occurs during physical erosion, then the ratio of mobile particles will deviate from the equivalent ratios in the source material. For example, if Al/Zr of the mobile particles are higher than that of soils, we can conclude that some process is preferentially mobilizing Al from the soil as particles in addition to physical erosion. In other words, Zr is preferentially retained in the system compared to Al. This process, then, has the same net effect as chemical

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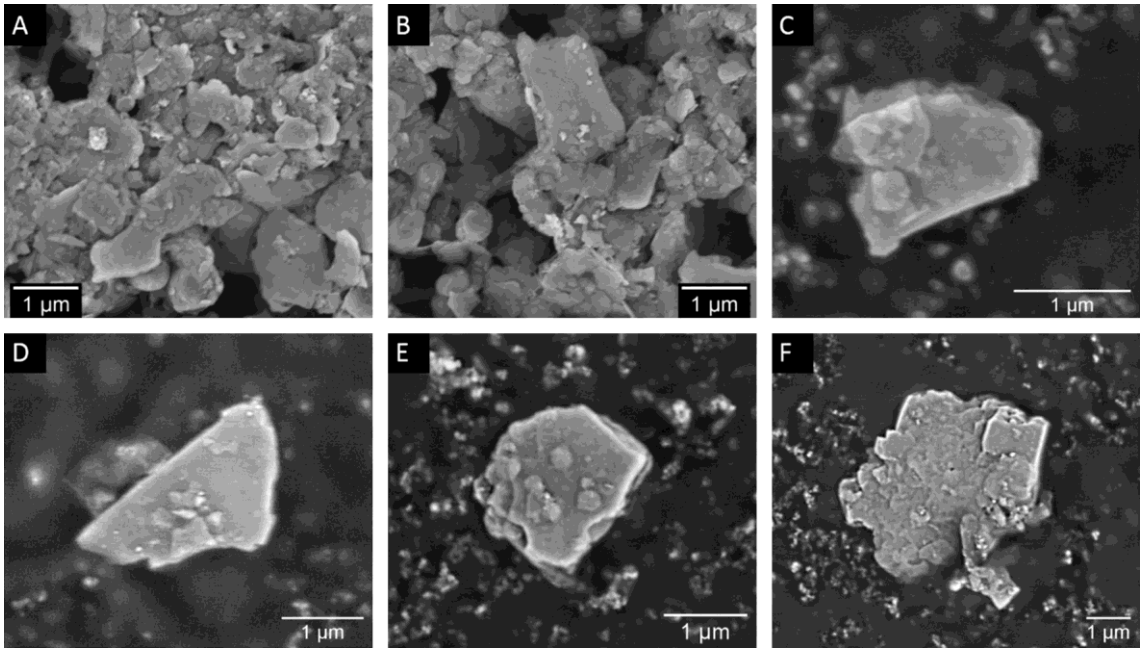

Fig. 1. Backscattered electron microscopy images of mobilized particles in stream recovered through ISCO® samplers in the Shale Hills catchment collected in February 2016 (A and B) and April 2015 (C, D, E, and F). The dominant mineral phase in these mobilized particles is micron-sized illite identified by energy dispersive X-ray spectroscopy (EDS). Quartz, Fe and Ti oxides, and amorphous Si and Al enriched particles (likely weathering products of illite and chlorite) were also occasionally observed. Zircon was not observed.

mobilization because it leaves behind a substrate of different elemental composition. In contrast, if Al/Zr of the mobile particles is lower than that of the soil, then Zr is preferentially mobilized as particles compared to Al, indicating "effective" chemical mobility of Zr.

In our work, we documented that the mobile particles always had higher Al/Zr and Fe/Zr than those of the soils. As seen in Table 1 in our original paper, for example, the average Al/Zr of stream particles (933; 759 (min.) - 1218 (max.)) is higher than the range observed for the soil (268-378) and parent bedrock (727; standard deviation = 65). Consistent with this, Fig. 4 in the original paper shows that $\tau_{Al,\ Zr}$ and $\tau_{Fe,\ Zr}$ of the stream particles were always greater than 0, indicating higher Al/Zr and Fe/Zr for the stream particles than for the parent bedrock.

In fact, based on extensive analysis of stream particles by scanning electron microscopy (SEM), we found that illite was preferentially mobilized as opposed to the other mineral particles (e.g., quartz, chlorite, zircon; Fig. 1). The preferential loss of illite is likely because of 1) its abundance in the mineral matrix (~40% in the parent bedrock); 2) its small size (typically smaller than 3 μm); and 3) its platy shape. Altogether, we concluded that Zr is "chemically" immobile.

Bern and Yesavage (2018) documented the chemistry of WDCs mobilized from Shale Hills soils through laboratory-extracted as a way to investigate particle transport out of the catchment. They used soil samples from 3 locations and maximum 1.05 m depth in the catchment. They extracted the WDCs by shaking 23 g of the Shale Hills soils in 207 g of ultrapure water for 10 minutes and centrifuging the mixture at 2000 rpm for 4 minutes. Then, the chemistry of the WDCs was used to calculate the elemental losses as colloids using the dual-phase mass balance model. Bern and Yesavage (2018) concluded that 40% of Zr in soil was mobilized as colloids as compared to the parent material.

Their estimation of the total Zr loss, however, may not necessarily implicate Zr's chemical mobility because their Zr concentrations of the WDCs may not representative of the particles that leave the catchment. One of the most interesting conclusions from our study is that colloid/particle transport at Shale Hills occurs not only from the augerable soil but also from the shallow fractured rock (Kim et al., 2018). However, they only focused on the top soil layer. Therefore, the chemistry of WDCs extracted from soil could differ from those from fractured rock where the Zr concentration is lower than that in the soil.

We also postulate that their measurements may estimate the maximum potential of colloidal losses because of their laboratory extraction approach. In natural systems, colloids are mobilized and then transported through the network of pore spaces and fractures in the soil and bedrock. This network can act like a filter because of its complicated tortuosity and heterogeneous structure and mineralogy. The shapes and sizes of colloids influence the colloid mobility and the optimal size and shape will vary depending on the network structure (e.g., Aramrak et al., 2013; Mohanty et al., 2015). For this reason, we argue that their method measures the maximum potential of the mobile colloids, and this may differ from what happens in the natural system.

2. Quantification of the particle losses

Bern and Yesavage also argue that the assumption behind the P_j calculation in our paper is flawed and therefore the P_j^* correction is incorrect. They argued that the actual assumption is that the ratio of a mobile element to Al for a mobile particle is the same as for parent bedrock, and not the same as for source soil. We disagree with Bern and Yesavage and therefore here we provide a full derivation of the P_j^* calculation.

We consider a weathering system with three groups of elements with different mobility: 1) elements such as Zr that are mobilized only by physical erosion (denoted in the equations below by subscript *Zr*); 2) elements that are mobilized by physical erosion and by preferential mobilization of "colloids" (denoted by subscript *i*); and 3) elements that are mobilized as "colloids" by both processes and also as solutes (denoted by subscript *j*). Here, physical erosion refers to mobilization of material with the same chemistry as the source material and "colloids" refers to any size of particles that move some elements more than others. Given

Table 1
Annual chemical weathering fluxes for elements as solutes and particles.

	Water year 2017[a] (total runoff 517 mm yr^{-1})								
	t km^{-2} yr^{-1}							kg km^{-2} yr^{-1}	
	Al	Ca	Fe	K	Mg	Si	sum	Zr	Ti
Solute	0.01	1.60	0.01	0.43	0.77	1.30	4.34	0.03	0.07
Particle	0.29	0.01	0.16	0.08	0.02	0.52	1.12	0.27	8.97
Total	0.30	1.61	0.17	0.51	0.79	1.82	5.46	0.29	9.04
Solid contribution (%)	96.6	0.4	95.6	15.8	2.8	28.5	20.5	91.0	99.2

[a] October 1, 2016 to September 30, 2017.

the definitions of the three types of elements described above, the equations describing mass balance between parent bedrock (denoted by subscript p) and the resultant regolith (denoted by subscript w) yield:

$$C_{Zr,p}m_p = C_{Zr,w}(m_w + m_e) \quad (1)$$

$$C_{i,p}m_p = C_{i,w}(m_w + m_e) + C_{i,c}m_c \quad (2)$$

$$C_{j,p}m_p = C_{j,w}(m_w + m_e) + C_{j,c}m_c + C_{j,s}m_s \quad (3)$$

where C and m are the elemental concentration (mass/mass) and mass, respectively, in the parent material or the regolith. The mass difference between parent bedrock and regolith is the integrated mass loss, m, of "colloids" (denoted by subscript c), of solute (denoted by subscript s), or of physically eroded material (denoted by subscript e).

Combining eqn (1) and (2), we can get an expression for the mass fraction of "colloid" loss compared to parent bedrock:

$$\frac{m_c}{m_p} = \frac{C_{i,p}}{C_{i,c}} - \frac{C_{i,w}}{C_{i,c}}\frac{C_{Zr,p}}{C_{Zr,w}} \quad (4)$$

Then, we can calculate the fractional mass loss of element j as "colloids", P_j^*:

$$P_j^* = \frac{C_{j,c}m_c}{C_{j,p}m_p} = \frac{C_{j,c}}{C_{j,p}}\left(\frac{C_{i,p}}{C_{i,c}} - \frac{C_{i,w}}{C_{i,c}}\frac{C_{Zr,p}}{C_{Zr,w}}\right)$$
$$= \left(\frac{C_{j,w}}{C_{i,w}}\frac{C_{i,p}}{C_{j,p}} - \frac{C_{j,w}}{C_{Zr,w}}\frac{C_{Zr,p}}{C_{j,p}}\right)\left(\frac{C_{i,w}}{C_{i,c}}\frac{C_{j,c}}{C_{j,w}}\right)$$
$$= \left(T_{j,i} - T_{j,Zr}\right)\left(\frac{C_{i,w}}{C_{i,c}}\frac{C_{j,c}}{C_{j,w}}\right) \quad (5)$$

If we choose i = Al as the second group element, then eq (5) is identical to eqn. (6) in our original paper. Using P_j^*, we estimated that the cumulative "colloid" fluxes were responsible for 58% of K and 24% of Mg loss for the overall weathering period.

Altogether, our study showed that losses of solid material can alter the soil and rock chemistry and such losses are not limited to the topsoil layer. For instance, Fig. 7 in our original paper revealed that such "colloid" losses occur in the weathered bedrock layer as well. Consistent with our conclusions, several previous studies also proposed an important role of "colloid" fluxes in the mass balance in Shale Hills based on the observations of the negligible levels of dissolved Fe, Al, and Ti in soil pore water and stream compared to observed depletions of these elements in the soil and weathered bedrock (Jin et al., 2010; Yesavage et al., 2012). Hasenmueller et al. (2017) also estimated a similar fractional contribution of "colloid" loss to the total weathering flux in the SSHCZO by analyzing the chemistry of material collected along fractures in weathered rock beneath the augerable soil layer.

3. Corrigendum to Table 2 of Kim et al. (2018)

Although not mentioned by Bern and Yesavage in their comment, we found errors in Table 2 of our original paper. Therefore, here we provide the correct version of the Table (reproduced as Table 1). Note that our original paper and this note were written based on this correct table; thus, our conclusions are not affected by the published errors in the original table.

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