Quantification of mass balance of colloidal material across lithologies and environments
Principal Investigator: Carleton Bern, Research Soil Scientist, USGS, Denver, Colorado (cbern@usgs.gov)

<u>Statement of Proposed Work</u>

Colloids, particles small enough to remain almost permanently in suspension, have long been recognized to play important roles in Critical Zone processes (Jin et al., 2010; McCarthy and McKay, 2004). Proportionately great surface area magnifies colloid influence on sorption and exchange, decreasing transport of components otherwise entrained in solution. In contrast, colloid mobility transports such components even while sorbed and redistributes insoluble components that form the colloid structure. Colloid redistribution plays roles in broader Critical Zone processes as fundamental as textural differentiation and B horizon formation (Jenny and Smith, 1935). Unfortunately investigating colloid redistribution in soil is difficult; hill slope flow paths are complex and *in situ* collection of mobile colloids in soil is challenging (McCarthy and McKay, 2004). Thus while colloid redistribution within and from soil is recognized as important, it has remained relatively unquantified.

The newly developed dual-phase mass balance model quantifies colloid redistribution in soils over pedogenic time scales (Bern et al., 2011; Bern et al., accepted pending revision). The model assumes that the sparing solubility of the high field strength elements Ti and Zr indicates their redistribution in solution is negligible. Support for that assumption comes from ≤ 1 ppb concentrations of Ti and Zr in ≤ 3 kDa filtrates of laboratory and *in situ* soil solutions. Therefore, deviation of the Ti/Zr ratio in a soil compared to its parent material traces redistribution of suspended solids (colloids) with a Ti/Zr ratio different from the parent material. Principles of mass balance can then be applied to quantify gains and losses of colloidal material using Ti/Zr ratios in a manner similar to isotope mixing models. Gains and losses of elements via solution can be quantified by difference. The required data are elemental compositions of soil, parent material, and colloids.

Thus far, the dual-phase mass balance model has been applied only along a single, slowly eroding (6.6 mm/kyr) catena in South Africa. There it shows that losses of colloids from upslope, clay-poor soil range up to 14% of mass relative to parent material, downslope gains of colloids in clay-rich soil can reach up to 52% relative to parent material, and places those changes in context relative to solution losses (Fig. 1). Clearly, colloidal redistribution is an important process at this site.

The work proposed here is laboratory extraction and analysis of soil colloids so that the dual-phase mass balance model can be implemented at four new sites. The results will support two lines of inquiry into the importance of colloid redistribution as a Critical Zone process. The two lines of inquiry are:

- Does the mass balance of colloidal Fe loss from Susquehanna Shale Hill Observatory (SSHO) soils match the Fe isotope mass balance from the same soils sufficiently to demonstrate reasonable accuracy for the quantification of each?
- How do magnitudes of colloid redistribution in soils derived from granitic material (including at Luquillo CZO) vary with climate and erosion regimes and compare to SSHO?

Previous work at SSHO has emphasized colloidal loss in the depletion of Fe from soils (Jin et al., 2010) and isotopically light Fe in bulk soils compared to parent material suggests that the colloids lost are isotopically heavy (Yesavage et al., 2012). Deviation of bulk soil Ti/Zr ratios from parent material also suggests that colloid losses are prevalent across SSHO hill slopes. It is proposed here to extract colloids from SSHO soils and determine both their elemental and Fe isotopic compositions. Elemental data will permit the quantification of Fe losses via colloids versus solution by using the new mass balance model. Determining the Fe isotopic composition for the colloids will allow predictions of that value (δ^{56}Fe = 0.8 ± 0.3‰) to be confirmed or refuted (Yesavage et al., 2012). Comparisons can then be made to see if

colloidal Fe mass balance matches Fe isotopic mass balance, thus providing a check on each or exposing where understanding could be improved.

The suggestion of isotopically heavy colloid losses from SSHO soils is at odds with the general assumption that particulate Fe in streams is isotopically light (Bergquist and Boyle, 2006; dos Santos Pinheiro et al., 2014; Fantle and dePaolo, 2004). Nevertheless, several recent studies have documented specific pools of isotopically enriched Fe in streams from around the world including Russia (Ilina et al., 2013), the United States (Escoube et al., 2009) and the Negro River of South America (dos Santos Pinheiro et al., 2014). At the moment, it is not clear why colloidal-sized Fe is light in some streams but heavy in others (dos Santos Pinheiro et al., 2014). Another benefit of the work proposed here is potential clarification of this issue for shale-derived colloidal material.

In addition to the SSHO, colloids from three other sites, having granitic as opposed to shale parent material, will also be extracted from archived samples and analyzed. Greater likelihood of parent material homogeneity makes granitic settings logical choices for early implementation of the dual-phase mass balance model. Ratios of Ti/Zr in elemental data from quartz diorite soils in different topographical locations at the Luquillo CZO provided by Stephen Porder suggest that colloid loss is an important process there (Mage and Porder, 2012). Ratios of Ti/Zr in elemental data from granitic hill slope soils from near the Feather River in California provided by Kyungsoo Yoo suggest that erosion rates (35–90 mm/kyr) influence the impact of colloidal redistribution on soils there (Yoo et al., 2011). Deep (7+ m) granitic weathering profiles in South Carolina, where the PI is studying rare earth element mobility, have Ti/Zr ratios that suggest depth dependence to colloid mobility. The climates (tropical to temperate) and erosion rates for these three new sites are substantially different from the slowly eroding, semi-arid South African catena where the model has been previously applied. Cross-site comparisons for granitic soils will yield insights into ranges of magnitude for colloidal redistribution and the influence of potential drivers of such redistribution as well as provide important context for interpreting the results at SSHO.

Laboratory extraction and analysis of colloids will be overseen by the PI and Tiffany Yesavage at USGS laboratories in Denver, Colorado. Tiffany has completed her PhD requirements at Penn State this spring. Tiffany is returning to Denver to live and that proximity will allow efficient collaboration on analyses, interpretation and writing. Analytical work should be complete by early 2015.

The ability to quantify colloidal redistribution in soil is relatively new. A check on colloid mass balance quantifications (through Fe isotopes) and exploration of environmental influence (across granitic soils) will demonstrate the applicability of the dual-phase mass balance model. Because the work will leverage samples and data held by collaborators, the small amount of support sought will allow substantial progress to be made and lay the foundation for more cross-cutting work to determine the importance of colloid redistribution within the Critical Zone.
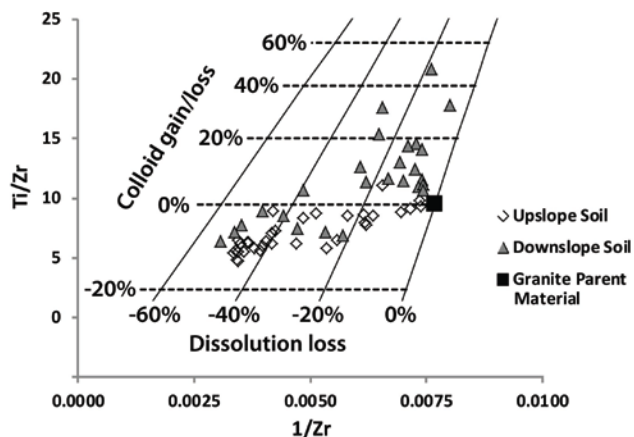

Figure 1. Ratios of 1/Zr and Ti/Zr for soil horizons and granitic parent material collected along a South African catena. Lines depict fractions of total mass gain or loss by solution and colloid redistribution as quantified using the dual-phase mass balance model.

References

Bergquist, B.A., Boyle, E.A., 2006. Iron isotopes in the Amazon River system: Weathering and transport signatures. Earth and Planetary Science Letters, 248: 54-68, doi:10.1016/j.epsl.2006.05.004.

Bern, C.R., Chadwick, O.A., Hartshorn, A.S., Khomo, L.M., Chorover, J., 2011. A mass-balance model to separate and quantify colloidal and solute redistributions in soil. Chemical Geology: doi:10.1016/j.chemgeo.2011.01.014.

Bern, C.R., Thompson, A., Chadwick, O.A., accepted pending revision. Quantification of colloidal and aqueous element transfer in soils: The dual-phase mass balance model. Geochimica et Cosmochimica Acta.

dos Santos Pinheiro, G.M., Poitrasson, F., Sondag, F., Cochonneau, G., Vieira, L.C., 2014. Contrasting iron isotopic compositions in river suspended particulate matter: the Negro and the Amazon annual river cycles. Earth and Planetary Science Letters, 394: 168-178, doi:10.1016/j.epsl.2014.03.006.

Escoube, R., Rouxel, O.J., Sholkovitz, E., Donard, O.F.X., 2009. Iron isotope systematics in estuaries: The case of North River, Massachusetts (USA). Geochimica et Cosmochimica Acta, 73: 4045-4059, doi:10.1016/j.gca.2009.04.026.

Fantle, M.S., dePaolo, D.J., 2004. Iron isotopic fractionation during continental weathering. Earth and Planetary Science Letters, 228: 547-562, doi:10.1016/j.epsl.2004.10.013.

Ilina, S.M. et al., 2013. Extreme iron isotope fractionation between colloids and particles of boreal and temperate organic-rich waters. Geochimica et Cosmochimica Acta, 101: 96-111, doi:10.1016/j.gca.2012.10.023.

Jenny, H., Smith, G.D., 1935. Colloid chemical aspects of clay pan formation in soil profiles. Soil Science, 39: 377-379.

Jin, L. et al., 2010. Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory. Geochimica et Cosmochimica Acta, 74: 3669-3691, doi:10.1016/j.gca.2010.03.036.

Mage, S.M., Porder, S., 2012. Parent material and topography determine soil phosphorus status in the Luquillo Mountains of Puerto Rico. Ecosystems, 16: 284-294, doi:10.1007/s10021-012-9612-5.

McCarthy, J.F., McKay, L.D., 2004. Colloid transport in the subsurface: Past, present, and future challenges. Vadose Zone Journal, 3: 326-337.

Yesavage, T.F., M.S. et al., 2012. Fe cycling in the Shale Hills Critical Zone Observatory, Pennsylvania: An analysis of biogeochemical weathering and Fe isotope fractionation. Geochimica et Cosmochimica Acta, 99: 18-38.

Yoo, K. et al., 2011. Evolution of hillslope soils: The geomorphic theater and the geochemical play. Applied Geochemistry, 26: S-149-S153, doi:10.1016/j.apgeochem.2011.03.054.

Proposed SSHO Interactions

The work on SSHO soils proposed here would support an informal collaboration underway between the PI and Susan Brantley (Lead-PI, SSHO) and Tiffany Yesavage (grad student, SSHO). Tiffany Yesavage has already selected soil samples from SSHO archives and completed some preliminary colloid extractions. Susan Brantley has committed to providing geochemical data on parent material and soils for implementation of the dual-phase mass balance model as well as additional archived samples if required (see letter of support). Extracted colloid material remaining at the end of the proposed study would be archived with the SSHO. The proposed work builds upon the detailed studies of iron geochemistry at SSHO by Brantley, Yesvage and others. It is envisioned that Tiffany Yesavage would lead authorship on a paper integrating the dual-phase mass balance model results for iron with iron isotope mass balance with at least the PI and Susan Brantley assisting as co-authors.

Although the Luquillo CZO is a separate entity from SSHO, both are part of the CZO network and work on Luquillo is proposed here. Stephen Porder is a Collaborator with the Luquillo CZO and has promised archived samples for colloid extraction and analysis as well as geochemical data on parent material and soils for implementation of the dual-phase mass balance model (see letter of support). Similarly, Kyungsoo Yoo has promised archived Feather River samples for colloid extraction and analysis as well as geochemical data on parent material and soils for implementation of the dual-phase mass balance model (see letter of support). It is not expected that sample material will remain after colloids are extracted from sample splits provided by these collaborators. However, if material remains it will be returned to be archived with the original samples. It is envisioned that the PI would be a lead author on a paper implementing the dual-phase mass balance model and making cross-site comparisons for these sites with granitic parent material with at least Tiffany Yesavage, Stephen Porder and Kyungsoo Yoo as co-authors.

All data collected on samples will be placed online at the SSHO or Luquillo websites if that is desired. Some guidance may be requested as some data will be derived from other research sites due to the cross-cutting nature of the proposed work.

<u>Results of prior support to work on SSHO</u>

SUMMARY PROPOSAL BUDGET

	FOR NSF USE ONLY		
ORGANIZATION U.S. Geological Survey	PROPOSAL NO.	DURATION (MONTHS)	
		Proposed	Granted
PRINCIPAL INVESTIGATOR/PROJECT DIRECTOR Carleton Bern	AWARD NO.		

A. SENIOR PERSONNEL: PI/PD, Co-PIs, Faculty and Other Senior Associates	NSF-Funded Person-months			Funds Requested By Proposer	Funds Granted by NSF (If Different)
List each separately with name and title. (A.7. Show number in brackets)	CAL	ACAD	SUMR		
1. Carleton Bern	0	0	0	$0	$
2.					
3.					
4.					
5.					
6. ( ) OTHERS (LIST INDIVIDUALLY ON BUDGET EXPLANATION PAGE)					
7. (1) TOTAL SENIOR PERSONNEL (1-6)	0	0	0	0	
B. OTHER PERSONNEL (SHOW NUMBERS IN BRACKETS)					
1. ( ) POSTDOCTORAL ASSOCIATES					
2. (1) OTHER PROFESSIONALS (TECHNICIAN, PROGRAMMER, ETC.)	1	0	0	2,400	
3. ( ) GRADUATE STUDENTS					
4. ( ) UNDERGRADUATE STUDENTS					
5. ( ) SECRETARIAL - CLERICAL (IF CHARGED DIRECTLY)					
6. ( ) OTHER					
TOTAL SALARIES AND WAGES (A + B)					
C. FRINGE BENEFITS (IF CHARGED AS DIRECT COSTS)					
TOTAL SALARIES, WAGES AND FRINGE BENEFITS (A + B + C)				2,400	
D. EQUIPMENT (LIST ITEM AND DOLLAR AMOUNT FOR EACH ITEM EXCEEDING $5,000.)					
TOTAL EQUIPMENT					
E. TRAVEL 1. DOMESTIC (INCL. CANADA, MEXICO AND U.S. POSSESSIONS)					
2. FOREIGN					
F. PARTICIPANT SUPPORT					
1. STIPENDS $					
2. TRAVEL					
3. SUBSISTENCE					
4. OTHER					
TOTAL NUMBER OF PARTICIPANTS ( ) TOTAL PARTICIPANT COSTS					
G. OTHER DIRECT COSTS					
1. MATERIALS AND SUPPLIES				1033	
2. PUBLICATION/DOCUMENTATION/DISSEMINATION					
3. CONSULTANT SERVICES					
4. COMPUTER SERVICES					
5. SUBAWARDS					
6. OTHER Analytical fees for samples				1,500	
TOTAL OTHER DIRECT COSTS					
H. TOTAL DIRECT COSTS (A THROUGH G)				4933	
I. INDIRECT COSTS (F&A) (SPECIFY RATE AND BASE) 50.667%				5,067	
TOTAL INDIRECT COSTS (F&A)					
J. TOTAL DIRECT AND INDIRECT COSTS (H + I)				10,000	
K. RESIDUAL FUNDS (IF FOR FURTHER SUPPORT OF CURRENT PROJECT SEE GPG II.D.7.j.)					
L. AMOUNT OF THIS REQUEST (J) OR (J MINUS K)				$10,000	$
M. COST SHARING: PROPOSED LEVEL $	AGREED LEVEL IF DIFFERENT: $				

PI/PD TYPED NAME AND SIGNATURE*	DATE	FOR NSF USE ONLY		
Carleton Bern		INDIRECT COST RATE VERIFICATION		
ORG. REP. TYPED NAME & SIGNATURE*	DATE	Date Checked	Date of Rate Sheet	Initials-ORG

NSF Form 1030 (10/99) *Supersedes All Previous Editions*   *SIGNATURES REQUIRED ONLY FOR REVISED BUDGET (GPG III.C)

Budget Justification

B.1. Other Professionals (Technician)
A student contract laboratory technician will work on the project
4 weeks * 40 hrs/week * $15/hr = $2,400

G.1. Materials and Supplies
Pall Macrosep Advance 3 kDa Centrifugal Ultrafilters and trace metal grade acids and for digestions are required to supplement supplies in the PI's lab $1033

G.6. Other
Fees for ICP-MS analysis of colloid digests and < 3 kDa filtrates, 50 samples * $20 per sample = $1000
Iron isotope analyses (consumable materials and instrument time), 5 samples * $100 per sample = $500

I. Indirect Costs
The indirect rate for the Crustal Geophysics and Geochemistry Science Center is 50.667%
$10,000 award * 50.667% = $5,066.67

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Professional Preparation

Virginia Tech	Biological Sciences	B.S.	1996
University of Colorado	Ecology and Evolutionary Biology	Ph.D.	2006

Appointments

Since 2010	Research Soil Scientist, U.S. Geological Survey
2008 – 2010	Mendenhall Postdoctoral Fellow, U.S. Geological Survey
2006 – 2008	Postdoctoral Researcher, University of California, Santa Barbara
2004 – 2006	Biologist, Stable Isotope Laboratory, U.S. Geological Survey
2001 – 2004	Physical Science Technician, Stable Isotope Laboratory, U.S. Geological Survey

Five Related Publications

Bern, C.R., Thompson, A., Chadwick, O.A. *Accepted pending revision*. Quantification of colloidal and aqueous element transfer in soils: The dual-phase mass balance model. Geochimica et Cosmochimica Acta.

Khomo, L., Bern, C.R., Hartshorn, A.S., Rogers, K.H. Chadwick, O.A. 2013. Chemical transfers along slowly eroding catenas developed on granitic cratons in southern Africa. Geoderma. doi:10.1016/j.geoderma.2013.03.023

Bern, C.R., Chadwick, O.A., Hartshorn, A.S., Khomo, L.M., Chorover, J. 2011. A mass-balance model to separate and quantify colloidal and solute redistributions in soil. Chemical Geology. doi:10.1016/j.chemgeo.2011.01.014

Bern, C.R. and White, A.F. 2011. A model for assessing, quantifying, and correcting for index element mobility in weathering studies. Applied Geochemistry. doi:10.1016/j.apgeochem.2011.03.016

Bern, C.R. and Chadwick, O.A. 2010. Quantifying colloid mass redistribution in soils and other physical mass transfers. In Birkle, P. and Torres-Alvarado, I.S. (eds.) Water-Rock Interaction. CRC Press, Boca Raton. pp. 765-768.

Five Other Significant Publications

Bern C.R., Breit, G.N., Healy, R.W., Zupancic, J. 2013. Deep subsurface drip irrigation using coal-bed sodic water: Part II. Geochemistry. Agricultural Water Management. doi:10.1016/j.agwat.2012.11.013

Bern, C.R., Brzezinski, M.A. Beucher, C., Ziegler, K., and Chadwick, O.A. 2010. Weathering, dust and biocycling effects on soil silicon isotope ratios. Geochimica et Cosmochimica Acta. doi:10.1016/j.gca.2009.10.046

Bern, C.R. 2009. Soil chemistry in lithologically diverse datasets: The quartz dilution effect. Applied Geochemistry, 24: 1429-1437, doi: 10.1016/j.apgeochem.2009.04.013

Bern, C.R., S. Porder and A.R. Townsend. 2007. Erosion and landscape development decouple strontium and sulfur in the transition to dominance by atmospheric inputs. Geoderma 142: 274-284, doi:10.1016/j.geoderma.2007.08.016

Bern, C.R., A.R. Townsend, and G.L. Farmer. 2005. Dominance of parent-material strontium in a tropical forest on highly weathered soils. Ecology 86(3): 626-632. doi:10.1890/03-0766

Synergistic Activities

Development of a mass balance model for use in soil and weathering studies that eliminates the immobile element assumption and distinguishes between dissolved and colloidal element transfers.

Teaching and curriculum development for Erosion: Process and Measurement at University of Denver, Fall 2012.

Collaborators & Other Affiliations

Alan R. Townsend (graduate advisor)	University of Colorado
Oliver A. Chadwick (postdoc advisor)	UC Santa Barbara
George Breit (Mendenhall advisor)	USGS
Susan Brantley	Penn State
Lesego Khomo	University of Cape Town
Anthony Hartshorn	Montana State
Stephen Porder	Brown University
Aaron Thompson	University of Georgia
Tiffany Yesavage	Penn State
Kyungsoo Yoo	University of Minnesota
Geneva Chong	USGS
Mark Engle	USGS/UT El Paso
Nora Foley	USGS
Anjana Shah	USGS
Ruth Wolf	USGS

<u>Summary of proposer's current/pending support</u>

Carleton Bern has no current or pending support from NSF or other sources external to the U.S. Geological Survey.