

AN ABSTRACT OF THE DISSERTATION OF

Elizabeth K. King for the degree of Doctor of Philosophy in Ocean, Earth, and Atmospheric Sciences presented on August 25, 2017.

Title: Understanding Molybdenum Isotope Dynamics in Terrestrial Environments

Abstract approved: _____
Julie C. Pett-Ridge

This dissertation works towards determining the mechanisms driving the Mo isotopic composition of soils, and how these signals may be used to refine the use of Mo as a proxy of biogeochemical processes. The first step towards quantifying Mo fractionation in soils is to determine the mechanisms controlling Mo accumulation, loss, and mobility. To do this, I first measured the abundance and isotopic composition of Mo across soil climatic gradients on the Hawaiian Islands. The Maui Climate Gradient (MCG) is a 410 kyr precipitation gradient where redox state (Eh) is well-constrained. I observed higher bulk soil Mo concentrations and greater mobilization of Mo in anoxic soils, and determined that Mo adsorption was two orders of magnitude greater onto organic matter relative to short range ordered (SRO) Fe- (oxyhydr)oxides. Since high rainfall coincides with an accumulation of organic matter, these results suggest a shift from Fe- (oxyhydr)oxides to organic matter control of Mo at high rainfall sites. I then focused on the Kona Climate Gradient (KCG), located on a 10 kyr lava flow where soils are undergoing initial stages of chemical weathering. Across the KCG, I observed net accumulation of Mo

with increasing precipitation in surface soil horizons, suggesting that atmospheric inputs were a significant source of Mo in soils. The isotopic composition of soil Mo is also offset from bedrock values, confirming that Mo isotope shifts are occurring. The isotopically lightest Mo signature is found in the driest sites, and the isotopically heaviest Mo signature is found in surface horizons of the wettest sites. To reconcile these observations, I measured the Mo isotopic composition of precipitation, groundwater, and vegetation and concluded that while the Mo cycle is significantly affected by isotopic fractionation mechanisms within soils, it is also modulated by atmospheric inputs and subsequent Mo adsorption onto organic matter.

My next research project followed up on these findings from Hawaiian soils by calculating the extent of Mo isotope fractionation during adsorption onto organic matter. At pH 4, fractionation between the solution and adsorbed phase ($\Delta^{98}\text{Mo}$) was 1.4‰ and fit an equilibrium fractionation model. As pH increased from 2 to 7, Mo adsorption onto IHA decreased, but the degree of fractionation increased to a maximum of 1.8‰. I compared laboratory results to Mo isotope patterns in precipitation, foliage, organic horizon, surface mineral soils, and bedrock for 12 forested sites across the Oregon Coast Range. Fractionation of precipitation-derived Mo onto the organic horizon aligned well with laboratory results, suggesting that organic matter influences the Mo isotope composition of soils by preferentially adsorbing light Mo. The magnitude and direction of Mo fractionation during adsorption onto organic matter is similar to fractionation of Mo onto Fe- and Mn-

(oxyhydr)oxides, which has implications for the interpretation of the sedimentary Mo record and its use as a paleoredox tracer.

In addition to organic matter adsorption and desorption processes, the dissolution of Fe- (oxyhydr)oxides, colloid dispersion, and shifts in pH have the potential to mobilize Mo and other trace metals in soil. To determine trace metal mobilization as a function of redox, soil mineralogy, and colloid dynamics, I measured trace metal mobilization via colloids and the aqueous phase during two consecutive, 8-day redox cycles. In soils with high clay content and low permeability, reducing conditions drove trace metal mobility. Comparatively, in soils with low clay content and high permeability, trace metal mobilization was independent of redox state. My results provide evidence that lithology remains an overarching factor governing trace metal mobility in soils. The Mo isotopic composition of the soil solid, colloids, and the aqueous phase did not reflect the redox history of soils, suggesting that the additional fractionation mechanisms such as organic matter and atmospheric inputs complicate the utility of Mo as a tracer of redox in soils.

My final research endeavor investigated the impact of Mo cycling in the terrestrial environment on the magnitude and isotope signature of the Mo flux to the oceans. I collected Mo from a series of rivers and groundwater sources along the Hawaiian Islands where the stage of chemical weathering varies as a function of lithological age. Groundwater dominates the Mo flux during initial stages of chemical weathering, and the dissolved Mo isotopic composition of groundwater is only slightly fractionated from bedrock. With increasing age, and stage of chemical

weathering, rivers become the main vector for water transport to the oceans. Rivers draining predominately shallow flowpaths have Mo isotopic signatures that reflect fractionation processes as Mo cycles through the terrestrial environment. However, the input of groundwater to riverine base flow overprints small-scale fractionation mechanisms and narrows the range of the isotopic signature of the global Mo flux.

The chapters of this dissertation seek to address the mechanisms driving isotope fractionation patterns during terrestrial biogeochemical cycling. My data shows that Mo is fractionated within soils during adsorption onto organic matter, and that the input of isotopically heavy Mo from atmospheric inputs is a previously unrecognized source of Mo to soils that may alter the trajectory of fractionation patterns. These conclusions suggest that the utility of Mo as a redox tracer in soils is suppressed by additional fractionation mechanisms. Nevertheless, these insights into Mo biogeochemical cycling contribute to better understanding and prediction of how riverine isotope signatures have likely varied as a function of chemical weathering throughout Earth's history.

©Copyright by Elizabeth K. King
August 25, 2017
All Rights Reserved

Understanding Molybdenum Isotope Dynamics in Terrestrial Environments

by
Elizabeth K. King

A DISSERTATION

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Doctor of Philosophy

Presented August 25, 2017
Commencement June 2018

Doctor of Philosophy dissertation of Elizabeth K. King presented on August 25, 2017

APPROVED:

Major Professor, representing Ocean, Earth, and Atmospheric Sciences

Dean of the College of Earth, Ocean and Atmospheric Sciences

Dean of the Graduate School

I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.

Elizabeth K. King, Author

ACKNOWLEDGEMENTS

I would like to thank my advisor Julie Pett-Ridge for the opportunity to embark on a research project where I have had the support and encouragement to combine my interests in terrestrial and aqueous biogeochemistry into a coherent dissertation. I would also like to thank my co-authors and committee members, who have spent countless hours discussing my data, helping me brainstorm, and encouraging me to follow the interesting, and sometimes not-so-interesting leads that arise in these meetings. I have also been fortunate to work in the W.M. Keck Collaboratory, a huge resource when it comes to sample preparation, data collection, and coping with the frustrations of method development.

Of course, I would not have been able to complete this degree without the love and encouragement of my family and friends. In particular, my Mom, Dad, and Samantha, have always been my “#1 fans”, reminding me that “great minds think differently” and I’m “braver than I believe”. Who knows where I would be without the flashcards, Mom! I would also be remiss not to thank Greg, for keeping me laughing and sane throughout this long, seemingly never-ending, graduate school journey. Finally, the friends, “roommates” and “officemates” I have collected in my years away from home have become family. From weekend hiking trips to trail runs to after-work beers, the relationships I have developed in Oregon (and maintained from afar, here’s looking at you Sal!) have provided me with endless support and stability. Thank you all!

CONTRIBUTION OF AUTHORS

Dr. Julie Pett-Ridge provided valuable assistance with the study design, data interpretation, synthesis, and countless edits for all the chapters of my dissertation.

Dr. Aaron Thompson assisted with the collection of data, experimental design, and participated in helpful discussions for Chapters 2, 3, and 5.

Ms. Caitlin Hodges assisted with data collection and provided helpful revisions for Chapter 2.

Dr. Oliver Chadwick helped with data collection and access to sampling locations for Chapter 3, and provided helpful insights during data interpretation and synthesis.

Dr. Steven Perakis provided foliage, organic horizon, and mineral soil horizon samples from the Oregon Coast Range for Chapter 4 and provided valuable comments and revisions to the manuscript

TABLE OF CONTENTS

	<u>Page</u>
Chapter 1: Introduction.....	1
1.1 Applications of the molybdenum isotope system	5
1.2 Complications for the molybdenum isotope system.....	7
1.3 Molybdenum in the terrestrial environment	8
1.4 Research strategies.....	10
Chapter 2: Towards understanding temporal and spatial patterns of molybdenum in the critical zone	15
Abstract	16
2.1 Introduction.....	17
2.2 Methods	19
2.3 Results and Discussion.....	23
2.3.1 MCG soil extractions	23
2.3.2 Kona soil climate sequence.....	29
2.4 Conclusion	30
2.5 Acknowledgements	31
Chapter 3: Molybdenum sources and isotopic composition during early stages of pedogenesis along a basaltic climate gradient.....	32
Abstract	33
3.1 Introduction.....	34
3.2 Methods	38
3.2.1 Study site: Kona Climate Gradient (KCG)	38
3.2.2 Sample collection.....	43

TABLE OF CONTENTS (Continued)

	<u>Page</u>
3.2.3 Element loss or gain.....	45
3.2.4 Extractions	46
3.2.5 Mo isotopic composition	47
3.3 Results	49
3.3.1 Concentration and mobility of molybdenum in soil profiles	49
3.3.2 Mo isotopic composition in soil profiles	51
3.3.3 Mo concentrations and isotopic compositions in foliage, groundwater, stream water, and precipitation	52
3.3.4 Selective extractions of Mo in soil	65
3.4 Discussion	65
3.4.1 Mo mobility across the KCG.....	65
3.4.2 Mo isotopic composition in bulk soil across the KCG	67
3.4.3 Mo isotopic mass balance.....	69
3.4.4 Terrestrial Mo cycling: Comparison with older soils.....	76
3.4.5 Implications for global Mo cycling	77
3.5 Conclusion	79
3.6 Acknowledgements	81
Chapter 4: Molybdenum isotope fractionation during adsorption onto organic matter	82
Abstract	83
4.1 Introduction.....	84
4.2 Methods	88
4.2.1 Insolubilization of humic acid and preparation of Mo stock solution	88

TABLE OF CONTENTS (Continued)

	<u>Page</u>
4.2.2 Sorption experiments	89
4.2.3 Oregon Coast Range samples	91
4.2.4 Mo isotopic composition	93
4.2.5 Data analysis	95
4.3 Results	96
4.3.1 Insolubilized humic acid experiment: Mo adsorption and isotopic composition	96
4.3.2 Mo dynamics in the Oregon Coast Range.....	100
4.4 Discussion	101
4.4.1 Mechanisms of Mo isotope fractionation on organic matter.....	101
4.4.2 Mo isotope fractionation during adsorption onto natural organic matter	108
4.4.3 Effect of plant uptake on the Mo isotopic composition	111
4.4.4 Relationship between soil Mo, carbon content, and pH	112
4.5 Conclusions and broader implications.....	116
4.6 Acknowledgements	117
Chapter 5: Interactions between lithology and redox cycling in controlling trace metal mobilization and Mo isotope dynamics in soils	118
Abstract	118
5.1 Introduction.....	120
5.2 Methods	124
5.2.1 Study sites and sample collection.....	124
5.2.2 Redox experiment.....	126

TABLE OF CONTENTS (Continued)

	<u>Page</u>
5.2.3 Chemical analyses	129
5.3 Results	131
5.4 Discussion	144
5.4.1 Importance of lithology on Fe mineralogy and redox.....	144
5.4.2 Trace metal cycling during redox oscillations	147
5.4.3 Mo partitioning during redox oscillations.....	149
5.5 Conclusions.....	153
5.6 Acknowledgements	154
Chapter 6: Reassessing the dissolved molybdenum isotopic composition of ocean inputs: The effect of chemical weathering and groundwater	155
Abstract	155
6.1 Introduction.....	157
6.2 Study Sites	161
6.3 Methods	167
6.4 Results	170
6.5 Discussion	177
6.5.1 Mo behavior during initial stages of chemical weathering.....	177
6.5.2 Mo behavior during intermediate- to late- stages of chemical weathering	183
6.5.3 Effect of soil redox conditions on shallow flowpaths	185
6.5.4 Mo in Critical Zone Observatories (CZOs)	188
6.5.5 Implications for global Mo fluxes.....	190
6.6 Conclusion	196

TABLE OF CONTENTS (Continued)

	<u>Page</u>
6.7 Acknowledgements	196
Chapter 7: Conclusion	197
Chapter 8: Bibliography.....	200
APPENDICES	227

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
Figure 2.1: Fe content (wt. %), carbon content (%), and redox state (Eh) as a function of precipitation (MAP) cross the Maui Climate Gradient.	22
Figure 2.2: Mo behavior before and after an artificial redox experiment as a function of MAP.	25
Figure 2.3: Mo content in a reducible (SRO mineral) and an oxidizable (organic) pool	28
Figure 2.4: Tau Mo values along the Kona climate sequence.	28
Figure 3.1: τ Mo depth profiles across the KCG	59
Figure 3.2: Mass-weighted, profile-integrated τ Mo and τ Ca calculations versus MAP.	60
Figure 3.3: Mass-weighted, profile-integrated τ Mo plotted against % $C_{org.}$	61
Figure 3.4: Mass-weighted, profile-integrated $\delta^{98}\text{Mo}$ plotted against % $C_{org.}$	62
Figure 3.5: $\delta^{98}\text{Mo}$ depth profiles across the KCG.	63
Figure 3.6: Mo released in the H_2O_2 extraction versus mass-weighted, profile-integrated a) τ Mo and b) $\delta^{98}\text{Mo}$	64
Figure 3.7: Box model of Mo inputs to the driest site along the KCG (MAP = 660 mm) (a) and the wettest site along the KCG (MAP = 2100 mm) (b).	75
Figure 4.1: Mo adsorption onto insolubilized humic acid (IHA) as a function of (a) time (hours) and (b) pH.	97
Figure 4.2: Mo isotopic composition ($\delta^{98}\text{Mo}$) of solution (open circles) and IHA (closed circles) versus (a) time (hours) and (b) pH.	97
Figure 4.3: Mo isotopic composition ($\delta^{98}\text{Mo}$) of foliage (triangles), O horizon (circles), and mineral soil samples (squares) for the Oregon Coast Range.	106
Figure 4.4: Elemental mass transfer of Mo (τ Mo) (a) and Mo isotopic composition ($\delta^{98}\text{Mo}$) (b) versus carbon content for mineral soil samples (0-10 cm) along the Oregon Coast Range.	107

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
Figure 4.5: Elemental mass transfer of Mo (τ Mo) (a) and Mo isotopic composition ($\delta^{98}\text{Mo}$) (b) versus pH for mineral soil samples along the Oregon Coast Range (OCR).	107
Figure 5.1: Mössbauer spectroscopy Fe phase abundances.	135
Figure 5.2: Al ($\mu\text{g g}^{-1}$ dry soil), Ti ($\mu\text{g g}^{-1}$ dry soil), Fe ($\mu\text{g g}^{-1}$ dry soil), and Mo (ng g^{-1} dry soil) concentrations during artificial redox experiment:	138
Figure 5.3: Ratio of the trace metal concentrations ([X]) at Bisley to Guaba Ridge during oxic half-cycle I (a), reducing half-cycle I (b), oxic half-cycle II (c), and reducing half-cycle II (d).	140
Figure 5.4: Coefficient of determination (R^2) based on linear regression analyses for trace metal solution concentrations versus Fe solution concentrations.	141
Figure 5.5: Mo isotopic composition ($\delta^{98}\text{Mo}$) during redox oscillations	143
Figure 6.1: Approximate location of sample sites across Hawaii (A) and North America (B). The Hawaiian Islands get progressively older along a northwest transect.	163
Figure 6.2: Mo concentration and $\delta^{98}\text{Mo}$ data for Hawaiian groundwater and rivers in Hawaii and the CZOs.....	174
Figure 6.3: A) Mo concentration and B) $\delta^{98}\text{Mo}$ data plotted as a function of approximate regolith age.	175
Figure 6.4: Mixing plot between seawater, Hawaiian basalt, and Mo leaching from soils.....	176
Figure 6.5: Hawaii water samples (groundwater = black, river water = white) compared to soil samples (brown diamonds) of similar ages	182
Figure 6.6: $\delta^{98}\text{Mo}$ and [Mo] values for the Kohala Peninsula, Hawaii (A), Kauai, Hawaii (B), and Luquillo, Puerto Rico (C) where there is a clear difference between Mo sourced from shallow flow and deep flow (groundwater).	187
Figure 6.7: $\delta^{98}\text{Mo}$ values plotted as a function of the inverse of Mo concentrations from a suite of studies reporting Mo isotope data for rivers.	192

LIST OF FIGURES (Continued)

<u>Figure</u>	<u>Page</u>
Figure 6.8: Direct plot of $\delta^{98}\text{Mo}$ values versus Mo discharge.	193

LIST OF TABLES

<u>Table</u>	<u>Page</u>
Table 2.1: Maui Climate Gradient site chemistry	24
Table 3.1: Kona Climate Gradient site physiography	42
Table 3.2: Soil and parent material element mobility and Mo isotopic composition	54
Table 3.3: profile integrated soil Mo data, mobility, and isotopic composition	56
Table 3.4: Precipitation, groundwater, and vegetation Mo concentrations and isotopic composition	57
Table 3.5: Soil selective extraction data	58
Table 3.6: Mo isotopic mass balance	74
Table 4.1: IHA experiment: Duration, pH, Mo adsorbed onto insolubilized humic acid (IHA) and fractionation of Mo isotopes	98
Table 4.2: Site properties for foliage, O horizon, and 0 – 10 cm mineral soils in the Oregon Coast Range	104
Table 4.3: Mo isotopic composition of precipitation, foliage, O horizon, mineral soil (0-10 cm) and bedrock in the Oregon Coast Range	105
Table 5.1: Luquillo CZO site chemistry	133
Table 5.2: Soil Fe phases based on Mössbauer spectroscopy	134
Table 5.3: Artificial redox experiment chemistry	137
Table 6.1: Mo geochemical data for groundwater and river samples	172

LIST OF APPENDICES

<u>Appendix</u>	<u>Page</u>
Appendix A. Supplementary material for “Molybdenum sources and isotopic composition during early stages of pedogenesis along a basaltic climate gradient”	228
A.1. Tephra calculations	228
A.2. Seawater contamination of groundwater	229
Appendix B. Supplementary material for “Molybdenum isotope fractionation during adsorption onto organic matter”	233
Appendix C. Supplementary material for “Interactions between lithology and redox cycling in controlling trace metal mobilization and Mo isotope dynamics in soil” ..	238
C.1. ⁵⁷ Fe Mössbauer spectroscopy of the Bisley and Guaba Ridge soils and the Ferrihydrite and Goethite standards	240
C.1.1. Introduction	240
C.1.2. Methods	240
C.1.3. Mossbauer spectral components in the Bisley and Guaba Ridge bulk soils	242
C.1.4. Mossbauer phase analysis of Bisley and Guaba Ridge bulk soils	243
Appendix D. Supplementary material for “Reassessing the dissolved molybdenum isotopic composition of ocean inputs: The effect of chemical weathering and groundwater”	254
Appendix E. Methodology details	260
E.1. Reducible pool (SRO Fe- and Mn-) (oxyhydr)oxides associated) extraction for soil Mo isotopes	260
E.2. Oxidizable pool (organic matter associated) extraction for soil Mo isotopes	261
E.3. Molybdenum column chemistry	262
E.4. Column wash justification	262

LIST OF APPENDICES (Continued)

<u>Appendix</u>	<u>Page</u>
E.5. Nu parameters.....	264
E.5.1. Mo double spike NICE code	266

LIST OF APPENDIX FIGURES

<u>Figure</u>	<u>Page</u>
Figure A.1: $\delta^{98}\text{Mo}$ versus Na concentrations of groundwater samples affected by seawater intrusion.....	232
Figure B.1: Percentage of Mo adsorbed as a function of the exact mass of IHA.	235
Figure B.2: Percentage of Mo adsorbed by IHA versus Mo isotopic composition ($\delta^{98}\text{Mo}$) from the time series experiment.	236
Figure B.3: O horizon Mo concentrations (a) and O horizon Mo isotopic composition ($\delta^{98}\text{Mo}$) (b) versus O horizon pH along the Oregon Coast Range.....	237
Figure C.1: Schematic of artificial redox experiment.	238
Figure C.2: ^{57}Fe Mössbauer spectra of the unreacted Bisley soil at 295K, 77K, and 4.8K.....	246
Figure C.3: ^{57}Fe Mössbauer spectra of the unreacted Guaba Ridge soil at 295K, 77K, and 4.8K.....	247
Figure E.1: Mo contamination on AG1 X-8 resin	263
Figure E.2: Nu standard reproducibility for A) Alfa Aesar, B) BCR-2, C) BHVO-2, and D) SDO-1 standards.....	265

LIST OF APPENDIX TABLES

<u>Table</u>	<u>Page</u>
Table A.1: Tephra influence on Mo mobility	230
Table A.2: Profile intergrated tephra influence.....	231
Table A.3: Groundwater influenced by seawater intrusion	231
Table B.1: Dissolved organic carbon concentrations	233
Table B.2: O horizon chemical parameters (Perakis et al., 2017).....	234
Table B.3: Regression statistics for O horizon chemical parameters (95% C.I.)	235
Table C.1: Trace metal bulk soil and bedrock chemistry ($\mu\text{g g}^{-1}$).....	239
Table C.2: Mossbauer spectroscopy parameters	248
Table C.3: Artificial redox experiment chemistry: Trace metals ($\mu\text{g g}^{-1}$)	250
Table C.4: $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ for full suite of metals analyzed in experiments	251
Table C.5: Correlation matrix for Bisley(red) and Guaba Ridge (blue)	252
Table D.1: Additonal geochemical data for groundwater and river samples from Hawaiian Islands and Critical Zone Observatories.....	254
Table D.2: Subsurface soil Mo data for Hawaii	257
Table D.3: Compilation of Mo data	258
Table E.1: Column chemistry.....	262
Table E.2: Mo column efficiency	263
Table E.3: Nu instrument settings	264
Table E.4: Nu Faraday Cup configuration	264

Chapter 1: Introduction

Understanding the environmental cycling of molybdenum (Mo) is of interest because Mo is an enzyme cofactor in a suite of biological processes, and its abundance and isotopic composition is driven by reduction-oxidation (redox) reactions, making Mo a potential tracer of biogeochemical processes. Biologically, Mo is an essential nutrient for over 30 enzymes in the nitrogen (N) and sulfur (S) cycles (Kendall et al., 2017), most notably the nitrogenase enzyme, used to convert nitrogen gas (N_2) to plant-available ammonium (NH_3) during N_2 -fixation (Bittner and Mendel, 2006). Recent evidence suggests that N_2 -fixation can be limited by Mo (Barron et al., 2008; Bellenger et al., 2011; Perakis et al., 2017; Silvester, 1989); therefore, quantifying the spatial and temporal scales of Mo mobility will improve the understanding of ecosystem nutrient limitation. Geochemically, Mo has seven stable isotopes that accumulate in environments at different rates as a function of redox state, coordination chemistry, and metal-ligand bonding. As such, the abundance and isotopic composition of Mo in various reservoirs is a potential indicator of past environmental conditions.

The paleo-environmental applications of Mo revolves around its speciation in aqueous systems and its dynamic redox behavior. Under typical oxic conditions, Mo is highly mobile as the soluble molybdate oxyanion (Mo(VI)O_4^{2-}), though molybdic acid (H_2MoO_4) and its oxyanion (HMoO_4^-) become increasingly abundant at $\text{pH} < 6$ (Alloway, 2013). Polynuclear molybdates (e.g. $\text{Mo}_6\text{O}_{19}^{2-}$, $\text{Mo}_7\text{O}_{24}^{6-}$, and $\text{Mo}_8\text{O}_{26}^{4-}$) also exist as minor species under the vast majority of environmental conditions (Mo

concentrations < 100 μM and pH 4 – 8) (Baes and Mesmer, 1976; Kendall et al., 2016; Wasylenki et al., 2011). Under reducing conditions, MoO_4^{2-} is transformed into a series of oxothiomoledate species ($\text{MoO}_{4-x}\text{S}_x^{2-}$) (Erickson and Helz, 2000). The complete conversion of $\text{MoO}_{4-x}\text{S}_x^{2-}$ to a tetrathiomoledate (MoS_4^{2-}) anion occurs when total sulfide concentrations ($\text{H}_2\text{S} + \text{HS}^- + \text{S}^{2-}$) range between 22 μM and 125 μM , which is equivalent to when $[\text{H}_2\text{S}]_{\text{aq}} > 11 \mu\text{M}$ at typical seawater chemical conditions (Erickson and Helz, 2000). Polynuclear Mo sulfide species also exist ($\text{Mo}_2\text{S}_7^{2-}$, $\text{Mo}_4\text{S}_{15}^{6-}$, and $\text{Mo}_4\text{S}_{13}^{2-}$), though it is believed that they do not contribute significantly to the Mo geochemistry of natural systems (Helz et al., 1996). The transformation of MoO_4^{2-} into $\text{MoO}_{4-x}\text{S}_x^{2-}$ is accompanied by increased particle reactivity and subsequent removal of aqueous Mo from anoxic and euxinic environments (Helz et al., 1996). Above the H_2S “switchpoint” ($[\text{H}_2\text{S}]_{\text{aq}} > 11 \mu\text{M}$), Mo is quantitatively removed from solution as MoS_4^{2-} . However, in many natural environments, this process is kinetically-limited, and instead Mo is removed via scavenging of particle-reactive $\text{MoO}_{4-x}\text{S}_x^{2-}$ species on iron (Fe)- sulfides and organic matter or via a reduction step to Mo(IV)-sulfide compounds (Helz et al., 2011, 2004). The various removal pathways of aqueous Mo from the water column and the accompanying Mo isotope fractionation that occurs is an active area of research.

Advances in mass spectrometry have made it possible to measure the Mo isotopic composition for a variety of sample types. The Mo isotopic composition is typically reported in delta notation ($\delta^{98}\text{Mo}$), as a ratio of $^{98}\text{Mo}/^{95}\text{Mo}$ in a sample relative to that of a standard. The data in this dissertation are reported relative to

the NIST 3134 standard. Molybdenum isotopes undergo mass-dependent fractionation because chemical bonds comprised of heavier isotopes have lower zero-point energies, and are less reactive compared to chemical bonds with lighter isotopes (Anbar and Rouxel, 2007; Tossell, 2005; Urey, 1947). These isotopic distinctions lead to different reaction rates, which ultimately creates kinetic fractionation effects, or can change the equilibrium constant of a chemical reaction thereby creating an equilibrium fractionation effect.

Molybdenum isotope fractionation has been observed during many abiotic and biotic processes. The largest fractionation is observed during Mo adsorption onto Fe- and manganese (Mn)- (oxyhydr)oxides. Laboratory experiments have determined that light Mo isotopes are preferentially adsorbed onto Fe- and Mn- (oxyhydr)oxides such that the isotopic offset between the solution and the mineral surface ($\Delta^{98}\text{Mo}$) is between 0.8‰ and 2.7‰ (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011, 2008), and is best modeled as an equilibrium fractionation effect (Barling and Anbar, 2004). The range in $\Delta^{98}\text{Mo}$ is a function of the crystallinity of the mineral surface whereby amorphous, short-range-ordered (SRO) minerals such as ferrihydrite exhibit lower fractionation factors compared to crystalline minerals such as goethite and hematite (Goldberg et al., 2009). The $\Delta^{98}\text{Mo}$ also varies as a function of pH such that the fractionation factor increases as pH increases (Goldberg et al., 2009).

The ultimate mechanism that leads to fractionation is thought to be the adsorption of minor Mo species enriched in light Mo isotopes from solution (Siebert

et al., 2003; Tossell, 2005; Wasylenki et al., 2011). Heavier isotopes have lower zero-point energies and more readily stay tetrahedrally-coordinated as stable molybdate (MoO_4^{2-}) anions. Lighter Mo isotopes preferentially undergo a transformation to octahedrally-coordinated minor species that will be more particle-reactive. Wasylenki et al., (2011) concluded that isotope fractionation between Mo in solution and Mo bound to Mn- (oxyhydr)oxides resulted from the fractionation between MoO_4^{2-} in solution and subsequent adsorption of polymolybdates ($\text{Mo}_6\text{O}_{19}^{2-}$) onto a protonated surface. Fractionation of Mo isotopes also occurs in sulfidic environments. As MoO_4^{2-} forms oxothiomolybdates ($\text{MoO}_{4-x}\text{S}_x^{2-}$) there is a 1.2‰ to 1.5‰ fractionation associated with each step along the reaction scheme ($\text{MoO}_4^{2-} \rightarrow \text{MoO}_3\text{S}^{2-} \rightarrow \text{MoO}_2\text{S}_2^{2-} \rightarrow \text{MoOS}_3^{2-} \rightarrow \text{MoS}_4^{2-}$), and the ultimate fractionation factor between MoO_4^{2-} and MoS_4^{2-} is 5.4‰ (Kerl et al., 2017; Tossell, 2005).

There is some evidence that isotope fraction occurs during Mo assimilation into N_2 -fixers. The soil bacterium, *A. Vinelandii*, preferentially incorporates light Mo during uptake leading to a fractionation factor of $\sim 0.45\text{‰}$ between cells and Mo solution (Liermann et al., 2005; Wasylenki et al., 2007). Fractionation is hypothesized to arise during uptake, which involves Mo chelation onto octahedrally-coordinated metal-ligands (Bellenger et al., 2008), or during Mo adsorption onto the cell membrane (Wasylenki et al., 2007). Additionally, Mo isotope fractionation has been observed during N_2 -fixation for the cyanobacteria, *A. Variabilis* (Zerkle et al., 2011). This fractionation arises because of the relative proportion of tetrahedrally-

coordinated Mo bound to storage proteins versus octahedrally-coordinated Mo bound to enzymes. Zerkel et al., (2011) also observed different fractionation factors during different growth periods for *A. Variabilis* such that high Mo demand and exponential growth during N₂-fixation leads to the depletion of tetrahedrally-coordinated Mo bound to storage proteins, and thus a greater fractionation between cells and their growth media ($\Delta^{98}\text{Mo}$ N₂-fixation = -0.9‰ versus $\Delta^{98}\text{Mo}$ non- N₂-fixation = -0.3‰). As a result of this variability in isotope signatures, it is difficult to predict the fractionation factor in environmental systems.

1.1 Applications of the molybdenum isotope system

The Mo isotope composition of various reservoirs provides information for a suite of environmental and Earth science studies. Such applications include using the Mo isotopic composition of chondrites to reconstruct planetary evolution and the fractionation processes that may arise during core formation (Burkhardt et al., 2014; Hin et al., 2013), and using the isotopic composition of molybdenites to constrain fractionation processes that arises during magmatic differentiation (Breillat et al., 2016; Greber et al., 2014; Hannah et al., 2007). However, the most comprehensively studied facet of the Mo isotope system is the fractionation that arises as Mo accumulates in marine sediments as a function of the redox state of the depositional environment.

The Mo isotope system has been used to reconstruct paleoredox conditions based on the differences in isotopic fractionation between oxic and euxinic conditions. This paradigm exists because Mo accumulation in marine sediments can

be defined by three sinks (McManus et al., 2006). Under oxic conditions, the removal of Mo from the dissolved phase occurs due to the adsorption of Mo onto Fe- and Mn- (oxyhydr)oxides. Because light Mo isotopes are preferentially adsorbed onto these mineral surfaces, there is an isotopic offset between Mo in seawater and Mo in oxic sediments of $\sim 3\text{‰}$. In the modern ocean, this leads to a sediment $\delta^{98}\text{Mo}$ value of $\sim -1.0\text{‰}$ and a seawater value of $\sim +2.1\text{‰}$ (Barling et al., 2001; Barling and Anbar, 2004; Brucker et al., 2009; Siebert et al., 2003; Wasylenki et al., 2008). Under euxinic conditions, where H_2S has accumulated to concentrations $> 11 \mu\text{M}$, there is a quantitative conversion of MoO_4^{2-} to MoS_4^{2-} and removal from the water column (Arnold, 2004; Barling et al., 2001; Erickson and Helz, 2000; Neubert et al., 2008; Vorlicek et al., 2004). This leads to a high Mo sedimentation rate, and an isotopic signature that is unfractionated relative to seawater values ($\delta^{98}\text{Mo} = +2.1\text{‰}$). The third sink occurs when bottom waters are anoxic but have not yet accumulated enough S concentrations for MoO_4^{2-} to be quantitatively converted to MoS_4^{2-} . Under these conditions, a range of $\delta^{98}\text{Mo}$ values have been observed as a result of adsorption onto Fe-S phases and/or oxythiomolybdate formation (Brucker et al., 2009; Goldberg et al., 2012).

The oceans are well-mixed with respect to Mo because the residence time of Mo is two orders of magnitude greater (440 kyr) than the ocean mixing time (1.5 kyr) (Miller et al., 2011). This allows scientists to create an isotopic mass balance where the isotopic composition of the Mo inputs (rivers) equals the outputs (sedimentary pathways), assuming steady state. As such it is assumed that rivers

have a known $\delta^{98}\text{Mo}$ value that reflects that of the average continental crust ($\delta^{98}\text{Mo} \sim +0.1\text{‰}$ to $+0.4\text{‰}$) (Dahl et al., 2010; Kendall et al., 2011, 2010, 2009; Willbold and Elliott, 2017). Thus, by knowing the Mo isotopic composition of rivers, oxic sediments, anoxic sediments, euxinic sediments, and seawater—which would be preserved in euxinic sediments—at the time of Mo deposition, it is possible to calculate the extent of global euxinia throughout Earth history (Kendall et al., 2016). However, in recent years, several studies have demonstrated that the assumptions made to use the Mo isotope system as a tracer of paleoredox may lead to oversimplifications that skew the interpretation of the sedimentary Mo record.

1.2 Complications for the molybdenum isotope system

Using Mo isotopes as a paleoredox proxy relies on the assumption that the input of Mo is a reflection of the isotopic composition of the continental crust (Anbar, 2004; Siebert et al., 2003). Yet, the direct measurement of riverine Mo isotopic compositions indicates that they are characterized by a wide range of $\delta^{98}\text{Mo}$ values ranging from -0.4‰ to $+2.1\text{‰}$, where the most fractionated Mo relative to bedrock was found in rivers with the lowest Mo concentrations (Archer and Vance, 2008). Studies from small catchments suggest that rivers with heavy $\delta^{98}\text{Mo}$ values reflect the preferential dissolution of minerals with heavy $\delta^{98}\text{Mo}$ signatures (Neubert et al., 2011; Voegelin et al., 2012). These studies have been further explored by laboratory experiments of bulk rock leach experiments that show that incongruent weathering generates a $\delta^{98}\text{Mo}$ flux consistent with the dissolution of individual mineral phases (Liermann et al., 2011; Voegelin et al., 2012). The observed

relationship between heavy $\delta^{98}\text{Mo}$ and sulfate and sulfide concentrations also support incongruent dissolution because the heavy $\delta^{98}\text{Mo}$ signature of many sedimentary rocks likely arises from heavy seawater signatures during Mo deposition in euxinic environments (Neubert et al., 2011).

Other studies have attributed the riverine $\delta^{98}\text{Mo}$ signature to Mo fractionation that occurs during soil formation. Because the chemistry of Mo is largely driven by adsorption processes, it is probable that during weathering, isotopically light Mo could be adsorbed to soils. In fact, preliminary soil Mo data exhibit isotopic offsets relative to the parent material from which they are derived (Siebert et al., 2015). These soils are both lighter and heavier than bedrock values, suggesting that adsorption of Mo to soils leads to significant fractionation. Because the rates of chemical weathering have changed over time it is important to quantify the mechanisms in the terrestrial environment to constrain the riverine flux and isotopic composition.

1.3 Molybdenum in the terrestrial environment

The ultimate source of Mo to low-temperature geochemical systems comes from the chemical weathering of minerals. In addition to the mineral molybdenite (MoS_2), Mo can be substituted into the crystal lattice of feldspars, biotite, pyroxenes, magnetite, volcanic glasses, and minerals containing titanium (Ti) and aluminum (Al) during primary mineral formation (Arnórsson and Óskarsson, 2007; Greaney et al., 2016; Gupta, 1997). The Mo isotopic composition ($\delta^{98}\text{Mo}$) of the average continental crust is between 0.0‰ to +0.4‰ (Willbold and Elliott, 2017),

though molybdenites, shales, and individual minerals have a much wider range (-1.7‰ to +2.3‰ (Breillat et al., 2016; Neubert et al., 2011).

Once liberated from primary minerals, Mo geochemistry is dominated by adsorption processes onto Fe- and Mn- (oxyhydr)oxides, clays, organic matter, and carbonates (Goldberg et al., 1996). At low pH, Mo is strongly adsorbed onto Fe- and Mn- (oxyhydr)oxides, particularly SRO phases such as ferrihydrite (Brinza et al., 2008), and maximum Mo adsorption occurs at $\text{pH} < 5$ (Goldberg et al., 1996). At higher pH, Mo enters the soil solution as the highly soluble MoO_4^{2-} oxyanion. Molybdenum desorption at high pH has been understood in the agricultural community as studies show that liming (calcium carbonate applications) increase Mo bioavailability (Gupta, 1997). Theoretically, reducing conditions, which lead to the dissolution of Fe- and Mn- (oxyhydr)oxides are often accompanied by an increase in pH associated with the release of OH^- ions, which can release Mo into the soil solution. Oxidizing conditions, on the other hand, lead to the precipitation of Fe- and Mn- (oxyhydr)oxides and are often accompanied by a decrease in pH associated with the hydrolysis, and thus can promote Mo adsorption. Organic substances also have a high affinity for Mo (Marks et al., 2015). A number of studies have determined that the adsorption of Mo onto organic matter can prevent Mo from leaching out of soils, and thus potentially increase Mo bioavailability (Bibak and Borggaard, 1994; Wichard et al., 2009). The adsorption of Mo onto organic matter has also been shown to be pH dependent, with decreasing Mo adsorption as the pH increases up

to 9 (Wichard et al., 2009). These conclusions suggest that soil Mo may be affected by both organic matter cycling and redox dynamics.

At the outset of this dissertation, very little was known about the isotopic composition of Mo in soils. Because adsorption processes in marine environments were known to drive isotope fractionation, it was hypothesized that fractionation during adsorption in soils would lead to similar patterns of fractionation (Archer and Vance, 2008). Voegelin et al., (2012) measured the Mo isotopic composition of a single sample of surface soil and roots from a single location and observed light Mo isotopes relative to bedrock. Complementary to this dissertation, Siebert et al., (2015) measured Mo isotope signatures in soils, hypothesizing about the influence of redox conditions, organic matter, and atmospheric inputs. They concluded that Mo isotope fractionation does indeed exist in terrestrial environments, and that multiple mechanisms likely fractionate Mo. Siebert et al., (2015) also highlighted areas where future Mo studies should focus, including the fractionation of Mo associated with adsorption of organic matter, quantifying the flux and isotopic composition of the different pools of Mo required to reconcile Mo accumulation in surface soils, and determining how well Mo isotopes record the redox history of a soil profile. Ultimately, understanding these additional mechanisms could help constrain how the Mo isotopic composition of rivers has changed over time.

1.4 Research strategies

The goal of this dissertation is to determine the mechanisms that fractionate Mo prior to delivery to the oceans. In doing so, I will help constrain how terrestrial

Mo fluctuations may have changed throughout Earth's history, and I will also determine the utility of the Mo isotope system in soils. My research is broken up into five discrete sections, each of which focuses on how Mo dynamics are affected by processes that drive chemical weathering and soil formation. Three of the five manuscript chapters (Chapters 2, 3, and 6) of my dissertation are focused on the Hawaii Age-Climate Matrix. Hawaii is a model ecosystem for studying the biogeochemical cycling of Mo because soil forming factors (relief, lithology, vegetation) can be kept constant while the effects of climate and age are determined (Chadwick et al., 1999; Vitousek, 2004a). Chapter 4 establishes the effect of organic matter on Mo isotope dynamics in the Oregon Coast Range, where vegetation type and lithology is well-constrained, and Chapter 5 uses a lithological gradient in the Luquillo Critical Zone Observatory to understand the effect of lithology on both Mo and trace metal dynamics in general.

The first step towards understanding Mo behavior in terrestrial systems is to determine where Mo is stored within a soil profile and the factors that drive Mo mobilization. To do this, Chapter 2 focuses Mo dynamics along the Maui Climate Gradient, a rainfall transect where soils become anoxic as precipitation increases (Miller et al., 2001; Schuur et al., 2001; Thompson et al., 2011). Extractions were performed to determine Mo concentrations within three pools: SRO Fe-(oxyhydr)oxides, organic matter, and residual soil. Next, soils were exposed to artificial reducing conditions to determine the flux of Mo from the soil solid during redox fluctuations. From this study, I concluded that higher concentrations of Mo

are mobilized in soils exposed to fluctuating redox conditions, but that organic matter drives long-term retention of Mo relative to SRO Fe- (oxyhydroxides). I also observed that increasing Mo concentrations aligned well with increasing rainfall, such that atmospheric inputs may be a significant source of Mo to the terrestrial environment.

Chapter 3 builds upon the results of Chapter 2 and traces Mo dynamics from a climate gradient along the Kona Coast on the main island of Hawaii, where soils are younger than the Maui Climate Gradient and undergoing initial stages of chemical weathering (Porder et al., 2007; Porder and Chadwick, 2009). The motivation behind choosing to focus on the Kona Climate Gradient was to capture Mo dynamics in soils where primary mineral dissolution, secondary mineral formation, and organic matter accumulation were all actively occurring. In this study, I measured both the accumulation of Mo and the Mo isotopic composition for a suite of seven soil profiles and constrained additional inputs of Mo to the soil system to create an isotopic mass balance. I observed Mo fractionation processes occurring in soils that led to the retention of light Mo and the leaching loss of heavy Mo. However, Mo fractionation patterns were modulated by the addition of isotopically-heavy atmospheric inputs in such a way that the driest sites exhibited the greatest Mo fractionation relative to bedrock and the wettest sites exhibited the smallest Mo fractionation relative to bedrock. Selective chemical extractions performed on these soils is consistent with results from Chapter 2 and previous

literature (Marks et al., 2015; Wichard et al., 2009) in which Mo adsorption onto organic matter drives Mo retention.

Chapters 4 and 5 focus on the mechanisms of fractionation as a function of organic matter and redox cycling. Laboratory experiments in Chapter 4 constrain the magnitude and direction of Mo isotope fractionation during adsorption onto organic matter, a previously unknown source of isotope fractionation, as a function of both time and pH. These results were then used to evaluate Mo isotope patterns in precipitation, foliage, organic horizon, surface mineral soil, and bedrock from 12 forested sites in the Oregon Coast Range. Molybdenum adsorbed onto organic matter is lighter than both mineral soil and foliage. The source of the Mo adsorbing onto organic matter is likely atmospheric, and fractionation patterns between organic matter and marine-derived precipitation are consistent with laboratory experiments. These results determine that Mo adsorption onto organic matter generates fractionation patterns comparable to Mo adsorption on Fe- and Mn-(oxyhydr)oxides (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011), potentially complicating the interpretation of the Mo sedimentary record. In Chapter 5, I focus on the redox dynamics of the Mo isotope system to determine whether Mo can be used to understand the integrated redox history of a soil. I compare the Mo isotope composition of colloids, aqueous Mo, and the soil solid for two contrasting lithologies exposed to a series of redox fluctuations. Ultimately, the Mo isotopic composition of the colloids and the aqueous phase were not adequate

predictors of the redox history of the soils, suggesting that additional fractionation mechanisms must be constrained to understand the redox behavior of Mo.

Finally, in Chapter 6, I use water samples from Hawaii and the United States network of Critical Zone Observatories (CZOs) to understand the effect that terrestrial Mo cycling has on the Mo signature of rivers and groundwater. In small catchments, the Mo isotopic composition of river water is highly variable, resulting from terrestrial fractionation processes included adsorption of Mo onto SRO Fe-(oxyhydr)oxides and organic matter, redox-mediated dissolution events, inputs from atmospheric sources, or mineral dissolution. However, this signal is suppressed by the input of groundwater Mo to rivers, which is less fractionated relative to bedrock and present at higher concentrations. Results from this study suggest that the range of Mo isotopic compositions throughout Earth's history may be constrained to a narrow range close to crustal values.

**Chapter 2: Towards understanding temporal and spatial patterns of molybdenum
in the critical zone**

Elizabeth King, Aaron Thompson, Caitlin Hodges, and Julie Pett-Ridge

ABSTRACT

Molybdenum (Mo) is a redox-sensitive trace metal that has been used to reconstruct reduction-oxidation (redox) conditions in marine sediments, and could potentially be used similarly in soils. Sedimentary Mo ultimately comes from the terrestrial weathering of bedrock during soil development (pedogenesis), but the mechanisms controlling Mo loss and mobility in soils are not well known. Here we present Mo concentration data from bulk soils and specific soil pools across two climatic gradients on the Hawaiian Islands, the Maui Climate Gradient (MCG) and the Kona Climate Gradient (KCG). The MCG is a well-established precipitation gradient that exhibits a decrease in soil redox potential (Eh) and iron (Fe) content and an increase in organic matter content with increasing rainfall. We expected to find lower Mo concentrations and lower Mo mobilization, as determined via a weakly acidic extraction, in highly reducing (greater rainfall) soils as a result of Fe reduction and near complete loss of Fe- (oxyhydr)oxides. However, we observe increasing Mo mobilization at higher rainfall sites, coinciding with a loss of Fe- (oxyhydr)oxides by reductive dissolution and the accumulation of soil organic matter, suggesting a shift from Fe- (oxyhydr)oxide control of Mo at low rainfall sites to predominately organic matter-control of Mo at high rainfall sites. Selective chemical extractions indicate that Mo concentrations are two orders of magnitude higher in the organic matter pool versus the short-range-ordered (SRO) Fe- (oxyhydr)oxide pool, corroborating the importance of Mo-organic matter interactions on overall soil Mo pools. We also find evidence for increasing Mo

retention in wetter soils along the KCG, which may be a result of increasing organic matter and Fe- (oxyhydr)oxide content. An alternate explanation is that higher rainfall contributes sufficiently greater marine-derived atmospheric input of Mo. The fact that there are consistent patterns with rainfall on both climate gradients illustrate the potential for Mo as a tracer of pedogenic and redox processes in soils and highlight the importance of constraining controls on Mo fluxes.

2.1 Introduction

Molybdenum (Mo) is a biologically, geochemically, and isotopically unique element that has the potential to be a powerful tracer of pedogenic processes. Biologically, Mo is an essential micronutrient because it is a co-factor for the nitrogenase and nitrogen reductase enzymes (Anbar, 2004). Geochemically and isotopically, Mo isotope signatures have been used to recreate paleoredox conditions preserved in marine sediments (Czaja et al., 2012; Kendall et al., 2011; Wille et al., 2007). In oxic sediments, light Mo isotopes preferentially absorb onto Fe- and manganese (Mn)- (oxyhydr)oxides, leaving oceans residually enriched in heavy Mo. As sediments become suboxic, the reductive dissolution of Fe- and Mn- (oxyhydr)oxides leads to the release of Mo into solution until sediments become euxinic and Mo re-precipitates as a thiomolybdate (MoS_4^{2-}) species (Anbar and Rouxel, 2007). The basis behind using Mo as a redox tracer is the observation that the abundance and isotopic signature of Mo in sediments should reflect the redox state of the environment.

To realize the full potential of this redox proxy, we must understand the behaviour of Mo in terrestrial environments. As bedrock weathers, Mo stored in the lithosphere enters soils where it is cycled through the environment via adsorptive and desorptive processes, and biological cycling, until it is eventually leached into rivers and the ocean. Dissolved Mo in rivers is isotopically heavy compared to bedrock (Archer and Vance, 2008). This may reflect the preferential absorption of light Mo isotopes onto Fe- or Mn- (oxyhydr)oxides in soils, incongruent dissolution of a heavy Mo bedrock source (trace sulphides), or another previously unconstrained pedogenic process that fractionates Mo (Archer and Vance, 2008; Neubert et al., 2011; Voegelin et al., 2012).

In order to understand the processes that fractionate terrestrial Mo, it is necessary to identify the soil solid phases hosting Mo, how Mo in each solid phase becomes mobilized, and how different solid phases react to changing redox conditions. We characterized the distribution of Mo among soil phases using selective chemical extractions targeted at the short-range-ordered (SRO) mineral pool—associated with Fe- and Mn- (oxyhydr)oxides—and the oxidizable pool—associated with organic matter—across a previously well-characterized soil redox gradient. We also quantified the leachable soil Mo pool and compared that to Mo mobilization following an artificial reduction experiment across the same soil gradient. The leachable soil pool is operationally defined as the Mo that would be mobilized in an acidic solution similar to soil pore water at these sites (pH 3.5) (Schuur and Matson, 2001). Finally, we paired this with an analysis of bulk soil Mo

loss or gain across a younger soil climosequence to gain insight into controls on soil Mo behaviour as a function of both age and climate.

2.2 Methods

The Hawaiian Islands are well suited for studying soil evolution because the state factors that drive soil formation (lithology, vegetation, climate, slope, and soil age) can be constrained (Chadwick et al., 1999). For this study, we focused on basalt-derived soils collected from two well-characterized climate gradients on the Hawaiian Islands. The Maui climate gradient (MCG) is a suite of 6 sites across a gradient of mean annual precipitation (MAP) that ranges from 2,020 – 5,050 mm yr⁻¹ on 410 thousand-year old (kyr) basalt at an elevation of 1370 m, and mean annual temperature of 16°C. Across the MCG, the reduction potential (Eh), and carbon (C) and Fe content are well correlated (Figure 2.1) (Miller et al., 2001; Schuur and Matson, 2001; Thompson et al., 2011, 2007). We selected four sites along the MCG at 2,200, 2,750, 3,350 and 4,050 mm MAP. A pit was dug at each site and two sets of soil samples (~ 8 g each) were collected from three depths (0 – 20 cm, 20 – 40 cm, 40 – 60 cm) at each site. These depths were chosen based on the visibility of redoximorphic features in order to capture the heterogeneity of redox conditions in tropical soils (Liptzin et al., 2011). One set was immediately extracted in a 1:5 (soil:solution) slurry in weakly acidic (pH 3.5) HCl to match the typical pH of pore water (Schuur and Matson, 2001). These acidified samples were shaken for 2 hours, centrifuged, and filtered through a 0.22 µm filter. The other set of samples were placed in vacutainers, flushed with N₂ gas, and left in the field for 48 hours to

simulate Fe- (oxyhydr)oxide reduction under *in situ* temperature conditions following a modification of methods outlined in Hall and Silver (2013). Following the 48-hour incubation, the soils were extracted in an identical manner to the first set. Bulk soil samples were also collected at each site in 1.75 mil polyethylene bags and stored in coolers until they were brought to the lab. Each horizon was subsequently homogenized and stored at 4°C before subjected to sequential extractions.

To test whether Mo was associated with Fe- (oxyhydr)oxides or organic matter, we performed a series of sequential chemical extractions on bulk soil. We targeted Mo associated with reducible, SRO mineral phases, and oxidizable, organic matter phases. Field moist samples from the surface depths of each site were subject to a 24-hour 0.5 M HCl extraction to target Mo bound to SRO Fe oxides as outlined in Wiederhold et al. (2007a). Between the reducible and oxidizable extractions, 20 mL of milli-Q water was added to the slurry, centrifuged, and decanted into the 0.5 M HCl extraction solutions. Next, soils underwent a H₂O₂ extraction to target oxidizable organic matter. All samples were filtered, evaporated, dissolved in 3% nitric acid (HNO₃), and analysed using Thermo X-Series II inductively coupled plasma mass spectrometer (ICP-MS).

Soil samples from a younger (10 kyr) soil climate gradient on the Kona coast of Hawaii (660 – 2,100 mm yr⁻¹ MAP) were also analyzed for Mo concentrations as well as other trace elements including Nb using ICP-MS. Concentrations were measured on the < 2 mm sieved fraction of the soil. Soil was microwave digested

(Anton Paar Multiwave 3000) in a $\text{HNO}_3\text{:HCl:HF}$ (1:3:1) solution. Tau (τ) calculations for the Kona soil climate sequence were calculated as:

$$\tau_{e,w} = \left\{ \left[\left(\frac{C_{e,s}}{C_{e,p}} \times \frac{C_{i,p}}{C_{i,s}} \right) - 1 \right] \times ff \right\} \times 100$$

where C is the profile weighted concentration of an element, and the subscript s , p , e , and i refer to the soil, parent material, element in question, and immobile element, respectively. The most immobile element for Hawaiian soils is niobium (Nb) (Kurtz et al., 2000). The ff variable refers to the fine earth fraction, or proportion of the total soil that was < 2 mm, which is used to convert the mass loss or gain that has occurred in the < 2 mm fraction of the soil to mass loss or gain on the basis of the total bulk soil (including gravel) (Porder et al., 2007). Parent material for these samples refers to the bedrock directly underneath the soil profile. Tau calculations are measurements of elemental loss from a soil profile, whereby a τ Mo value of -100% implies that soil profile has lost all of what was originally present in the parent material. Tau calculations were not performed on the MCG given uncertainty regarding the Mo/Nb ratio of known dust inputs that impact the older Maui soils.

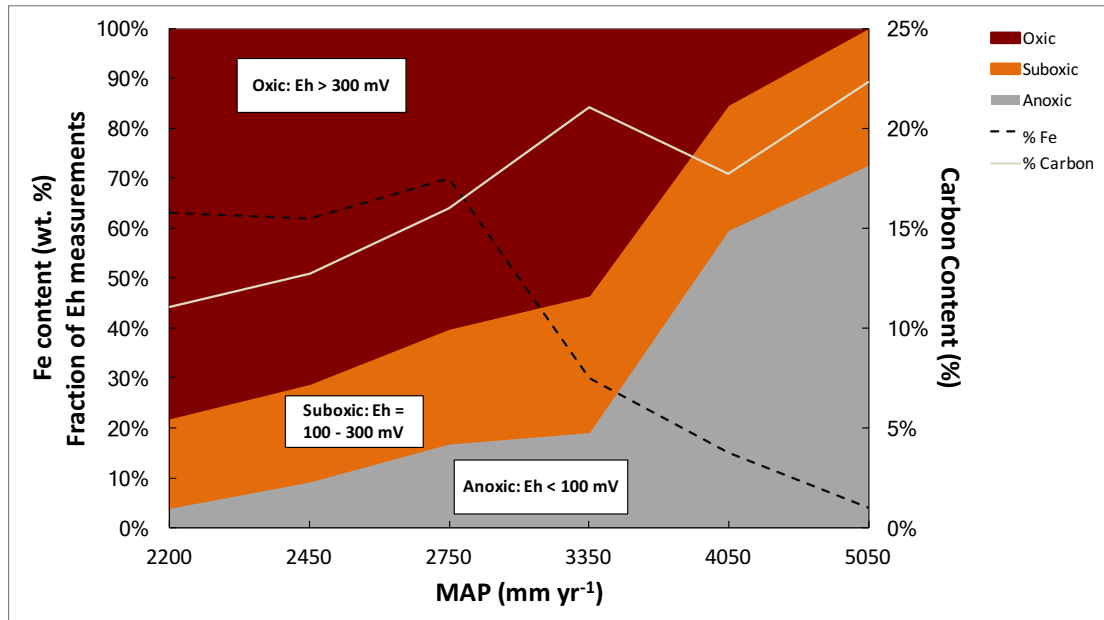


Figure 2.1: Fe content (wt. %), carbon content (%), and redox state (Eh) as a function of precipitation (MAP) cross the Maui Climate Gradient.

Eh, % Fe (dotted line), and % Carbon (solid line) across the MCG adapted from Miller et al., (2001) and Thompson et al., (2011). The shading corresponds to oxic soils (Eh > 300), suboxic soils (Eh 100-300), and anoxic soils (Eh < 100) and the duration (annual percentage) that each site was subject to those conditions (Schnuur et al., 2001).

2.3 Results and Discussion

2.3.1 *MCG soil extractions*

Bulk soil Mo concentrations decreased with increasing precipitation from an average of $9.61 \mu\text{g g}^{-1}$ at the driest site (Site 1, MAP = $2,200 \text{ mm yr}^{-1}$) to $0.28 \mu\text{g g}^{-1}$ at the wettest site (Site 5, MAP = 4050 mm yr^{-1}) (Table 2.1). On average, leachable Mo increased with increasing rainfall across the MCG from 0.36 ng g^{-1} at the driest site to 1.54 ng g^{-1} at the wettest site. Following anoxic incubation, leachable Mo exhibited similar trends, whereby Mo concentrations increased from 0.96 ng g^{-1} at the driest site to 3.38 ng g^{-1} at the wettest site (Figure 2.2a). When the leachable Mo extractions were broken down by depth surface (0 – 20 cm), shallow subsurface (20 – 40 cm), and deep subsurface (40 – 60 cm), the wetter sites had the most leachable Mo in the surface and shallow subsurface while the drier sites have low leachable Mo overall, but the greatest Mo release was observed following the artificial reduction experiment in the deep subsurface (Figure 2.2b-d). Since we chose our sampling depths based on the visibility of redoximorphic features, the variability at each sample point is a testament to the heterogeneity of redox processes in tropical soils (Hall et al., 2016, 2013; Liptzin et al., 2011), and this dataset highlights the range of Mo mobility within a complex soil profile (Figure 2.2).

Table 2.1: Maui Climate Gradient site chemistry

Site	Depth cm	Bulk Soil Fe ^a wt. %	Bulk Soil C ^a %	Bulk Soil Mo ^b μg g ⁻¹	Field Conditions	Artificial Reduction
					Mo ng g ⁻¹	Mo ng g ⁻¹
1	7-19	14.4	21.8	9.61	0.55	0.56
1	19-39	21.6	22.7	12.44	0.20	0.78
1	39-60	22.5	21.1	n.a.	0.32	1.52
3	18-20	11.5	23.5	5.38	1.11	1.02
3	20-29	22.0	21.0	8.42	0.17	1.01
3	29-60	2.5	26.3	9.84	0.91	4.29
4	6-12	1.3	55.5	1.81	1.68	2.25
4	12-32	3.2	23.1	10.83	0.03	2.39
4	32-60	1.1	24.4	10.16	0.57	2.62
5	20	0.1	75.1	0.28	4.07	6.33
5	20-35	9.9	39.9	1.99	0.01	3.23
5	35-50	9.2	23.1	5.62	0.55	0.59

^aScribner et al., (2006)^bSubsurface Mo concentrations from Siebert et al., (2015)

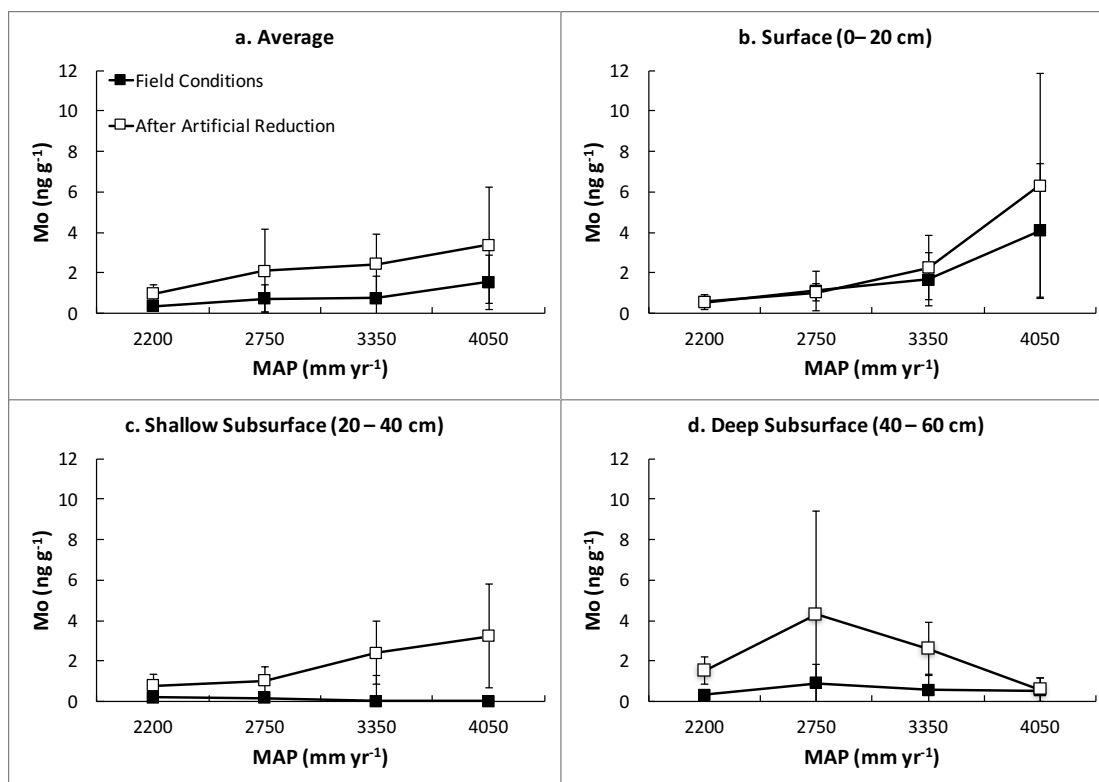


Figure 2.2: Mo behavior before and after an artificial redox experiment as a function of MAP.

Mo concentrations (ng Mo g⁻¹ soil) in a leachable extraction (pH ~ 3.5) averaged over soil profile (a) and then divided into surface soils (0 – 20 cm) (b), shallow subsurface soils (20 – 35 cm), and deep subsurface soils (35 – 60 cm). Closed squares indicate extractions collected in field conditions and open squares indicate extractions collected after a 48-hour artificial reduction experiment. Error bars indicate standard deviation between triplicate analyses at each depth.

The dominant control of Mo mobility in soils are considered to be adsorption onto Fe- and Mn- (oxyhydr)oxides and organic matter (Wichard et al., 2009). In our study, Mo concentrations in the leachable soil extractions increased with increasing rainfall along the MCG, despite lower concentrations of bulk soil Mo (Table 2.1, Figure 2.2a). This may reflect Mo associated with organic matter, which is more abundant in wet soils due to slower decomposition (Schuur, 2001). Alternatively, increases in leachable Mo with increasing rainfall may reflect a shift in the crystallinity of Fe- (oxyhydr)oxides. Both the overall abundance and degree of crystallinity of Fe-oxyhydroxides decrease with increasing rainfall along the MCG (Thompson et al., 2011), such that SRO Fe- (oxyhydr)oxides dominate the Fe pool in wetter sites. The fluctuating redox conditions experienced by SRO Fe-oxyhydroxides in wetter MCG soils provide dynamic and transient surface area for Mo adsorption, and this Mo may be especially susceptible to mobilization when exposed to weak acid leaching and short-term reducing conditions.

We used selective chemical extractions to help determine the specific soil phases hosting Mo in the MCG soils. In the reducible, SRO Fe- (oxyhydr)oxide targeted 0.5 M HCl extraction, Mo concentrations increased from 2.6 ng g⁻¹ at the driest site to 6.0 ng g⁻¹ at site 4 (the second wettest site) followed by a sharp decrease to 2.0 ng g⁻¹ at the wettest site (Figure 2.3). Mo concentrations in the H₂O₂ oxidizable extraction were two orders of magnitude larger than the SRO mineral phase pool and increased from 124.6 ng g⁻¹ at the driest site to 625.1 ng g⁻¹ at the wettest site (Figure 2.3). These results are in agreement with a recent X-ray

spectroscopy study finding strong organic matter control of Mo storage in soils (Wichard et al., 2009). Comparing our *in situ* leachable extraction with laboratory sequential extractions, it seems that Fe- (oxyhydr)oxide reductive dissolution is the main driver of short-term Mo mobility. In drier sites, the reductive dissolution of more crystalline Fe phases may not release as much Mo because there is either less surface area for Mo to adsorb to or the timescale of our artificial reduction event did not capture a full dissolution episode for these highly-ordered minerals. The data from the drier sites supports this since the most Mo is leached from the deep subsurface soil horizons, where Fe- (oxyhydr)oxide content is greatest (Table 2.1, Figure 2.2c-d). Alternatively, at wetter sites, the persistence of highly disordered SRO Fe minerals may lead to mineral-organic matter complexes in surface soils with high surface area for Mo adsorption (Thompson et al., 2011), which is why the greatest leachable Mo is collected in the surface and shallow subsurface of the wetter sites (Figure 2.2b-c). This Mo pool would be more mobile on shorter timescales, or easily reduced during high rainfall events (Thompson et al., 2011), leading to the mobilization of more Mo compared to drier sites. Nevertheless, in all the soils we analyzed, organic matter represents a larger Mo pool, and thus changes in organic matter abundance in soil over time will therefore play an important role in soil Mo mobility.

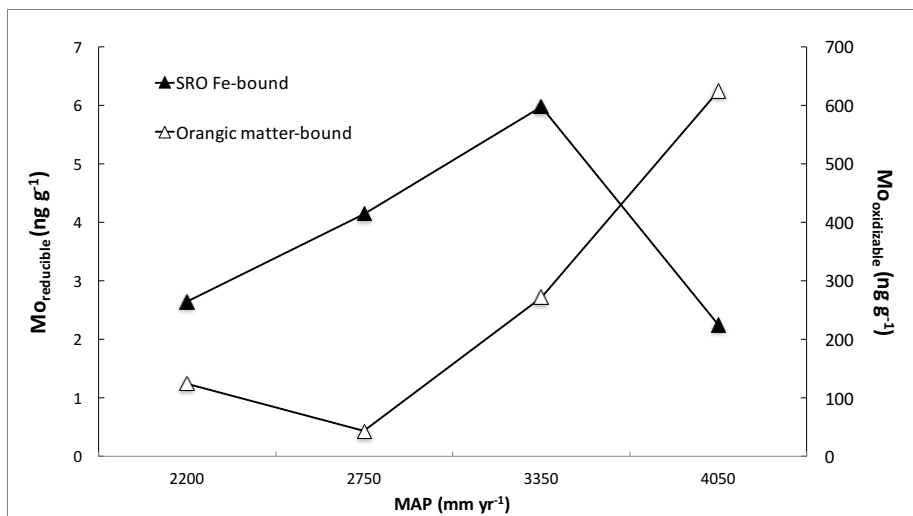


Figure 2.3: Mo content in a reducible (SRO mineral) and an oxidizable (organic) pool Mo concentrations (ng Mo g⁻¹ soil) in a 0.5 M HCl extraction (left axis, 0-7 ng g⁻¹) and a H₂O₂ oxidizable extraction (right axis, 0-700 ng g⁻¹). Closed triangles indicate the SRO-mineral pool and open triangles indicate the oxidizable pool. Note the oxidizable pool (right axis) is two orders of magnitude larger than the SRO-mineral pool.

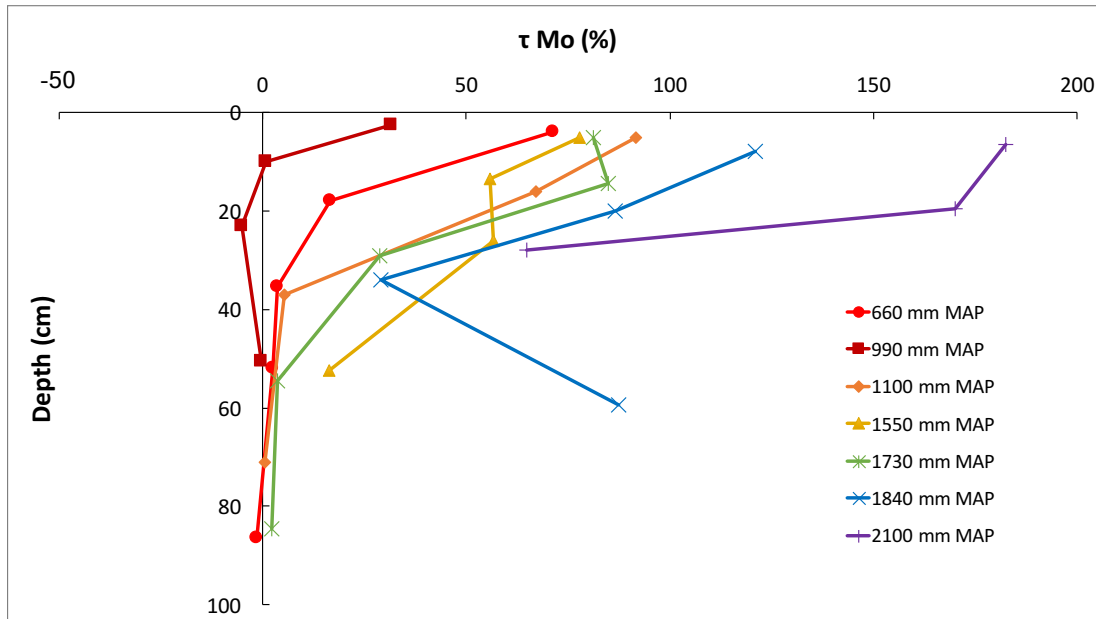


Figure 2.4: Tau Mo values along the Kona climate sequence. A negative tau value indicates Mo loss and a positive tau values indicates Mo enrichment.

2.3.2 Kona soil climate sequence

Mo mobility based on τ Mo calculations from the 10 kyr Kona soil climate sequence reflects percent loss (negative values) or percent gain (positive values) of Mo with respect to the underlying parent material (Figure 2.4). The driest sites show a Mo gain of +71% at the surface while the wettest sites show a Mo gain of +182% at the surface (Figure 2.4). At depth, τ Mo values for every profile approach 0% indicating no net loss or gain. Mo leaching losses are expected at the KCG, reflecting rapid weathering of volcanic glass (Porder et al., 2007) and subsequent leaching of MoO_4^{2-} . At the Kona sites, organic matter (% C) increases with increasing rainfall but there is also an increase in SRO minerals along the KCG based on oxalate-extractable Fe and Al (NCSS, 2015). This is likely a result of enhanced weathering at higher rainfall sites (Chorover et al., 2004). Much like Mo patterns on the MCG, enrichment of Mo in wetter sites on the KCG may be a result of increased Mo-SRO-organic matter interactions retaining Mo in the soil. Because the KCG is younger than the MCG, there may not have been sufficient formation of SRO minerals in the drier sites leading to a lower sorption capacity of Mo onto surface soils.

One hypothesis for the ultimate source of soil Mo is that there is a marine-derived atmospheric input of Mo. Preliminary results from the Oregon Coast Range (Marks et al., 2015) show enriched levels of Mo in rainwater ($2.3 - 9.8 \text{ pg g}^{-1}$). Mo in rainwater is presumably marine-derived in the Oregon Coast Range as there are few known atmospheric anthropogenic sources of Mo to this region. Since the Hawaiian Islands are also relatively undisturbed, marine-derived Mo from this region may be

similar. In that case, assuming an average concentration of 5.9 pg g^{-1} , the Mo precipitation flux across the KCG soils varies from $3.7 \text{ g km}^{-2} \text{ yr}^{-1}$ at the driest site (660 mm yr^{-1}) to $14.0 \text{ g km}^{-2} \text{ yr}^{-1}$ at the wettest site (2100 mm yr^{-1}). The bulk soil pool for these sites range from 350 kg km^{-2} at the driest site to 769 kg km^{-2} at the wettest site. Thus, over the 10 kyr age of the Kona samples, the precipitation flux of Mo could contribute 10 – 20% of the bulk soil pool and account for enrichment over basalt Mo concentrations.

2.4 Conclusion

The combination of bulk soil and specific soil pool Mo abundances is an informative tool for identifying and quantifying the different pedogenic processes that contribute to chemical weathering. Mo concentration data from chemical extractions constrains what soil pools are active during different environmental conditions such as redox. Our results from the MCG soils indicate that Fe reduction drives short-term Mo mobility, but organic matter hosts a much larger fraction of the soil Mo reservoir. On the younger KCG soils, we find significant loss of Mo occurs in early stages of weathering on drier soils (660 mm yr^{-1} mean annual precipitation), but that losses are minimal and even gains are apparent in wetter soils (up to 2100 mm yr^{-1} mean annual precipitation). An additional Mo input from marine-derived precipitation may also contribute to Mo bulk soil concentrations at higher rainfall. This study is the first of its kind to examine Mo availability across both a soil rainfall and soil age gradient. The patterns in Mo concentrations illustrate the potential of

this tracer for recording weathering fluxes, secondary Fe mineral dynamics, and biologic activity in soils.

2.5 Acknowledgements

This research was supported by NSF EAR-1053406 to Aaron Thompson and Julie Pett-Ridge and by the ARCS Scholar Award (Portland Chapter) to Elizabeth King. We thank Oliver Chadwick for sharing the Kona Climate Gradient samples and Heraldo Farrington for field assistance.

**Chapter 3: Molybdenum sources and isotopic composition during early stages of
pedogenesis along a basaltic climate gradient**

Elizabeth King, Aaron Thompson, Oliver Chadwick, and Julie Pett-Ridge

ABSTRACT

Molybdenum (Mo) is an essential micronutrient and redox sensitive trace metal that has the potential to be a tracer of pedogenic processes. Globally, riverine $\delta^{98}\text{Mo}$ values (based on $^{98}\text{Mo}/^{95}\text{Mo}$ relative to NIST SRM 3134) are heavy relative to bedrock, suggesting that soils may retain light Mo isotopes, however, the mechanisms governing the sources and fates of Mo in soils are poorly understood. We investigated soil Mo abundance and isotopic composition as a function of climate along a well-constrained climosequence on a 10 kyr lava flow in Hawaii receiving 660 to 2,100 mm yr⁻¹ mean annual precipitation (MAP). We assessed Mo abundance and isotopic composition as a function of soil organic matter (OM) content, short-ranged-ordered (SRO) iron (Fe) (oxyhydr)oxide abundance, and Mo loss/gain. We find net accumulation of Mo across all soils (up to +139% gain) that is positively correlated with increasing MAP. The highest Mo gains are in surface soil horizons, and are correlated with high OM content. The isotopic composition of soil Mo deviates from underlying basaltic bedrock, which ranges from $\delta^{98}\text{Mo}$ values of -0.11‰ to -0.26‰. Soil Mo isotopic values are lightest at the dry sites ($\delta^{98}\text{Mo}$ = -0.63‰) and become heavier with increasing precipitation (up to $\delta^{98}\text{Mo}$ = +0.03‰). Samples with the heaviest $\delta^{98}\text{Mo}$ values are from horizons with the largest net gains of Mo relative to bedrock, which also have higher OM content. In order to further constrain Mo fluxes into and out of the soil system, we measured Mo isotope ratios in local rainwater (average $\delta^{98}\text{Mo}$ = +1.11‰), groundwater (average $\delta^{98}\text{Mo}$ = +0.14‰), and vegetation ($\delta^{98}\text{Mo}$ values between -0.18‰ and +0.64‰). We propose

that Mo in these soils is substantially augmented by additions from precipitation, volcanic fog, and potentially anthropogenic inputs of Mo, and that retention of these inputs within soils is likely related to interactions with soil OM. The large atmospheric Mo input strongly modulates the $\delta^{98}\text{Mo}$ values of dissolved Mo fluxes from soil to values only slightly heavier than bedrock. These patterns illustrate the potential for Mo as a tracer of atmospheric inputs and pedogenic processes in soils and help elucidate the mechanisms that drive heavy $\delta^{98}\text{Mo}$ values in the global riverine Mo flux.

3.1 Introduction

The molybdenum (Mo) isotope system has the potential to trace soil processes including redox fluctuations, soil organic matter cycling, and atmospheric inputs. Mo incorporated into primary minerals in bedrock enters soil pore waters via chemical weathering. Once released, Mo is susceptible to leaching from soils, typically as the soluble oxyanion molybdate (MoO_4^{2-}) (Arnórsson and Óskarsson, 2007; Gupta, 1997). However, Mo may be retained in soils by adsorption onto soil organic matter (OM) and iron (Fe) (oxyhydr)oxides (Kabata-Pendias, 2010; King et al., 2014; Marks et al., 2015; Siebert et al., 2015). The mobility and speciation of Mo are particularly sensitive to redox conditions, as Mo is stable in multiple oxidation states (+III to +VI) over a relatively small range of reduction potentials (Anbar, 2004). Additionally, Mo has important biological roles as an essential micronutrient, and may limit N_2 fixation in some terrestrial ecosystems (Barron et al., 2008; Bellenger et al., 2014; Jean et al., 2013; Silvester, 1989; Wurzbürger et al., 2012). Each of these

soil processes and their accompanying changes in oxidation state and/or speciation has the potential to induce Mo isotopic fractionation. Mo isotopes may therefore provide records of pedogenic conditions and insight into how soils function.

The global riverine isotopic signature of dissolved Mo spans a wide range of positive $\delta^{98}\text{Mo}$ values (+0.15‰ to +2.40‰, reflecting differences in $^{98}\text{Mo}/^{95}\text{Mo}$ ratios, reported relative to NIST SRM 3134), with a discharge-weighted mean $\delta^{98}\text{Mo}$ of +0.5‰ (Archer and Vance, 2008). In contrast, $\delta^{98}\text{Mo}$ values for igneous rocks range from -0.3‰ to +0.4‰ (Pearce et al., 2009; Siebert et al., 2015; Voegelin et al., 2012). Thus, some mechanism—operating during chemical weathering or riverine transport of dissolved and particulate Mo—generates dissolved Mo with heavier isotopic values than the presumed source material (Liermann et al., 2011; Neubert et al., 2011; Pearce et al., 2010; Wang et al., 2015). Limited available soil Mo isotope data span both lighter and heavier than underlying bedrock (Siebert et al., 2015; Voegelin et al., 2012), suggesting that multiple mechanisms may control Mo isotope fractionation in soil.

The dynamics of the Mo isotopic system was first used in studies of marine sediments with the goal of reconstructing paleoredox environments (Barling and Anbar, 2004; Siebert et al., 2003). Under oxic conditions in marine sediments, the isotopic fractionation of Mo is driven by the adsorption of Mo onto iron (Fe)- and manganese (Mn)- (oxyhydr)oxides, which preferentially scavenge light Mo ($\delta^{98}\text{Mo} \sim -0.7\text{‰}$). Under euxinic conditions—anoxic conditions where hydrogen sulfide (H_2S) is present—Mo is hypothesized to be nearly quantitatively removed from solution as

Mo-S thiomolybdate complexes, and sediments reflect the isotopic composition of the bulk solution (Barling et al., 2001; Dahl et al., 2010, 2008; Neubert et al., 2008). Ocean paleoredox studies have relied on the assumption that the riverine input of Mo, the largest source of Mo to the marine environment, has remained constant and reflects the isotopic composition of continental rocks (Anbar and Rouxel, 2007; Barling et al., 2001; Siebert et al., 2003), yet this has not been supported by global river Mo isotopic compositions (Archer and Vance, 2008). Thus, characterizing the influence of terrestrial processes on Mo isotopic fractionation has the potential to improve the interpretation of Mo isotope records used in marine anoxia studies.

Another source of uncertainty in Mo dynamics is the role of atmospheric transport, which has long been recognized as a source of trace metals into both the marine and terrestrial environments (Duce and Tindale, 1991; Nicholson et al., 2003), and has specifically been observed in remote locations such as Hawaii (Monastera et al., 2004; Stewart et al., 2001; Teutsch et al., 1999). Even in these low-dust environments it is not feasible to consider soil as the residuum of weathering reactions operating solely on underlying parent material, but instead it must be considered as an interface where in situ weathering products mix with atmospheric inputs which themselves may undergo weathering. Although compounds entering the interface from above or below are modified by mineral dissolution, precipitation, and sorption processes, it may be possible to use differences in the isotopic composition of specific elements to evaluate the long-term mixing of input sources (Kurtz et al., 2001; Stewart et al., 2001). Recent studies suggest that trace

concentrations (pg g^{-1}) of Mo in precipitation may be a significant input of Mo to soils over pedogenic timescales (Marks et al., 2015; Siebert et al., 2015).

Atmospheric transport of Mo is largely unconstrained but may be significant for its availability as a micronutrient, its adsorption onto secondary mineral phases that also evolve as soils age, and its transport from terrestrial to marine environments.

Sources of atmospheric Mo include fossil fuel combustion, marine-derived aerosols, continental dust, and volcanic fog (vog) (Marks et al., 2015; Mather et al., 2012; Sansone et al., 2002; Tsukuda et al., 2005).

This study examines sources of Mo, the drivers of Mo retention, and controls on Mo isotopic composition in soils. We focus on soils developed on young (10 kyr) lava flows in Hawaii, and we examine how Mo in these soils varies as a function of climate. In addition to characterizing soil Mo, we measured the Mo isotope composition of inputs to and losses from the soil including bedrock, precipitation, vegetation, and groundwater discharge. We also performed sequential chemical extractions on surface soils targeting Mo associated with SRO minerals, OM, and bulk soil to constrain the distribution of Mo within the soils. Using an isotopic mass balance model, we calculate that atmospheric inputs account for a large proportion of the Mo flux into and out of soils, and are capable of shifting solid phase isotopic patterns relative to bedrock.

3.2 Methods

3.2.1 *Study site: Kona Climate Gradient (KCG)*

The Hawaiian Islands are well suited for studying pedogenic processes because the state factors that drive soil formation (climate, vegetation, relief, bedrock, and time) can be easily constrained (Chadwick et al., 1999; Vitousek, 2004b). The Hawaiian Islands form as the Pacific tectonic plate drifts over a stationary hot spot, tapping lava from the upper mantle creating a relatively homogenous lithology. Furthermore, Hawaii's geographic isolation results in low biodiversity and reduces external anthropogenic atmospheric inputs (Vitousek, 2004b). Hawaiian soil development studies can target elevation and precipitation gradients on same-age lava flows to measure the effect of climate on pedogenesis, or they can target sites with similar climate across multiple lava flows to study the effect of age on pedogenesis (Chadwick et al., 2003, 1999; Chorover et al., 2004; Vitousek et al., 1999).

This study focuses on a suite of seven sites from a well-characterized climate gradient (Kona Climate Gradient, or KCG) along 10 kyr lava flows on the western slopes of the Mauna Loa and Hualalai volcanoes on Hawaii's Kona Coast (see Porder and Chadwick, 2009 and Porder et al., 2007 for KCG topographic map). Mauna Loa and Hualalai are shield volcanoes with gentle, stable slopes ($< 15^\circ$) that minimize erosion and thus their soils represent continuous pedogenesis (Chadwick et al., 2009; Porder et al., 2007). The two volcanic sources create a patchwork of a'a flows along the Kona Coast that vary moderately in chemical composition, with Mauna Loa

basalt being tholeiitic in nature and Hualalai basalt being alkalic in nature (Sherrod et al., 2007). Based on radiocarbon dating of charcoal extracted from beneath the flows (Wolfe and Morris, 1996), KCG 3, 4, and 6 are located on a 5 – 10 kyr Mauna Loa tholeiitic flow, KCG 7, 10, and 11 are located on a slightly older > 11 kyr Mauna Loa tholeiitic flow, and KCG 9 is located on a 5 – 10 kyr Hualalai alkalic flow (Sherrod et al., 2007) (Table 3.1). Initial soil development along the KCG is influenced by the addition of tephra from younger volcanic eruptions. Tephra settles into the void space of a'a clinkers and early in pedogenesis it is the preferential weathering of these tephra fines over a'a clinkers that creates a soil layer. Over time the weathering zone propagates downwards creating subsoil horizons where weathered a'a clinkers predominate. The KCG has received alkalic tephra from the Hualalai Volcano over the past 5 kyr (Porder et al., 2007). This input contributes to the bedrock for the soil profiles. In our case, the close proximity of the soil sites to one another (< 7.5 km separates the most disparate sites) means that each site has received similar amounts of tephra so that comparisons between sites are valid. Assuming the chemical composition of the tephra input is identical to the chemical composition of the Hualalai flow from which it was produced, the amount of mass loss can be calculated from the amount of tephra bedrock input into the system (Porder et al., 2007) (Tables A.1 and A.2).

The soils in this study are primarily Mollisols (Andic Haplustolls) at the driest sites (MAP < 1100 mm), characterized by OM accumulation and weak development of SRO secondary minerals, and Andisols (Typic Hydrudands) at the wetter sites

(MAP > 1100 mm), also characterized by OM accumulation in the surface and more significant development and accumulation of SRO secondary minerals and clays. The sites originally hosted Hawaiian dryland and mesic forest. Currently, the vegetation at the dry end of the KCG is dominated by exotic grass species (*Megathryrsus* spp) and the non-native low tree Kiawe (*Prosopis* spp), and the vegetation at the wet end of the KCG is dominated by the native Ohia (*Metrosideros* spp) and the Guava (*Psidium* spp) trees and Christmas berry (*Schinus* spp) (NCSS, 2015). Precipitation increases with elevation from 660 mm yr⁻¹ mean annual precipitation (MAP) at 32 m elevation to 2,100 mm yr⁻¹ MAP at 600 m elevation. Precipitation for each site was determined using the Rainfall Atlas of Hawaii (Giambelluca et al., 2013) and cross-referencing historical records of precipitation as a function of elevation for the last 47 years provided by local landowners. The orographic gradient is controlled by overall island topography and land-sea wind patterns and has remained similar in magnitude throughout the Holocene (the entirety of the soil development) (Hotchkiss et al., 2000). Slightly different precipitation values were reported in Porder et al. (2007), Porder and Chadwick (2009), and Chadwick et al. (2009) based on an older version of the Rainfall Atlas of Hawaii (Giambelluca et al., 1986). Mean annual temperatures are similar among sites, averaging 18°C at the higher elevation sites and 23°C at the lower elevation sites (Table 3.1). The leeward side of Hawaii, where the KCG is located, has no permanent streams due to the high permeability of young a'a basalt bedrock. Precipitation infiltrates into soils and is leached via the groundwater flux to the ocean. As a result, groundwater is the major transport

vector for products of chemical weathering and soil leaching for these sites (Schopka and Derry, 2012).

King et al. (2014) found that significant loss of Mo occurs during early stages of weathering in basaltic soils. Therefore studying young soils, where weathering fluxes are higher (Porder et al., 2007), should provide a clearer picture of isotope behavior in the pedogenic environment and be more relevant to understanding terrestrial fluxes to the ocean. The KCG is an ideal setting for early-stage weathering research because it captures the major primary to secondary mineral transformations, which are completed by the time Hawaiian soils are 20 kyr and older (Vitousek et al., 1997). We anticipate the KCG will represent a transition zone between Mo loss as a highly mobile oxyanion and Mo adsorption as SRO Fe (oxyhydr)oxides and OM accumulate. Base saturation declines from 100% to 13.5% and extractable Fe (a proxy for secondary mineral formation) increases from 48% to 91% of total Fe with increasing MAP (NCSS, 2015). In addition, because the KCG is < 20 kyr, Asian dust inputs, which could significantly alter the Mo budget and isotope signature, are likely minor (Porder et al., 2007) allowing us to better constrain the role of non-dust atmospheric inputs.

Table 3.1: Kona Climate Gradient site physiography

Site	Mean Annual Precipitation (mm)	Mean Annual Temperature (°C)	Elevation (m)	Vegetation	Soil Classification	Geology (Age)	Easting	Northing
3	660	23	32	Koa haole Kiawe Guineagrass	Clayey-skeletal, parasesquic, isohyperthermic Andic Haplustols	A'a lava flow from Mauna Loa (5-10 kyr)	189703	2162165
4	990	22	133	Kiawe Guineagrass	Clayey-skeletal, parasesquic, isohyperthermic Andic Haplustols	A'a lava flow from Mauna Loa (5-10 kyr)	190686	2162505
6	1100	21	323	Lantana Guineagrass Kiawe	Hydrous- skeletal, ferrihydritic, isothermic Typic Hydrudands	A'a lava flow from Mauna Loa (5-10 kyr)	191787	2162824
7	1550	20	482	Kikuyugrass	Hydrous- skeletal, ferrihydritic, isothermic Typic Hydrudands	A'a lava flow from Mauna Loa (11 kyr)	193177	2163105
9	1730	18	909	Kikuyugrass Guava Christmasberry Ohia lehua	Hydrous- skeletal, ferrihydritic, isothermic Typic Hydrudands	A'a lava flow from Hualalai (5- 10 kyr)	196671	2163617
10	1840	19	585	Guava Christmasberry Ohia lehua	Hydrous- skeletal, ferrihydritic, isothermic Typic Hydrudands	A'a lava flow from Mauna Loa (11 kyr)	193895	2163147
11	2100	19	711	Guava Christmasberry Ohia lehua	Hydrous- skeletal, ferrihydritic, isothermic Typic Hydrudands	A'a lava flow from Mauna Loa (11 kyr)	195049	2163542

3.2.2 Sample collection

Mineral soil samples were collected by horizon from backhoe dug soil pits until reaching soil rock too solid to excavate (Porder et al., 2007). Bedrock was collected from road cuts and visually unweathered lava flows surrounding the soil pits based on the USGS Geologic Map of the State of Hawaii (Sherrod et al., 2007). First-year foliage was collected from the dominant vegetation types at the dry, intermediate, and wet sample sites (predominately Ohia, Kiawe, and grass species). Groundwater samples were collected from a total of seven wells in the Kona region in July 2015 using 1-L acid-washed plastic bottles. Soil and bedrock samples were shipped to University of California, Santa Barbara for preliminary analyses. Soils were dried overnight at 105°C, sieved at < 2 mm to separate the fine-earth fraction from the coarse fragments. Samples were analyzed for basic soil properties including bulk density, pH, major elemental composition, water content, % organic carbon (% C_{org}), and oxalate (amorphous, non-crystalline Fe) and dithionate-citrate (pedogenic Fe) extractable and total Fe content (Fe_{ox} , Fe_d , and Fe_{total}) before being sent to the W.M. Keck Collaboratory for Plasma Spectrometry at Oregon State University for further trace metal analysis. Bulk density and major element composition were previously reported in Porder et al. (2007) and Porder and Chadwick (2009). To prepare for trace metal analysis, soil and foliage subsamples were ashed at 600°C for four hours to oxidize the sample. Soil, foliage, and bedrock samples were powdered in a trace-metal-free agate ball mill. An aliquot of each sample (200 mg) was digested in a mixture of concentrated HF-HCl-HNO₃ (1:3:1 solution) in an Anton

Paar microwave oven. Digested samples were refluxed twice in concentrated HNO_3 , then dried on a hot plate and re-suspended in a 0.5 M HNO_3 solution for elemental analysis. Groundwater and stream water samples were acidified and filtered through 0.2- μm filters before they were dried on a hot plate and re-suspended in a 0.5 M HNO_3 solution. Elemental concentrations including Mo and niobium (Nb) were measured on a Thermo X-Series II Inductively Coupled Plasma Mass Spectrometer (ICP-MS) and major elements (Ca, K, Mg, Na, Si, P, and Al) were measured on a Teledyne Leeman Prodigy ICP-OES. Procedural blanks were subtracted from reported data and always < 1 ng Mo. Mixed element solution standards were used as calibration standards and USGS rock standards (BHVO-2 and BCR-2 basalts) were monitored for quality control and agreed with published concentrations within 5% and 6%, respectively (Li et al., 2014).

Precipitation was collected at a site 3 km away from the KCG that receives the same amount of precipitation as our intermediate MAP soil sites. Precipitation collectors consisted of a large plastic funnel attached to an acid-washed, 1-L Nalgene bottle attached to 1 m wooden stakes that were placed in the field only during rain events. Only deploying the collectors during the rain events minimized any inputs from dry deposition and volcanic fog. In total, 4 L of precipitation was collected over six rain events. A second set of precipitation collectors were deployed in Hilo, Hawaii over a two-week period to collect 8 L of precipitation. Precipitation and groundwater samples were acidified and filtered through 0.2- μm filters before they were dried down on a hot plate and re-suspended in a 0.5 M HNO_3 solution.

3.2.3 Element loss or gain

To determine fractional mass loss or gain of Mo relative to basalt bedrock, we compared the concentrations of Mo at each site and depth to that of an immobile element. In basalt-derived Hawaiian soils, the least mobile element is Nb (Kurtz et al., 2000). The fraction of an element lost or gained relative to the bedrock can be expressed in terms of “ τ ”:

$$\tau = \left[\left(\frac{C_{j,w} \cdot C_{i,p}}{C_{i,w} \cdot C_{j,p}} \right) - 1 \right] \cdot ff \cdot 100 \quad (1)$$

C is the concentration of an element, w refers to the weathered material, p refers to the bedrock, i refers to the immobile element (Nb), j refers to the element of interest, and ff is the fraction of soil mass in the < 2 mm range (Kurtz et al., 2000; Porder et al., 2007). In this case, we assume the bedrock is the basalt we collected from nearby road cuts and lava flows across the KCG. We chose not to average bedrock concentrations KCG in order to precisely calculate τ values with the respective tholeiitic or alkalic flow. A tau value of +100% implies 100% gain of an element relative to bedrock and a tau value of -100% implies 100% loss of an element relative to bedrock. By multiplying τ by the bulk density (ρ_h) and thickness (z_h) of each horizon and then summing over the entire soil profile we calculated mass-weighted profile averages for elemental loss and gain:

$$\tau_{int} = \sum \left(\frac{\tau \cdot z_h \cdot \rho_h}{\sum (z_h \cdot \rho_h)} \right) \quad (2)$$

We also calculated the absolute mass gain or loss of Mo per unit volume of bedrock (N_{Mo}) (relative to Nb) (Brimhall et al., 1992; Pett-Ridge et al., 2007; Porder et al., 2007). The τ of a given horizon was multiplied by the abundance of Mo (the element of interest) in bedrock and the thickness of that soil horizon. This represents the fraction of Mo gain or loss as bedrock is transformed into a horizon:

$$N_{Mo} = \frac{\tau}{100} \cdot C_{j,p} \cdot \rho_p \cdot z_h \quad (3)$$

Mass-weighted absolute mass gain/loss was calculated by summing the N_{Mo} of each horizon. Error was propagated through the calculations assuming a 5% uncertainty on concentration values.

3.2.4 Extractions

Mo distribution among soil pools was determined based on operationally defined chemical extractions from the surface horizons at each site across the KCG. The following extraction methods were chosen based on previous experiments looking at metal partitioning in soils and to avoid any additional isotope fractionation that could arise from the incomplete dissolution of target phases (Marks et al., 2015; Siebert et al., 2015; Ure et al., 1993; Wiederhold et al., 2007a, 2007b, 2006); however, we are only focusing on Mo concentrations in each extraction in this study. The first extraction targeted soluble Mo, exchangeable Mo, and Mo adsorbed onto SRO Fe-(oxyhydr)oxides. In this extraction, 20 g of sieved (< 2

mm) bulk soil was combined with 100 mL 0.5 M ultrapure HCl and shaken for 24 hours, following the procedure used in Siebert et al. (2015). The second extraction targeted Mo associated with OM and uses the pellet collected from the 0.5 M HCl extraction and acidified hydrogen peroxide (H_2O_2) (Marks et al., 2015; Ure et al., 1993). The solutions were heated in an 85°C water bath and H_2O_2 (adjusted to pH 2) was added in 10 mL incremental amounts every 60 minutes until oxidation was no longer evident. To prevent re-adsorption of Mo species, 10 mL of 3.2 M NH_4OAc was added at the end of the extraction procedure. Samples were centrifuged at 3400 rpm for 20 minutes and the supernatant was collected, filtered using 0.2 μm syringe top filters, evaporated to dryness, and re-suspended in 0.5 M HNO_3 . An aliquot (~0.2 g) of the final pellet was dissolved in an ultrapure HF-HCl-HNO_3 (1:3:1 solution) in an Anton Paar microwave oven and represented the “residual Mo pool”, or Mo associated with primary silicate phases, Ti oxide phases, and secondary mineral phases resistant to the extractions. Elemental concentrations of Mo of the three extractions were measured on a Thermo X-Series II ICP-MS. Procedural blanks for the extractions were always < 6 ng Mo.

3.2.5 Mo isotopic composition

Mo isotope measurements were performed on a Nu Plasma MC-ICP-MS at Oregon State University using the procedure outlined in Siebert et al., (2001). The double spike procedure allows correction for both laboratory and instrumental mass fractionation. Following digestion and Mo concentration measurements, samples were spiked with a ^{97}Mo - ^{100}Mo double-spike targeted to yield a $^{97}\text{Mo}/^{98}\text{Mo}$ ratio of 3

(Siebert et al., 2001). A range of $^{97}\text{Mo}/^{98}\text{Mo}$ ratios were tested and the isotopic results were found to be stable across a range of 1 to 10. Spiked samples were refluxed in 0.5 M HNO_3 to allow for homogenization, dried down, and re-dissolved in 6 – 10 mL of a 1M HF – 0.5 M HCl solution. To ensure complete oxidation, 200 μL of H_2O_2 was added to each sample. To separate Mo from the soil matrix, we followed the Mo column chromatography outlined in Pearce et al. (2009) with minor adaptations. The Bio-Rad AG1-X8 anion resin contained high Mo blanks, so an additional step of cleaning the resin with 200 mL of 1 M HCl was adopted. We also achieved greater Mo sample recovery when the final elution step was changed from 10 mL 3 M HNO_3 to 30 mL 1 M HCl. For samples with a complex matrix, including bulk soils and bedrock, column chromatography was repeated twice to ensure complete separation of Mo from the solution matrix. Sample recovery was > 90% for BHVO-2 and Alfa Aesar Mo standards, and procedural blanks were less than 5 ng Mo with the improved resin cleaning.

Isotope measurements are made relative to NIST SRM 3134 (Lot No.: 891307), which has recently been proposed to serve as the zero-delta reference material for Mo isotopes (Goldberg et al., 2013; Greber et al., 2012). Data are presented in delta notation ($\delta^{98}\text{Mo}$) for $^{98}\text{Mo}/^{95}\text{Mo}$ ratios:

$$\delta^{98}\text{Mo} = \left[\frac{\frac{^{98}\text{Mo}}{^{95}\text{Mo}}_{\text{sample}}}{\frac{^{98}\text{Mo}}{^{95}\text{Mo}}_{\text{NIST SRM 3134 standard}}} - 1 \right] \cdot 1000 \quad (4)$$

For soil samples, we calculated mass weighted soil profile averages for the $\delta^{98}\text{Mo}$ isotopic composition by multiplying $\delta^{98}\text{Mo}$ by the Mo concentration ($C_{\text{Mo},h}$), bulk density (ρ_h) and thickness (z_h) of each horizon and then summing over the entire soil profile (z_t):

$$\delta^{98}\text{Mo}_{\text{int}} = \sum \frac{(\delta^{98}\text{Mo}_h \cdot C_{\text{Mo},h} \cdot \rho_h \cdot z_h)}{(C_{\text{Mo},\text{tot}} \cdot \rho_t \cdot z_t)} \quad (5)$$

An Alfa Aesar ICP standard solution (Specpure[®] Product No.: 35758 (Lot No.: 23-16504a)) was used as our in-house standard ($\delta^{98}\text{Mo} = -0.17 \pm 0.03\text{‰}$ (2σ ; 55 analyses/6 analytical sessions)). In agreement with previous results, repeated measurement of USGS standards BCR-2, BHVO-2, and SDO-1 yielded $\delta^{98}\text{Mo}$ values of $-0.05 \pm 0.10\text{‰}$ (2σ ; 12 analyses/4 analytical sessions), $-0.10 \pm 0.15\text{‰}$ (2σ ; 5 analyses/3 analytical sessions), and $+0.86 \pm 0.01\text{‰}$ (2σ ; 6 analyses/3 analytical sessions) (Goldberg et al., 2013; Pearce et al., 2009; Skierszkan et al., 2015). All samples were measured at least twice during an analytical session, and when averaged had reproducibility within $< 0.1\text{‰}$. Repeated analysis of bulk KCG soil samples on two separate days were reproduced within 0.15‰ (2σ).

3.3 Results

3.3.1 *Concentration and mobility of molybdenum in soil profiles*

Bulk soil Mo concentrations ranged from $0.44 \mu\text{g g}^{-1}$ to $3.32 \mu\text{g g}^{-1}$ while bulk soil Nb concentrations ranged from $7 \mu\text{g g}^{-1}$ and $28 \mu\text{g g}^{-1}$. Bedrock was collected from three different sites, corresponding to the three different lava flows across the

Kona Climate Gradient (KCG). Bedrock from site 3 had a Mo concentration of $0.67 \mu\text{g g}^{-1}$ and a mean Nb concentration of $14.80 \mu\text{g g}^{-1}$. Bedrock from site 3 was used as the bedrock basalt for KCG 3, KCG 4, and KCG 6. Bedrock from site 7 had a mean Mo concentration of $0.25 \mu\text{g g}^{-1}$ and a mean Nb concentration of $7 \mu\text{g g}^{-1}$ and was used as the bedrock basalt for KCG 7, KCG 10, and KCG 11. Bedrock from site 9 was used as the bedrock basalt for KCG 9 and had a mean Mo concentration of $0.46 \mu\text{g g}^{-1}$ and a mean Nb concentration of $4 \mu\text{g g}^{-1}$ (Table 3.2).

Calculations of τ Mo for individual soil horizons ranged from -5% at KCG 4 to +182% at KCG 11 (Table 3.2). Surface horizons exhibited the greatest enrichment of Mo with respect to bedrock and range from +31% at KCG 4 to +182% at KCG 11 (Table 3.2, Figure 3.1). τ Mo values decrease with depth, generally reaching values within error of the bedrock (τ Mo = 0%) in the deepest horizons (Table 3.2, Figure 3.1). τ_{int} Mo values revealed net enrichment of Mo across the KCG ranging from +1% at the dry end of the KCG (KCG 4) to +79% at the wet end of the KCG (KCG 10) (Table 3.3, Figure 3.2). Our τ Mo calculations showed increasing Mo enrichment with increasing MAP and a negative correlation with other rock-derived mobile elements in soils including calcium (τ_{int} Ca) ($r^2 = 0.86$ and 0.75 , $p = 0.003$ and 0.01 , respectively) (Table 3.3, Figure 3.2). While a significant positive correlation existed between profile-integrated τ Mo and % C_{org} ($r^2 = 0.70$, $p = 0.02$) (Figure 3.3); no significant correlations existed between profile-integrated τ Mo and Fe_{ox} , Fe_d , Fe_{tot} or pH.

We investigated the potential effect that additional tephra input has on the Mo/Nb ratio, and thus τ Mo, by incorporating Mo and Nb concentrations from a

nearby 5 kyr Hualalai outcrop into τ Mo calculations operating under the assumption that the composition of tephra reflects the chemical composition of bedrock and that the 5 kyr Hualalai material is the most likely potential tephra input (Tables A.1 and A.2). Porder et al. (2007) estimated that $40\% \pm 10\%$ void space along the KCG can be filled by tephra, which would subsequently be an additional source of parent material for soil production. We defined bedrock Mo and Nb concentrations as a combination of tephra and bedrock sources ranging from 30% to 50% possible tephra input. Considering this effect, τ Mo values changed by an average of 5% (maximum of 17%) and remained within the propagated error for τ Mo (Tables A.1 and A.2).

3.3.2 Mo isotopic composition in soil profiles

Bedrock samples from sites 3, 7, and 9 had $\delta^{98}\text{Mo}$ values of -0.26‰, -0.11‰, and -0.19‰, respectively (Table 3.2). The general pattern of bulk soil $\delta^{98}\text{Mo}$ isotopic values showed that soils at the drier end of the KCG (KCG 3, 4, 6, and 7) had $\delta^{98}\text{Mo}$ isotopic values lighter than bedrock ($\delta^{98}\text{Mo}$ range: -0.63‰ and -0.28‰) and soils at the wetter end of the KCG (KCG 9, 10, and 11) had $\delta^{98}\text{Mo}$ isotopic values similar to bedrock ($\delta^{98}\text{Mo}$ values of -0.26‰ to -0.11‰) or heavier (up to +0.03‰) (Table 3.2). Mass-weighted profile-integrated $\delta^{98}\text{Mo}$ isotopic compositions ranged from -0.53‰ to -0.07‰ (Table 3.3). Similar to the τ Mo data (e.g., Figure 3.3), a significant positive correlation was found between profile-integrated $\delta^{98}\text{Mo}$ and % C_{org} ($r^2 = 0.65$, $p = 0.02$) (Figure 3.4). No significant correlations were found between profile-integrated $\delta^{98}\text{Mo}$ and Fe_{ox} , Fe_{d} , or Fe_{tot} .

Depth profiles of bulk soil $\delta^{98}\text{Mo}$ did not have consistent trends with depth (Figure 3.5). Subsurface horizons sites 3, 7, and 11 were lighter than surface horizons. However, excursions from this trend emerge in subsurface horizons at KCG 3, 6, and 10 where one or more subsurface horizons exhibited heavier $\delta^{98}\text{Mo}$ isotopic values than surface horizons.

3.3.3 Mo concentrations and isotopic compositions in foliage, groundwater, stream water, and precipitation

Foliar Mo concentrations ranged from 45.2 ng g^{-1} to 166.2 ng g^{-1} , with an average Mo concentration of 94.8 ng g^{-1} . $\delta^{98}\text{Mo}$ isotopic values were highly variable, even within sites, and ranged from -0.18‰ to $+0.64\text{‰}$ (Table 3.4). No significant correlations between foliar Mo concentrations or foliar $\delta^{98}\text{Mo}$ isotopic values and surface Mo concentrations, τ_{int} Mo, or soil $\delta^{98}\text{Mo}$ isotopic values were evident.

Precipitation collected from the Kona coast had a Mo concentration of 5.85 pg mL^{-1} and precipitation collected from Hilo has a Mo concentration of 7.64 pg mL^{-1} (Table 3.4). Multiplying the average Mo concentration in precipitation by the MAP flux for each site yielded an average Mo precipitation flux between $5.2 \text{ } \mu\text{g cm}^{-2} \text{ yr}^{-1}$ at the dry end of the KCG to $16.0 \text{ } \mu\text{g m}^{-2} \text{ yr}^{-1}$ at the wet end of the KCG. The Mo isotopic composition of the precipitation was consistently heavier than bulk soil and bedrock with $\delta^{98}\text{Mo}$ values of $+1.20\text{‰}$ for the Kona coast precipitation sample and $+1.02\text{‰}$ for the Hilo precipitation sample (Table 3.4). Groundwater Mo concentrations ranged from 0.45 ng mL^{-1} to 4.86 ng mL^{-1} with an average Mo concentration of 2.55 ng mL^{-1} . The isotopic composition of groundwater was heavier

than bedrock with $\delta^{98}\text{Mo}$ values ranging from 0.00‰ to +1.17‰ (Table 3.4). There was evidence of seawater intrusion in our groundwater samples collected closest to the coast during a flooding tide so these samples are not included in our discussion of fluxes from soils to the ocean (Table A.3).

Table 3.2: Soil and parent material element mobility and Mo isotopic composition

Sample name	Depth range	Density (ρ)	Fraction Fines (ff)	Mo	Nb	Absolute Mass Gain (N_{Mo})	τ Ca
	cm	$g\ cm^{-3}$		$\mu g\ g^{-1}$	$\mu g\ g^{-1}$	$\mu g\ cm^{-2}$	%
<i>KCG 3</i>							
A1	0--8	0.70	0.8	0.61	7.0	5.1	-35.2
A2/2C2	8--28	0.71	0.7	0.67	12.0	3.0	-42.9
B1/2C3	28--43	0.83	0.5	0.68	14.0	0.5	-30.4
B2/2C4	43--61	0.70	0.3	0.73	15.0	0.4	-20.7
B4/2C6	74--99	0.74	0.2	0.45	11.0	-0.3	-2.4
PM 3		1.35		0.67	14.8		
<i>KCG 4</i>							
A1	0--5	0.74	1.0	0.72	12.0	1.4	-80.9
A2	5--15	0.82	0.9	0.68	15.0	0.1	-78.8
Bw1/2C1	15--31	0.85	0.3	0.61	17.0	-0.7	-22.4
Bw2/2C2	31-70	0.80	0.1	0.44	10.0	-0.1	-7.9
<i>KCG 6</i>							
A1	0--10	0.60	0.9	1.43	16.0	8.2	-80.0
A2	10--22	0.70	0.9	1.29	16.0	7.2	-73.6
Bw1/2C2	22--52	0.75	0.2	0.80	14.0	1.4	-17.8
Bw2/2C3	52--90	0.80	0.2	0.46	10.0	0.2	-11.8
<i>KCG 7</i>							
A1	0--10	0.80	0.9	1.64	16.0	2.5	-87.1
A2	10--17	0.78	0.9	1.69	19.0	1.3	-87.1
Bw1	17--35	0.55	0.9	1.97	22.0	3.3	-88.7
Bw2/2C1	35--70	0.60	0.3	1.09	12.0	1.9	-24.1
PM 7		1.35		0.24	4.4		
<i>KCG 9</i>							
A1	0--10	0.64	0.9	2.17	17.0	5.0	-81.4
A2	10--19	0.70	1.0	2.73	22.0	4.7	-96.0
BW1	19--39	0.76	1.0	2.43	28.0	3.5	-97.3
Bw2/2C1	39--70	0.74	0.2	0.92	11.0	0.7	-14.4
0	70--99	0.70	0.1	0.77	8.0	0.5	-4.5
PM 9		1.35		0.46	6.8		
<i>KCG 10</i>							
A1	0--16	0.80	0.9	2.66	20.0	6.3	-82.2
A2	16--24	0.82	0.8	2.75	24.0	2.3	-78.4
Bw1/2C1	24--44	0.77	0.7	1.91	24.0	1.9	-64.0
Bw2/2C2	44--75	0.70	0.5	3.32	22.0	8.8	-49.1
<i>KCG 11</i>							
A1	0--13	0.80	1.0	2.95	19.0	7.7	-96.1
A2	13--26	0.70	1.0	3.26	22.0	7.2	-96.2
Bw1/2C1	26--50	0.70	0.7	2.45	23.0	5.1	-68.1

Table 3.2 (continued): Soil and parent material element mobility and Mo isotopic composition

Sample name	τ Mo	$\delta^{98}\text{Mo}$		C_{org}	Fe_{ox}	Fe_d	Fe_{tot}	pH
	%	‰	2 s.d.	%	g kg^{-1}	g kg^{-1}	g kg^{-1}	$\text{H}_2\text{O } 2:1$
<i>KCG 3</i>								
A1	71.2	-0.29	0.11	8.64	26	43	100	7.4
A2/2C2	16.7	-0.49	0.04	14.59	18	28	140	6.7
B1/2C3	3.7	-0.28	0.07	6.62	25	50	135	8.3
B2/2C4	2.5	-0.53	0.07	4.99	19	55	150	8.1
B4/2C6	-1.4	-0.39	0.10	2.06	4	31	105	7.9
PM 3		-0.26	0.09					
<i>KCG 4</i>								
A1	31.4	-0.38	0.04	10.1	21	55	136	6.9
A2	0.8	-0.38	0.03	6.13	40	66	165	7.3
Bw1/2C1	-5.2	-0.46	0.14	3.25	49	74	167	7.6
Bw2/2C2	-0.3	-0.53	0.08	0.84	13	39	149	7.8
<i>KCG 6</i>								
A1	91.5	-0.61	0.06	8.61	30	80	151	5.7
A2	67.1	-0.61	0.12	5.48	31	72	165	5.8
Bw1/2C2	5.4	-0.36	0.06	3.77	42	56	167	6.4
Bw2/2C3	0.5	-0.63	0.11	2.67	32	99	138	6.9
<i>KCG 7</i>								
A1	77.9	-0.33	0.11	12.02	42	111	171	7.1
A2	55.7	-0.38	0.04	8.94	42	91	184	5.8
Bw1	56.7	-0.39	0.06	6.99	60	95	201	6.3
Bw2/2C1	16.4	-0.60	0.03	5.44	41	92	166	6.1
PM 7		-0.11	0.08					
<i>KCG 9</i>								
A1	81.2	-0.18	0.10	22.79	50	97	147	5.6
A2	85.0	-0.15	0.10	18.83	57	118	196	5.8
BW1	28.8	-0.20	0.11	12.82	73	178	238	5.7
Bw2/2C1	3.7	-0.29	0.02	8.85	45	68	130	5.4
0	2.2	-0.24	0.01	5.21	26	43	93	5.8
PM 9		-0.19	0.09					
<i>KCG 10</i>								
A1	121.0	-0.07	0.08	16.63	54	126	210	6.3
A2	86.6	-0.10	0.11	12.23	78	106	235	5.6
Bw1/2C1	29.0	-0.22	0.03	11.25	65	137	231	5.5
Bw2/2C2	87.4	-0.01	0.04	8.76	91	160	229	5.5
<i>KCG 11</i>								
A1	182.4	0.03	0.06	15.17	47	123	224	5.9
A2	170.1	-0.41	0.04	13.89	65	93	239	5.6
Bw1/2C1	64.9	-0.45	0.11	12.58	61	108	193	5.7

τ values calculated using Nb as immobile element

Fe_{ox} , Fe_d , Fe_{tot} , pH, and % C_{org} reported in Porder et al., (2007) and Porder and Chadwick, (2009)

Table 3.3: profile integrated soil Mo data, mobility, and isotopic composition

Sample name	Depth range (cm)	Bulk Soil Mo $\mu\text{g cm}^{-2}$	Absolute Mass Gain (N_{Mo}) $\mu\text{g cm}^{-2}$	τ Mo %	$\delta^{98}\text{Mo}$ ‰	2 s.d.
KCG 3	0--99	38.9	8.7	10.9	-0.41	0.19
KCG 4	0--70	30.1	0.6	0.8	-0.47	0.17
KCG 6	0--90	51.4	17.0	18.5	-0.53	0.19
KCG 7	0--70	64.8	9.0	41.3	-0.45	0.13
KCG 9	0--99	643.1	14.5	20.9	-0.23	0.18
KCG 10	0--75	153.5	19.3	79.0	-0.07	0.15
KCG 11	0--50	101.5	20.0	75.2	-0.30	0.13

Table 3.4: Precipitation, groundwater, and vegetation Mo concentrations and isotopic composition

Sample name	Mo ng g ⁻¹	$\delta^{98}\text{Mo}$ ‰	Mo 2 s.d.
<i>Precipitation</i>			
Kona	0.008	1.20	0.07
Hilo	0.006	1.02	0.08
<i>Average</i>	0.007	1.110	
<i>Groundwater</i>			
4161-01*	0.46	1.06	0.06
4161-02*	1.29	1.01	0.04
4061-01*	2.51	1.17	0.04
PW1	2.13	0.20	0.04
PW3	1.83	--	--
PW4	2.07	0.00	0.06
PW7	3.92	0.11	0.05
IW5	4.86	--	--
Puu Lani	3.59	0.26	0.03
Puu Waa Waa	2.84	--	--
<i>Average</i>	3.033	0.142	
<i>Vegetation</i>			
KCG 3 Kiawe	93.89	-0.05	0.06
KCG 3 Koa Haole	88.67	0.34	0.04
KCG 7 Kikuyu grass	166.24	0.64	0.06
KCG 9 Desmodium	60.44	--	--
KCG 9 Ohia	137.50	-0.18	0.05
KCG 11 Ohia	71.42	0.50	0.07
<i>Average</i>	103.03	0.25	

Kona precipitation was collected between November 2014 and January 2015

Hilo precipitation was collected in July 2015

*Samples influenced by seawater intrusion not included in average

Table 3.5: Soil selective extraction data

Sample name	Depth range (cm)	Mo in 0.5M HCl extraction ng g ⁻¹	% of total Mo	% of total Fe	Mo in H ₂ O ₂ extraction ng g ⁻¹	% of total Mo	% of total C _{org}	Mo in Residue ng g ⁻¹
KCG 3	0--8	0.9	0.2	6.0	100.3	23.7	86.1	322.0
KCG 4	0--5	0.5	0.1	6.8	59.6	9.7	82.3	553.6
KCG 6	0--10	1.9	0.2	14.2	130.7	11.0	83.4	1057.0
KCG 7	0--10	0.5	0.0	2.5	187.5	9.7	77.2	1745.6
KCG 9	0--10	1.4	0.1	6.0	209.1	8.3	73.2	2312.1
KCG 10	0--16	1.3	0.1	4.7	222.5	10.1	77.7	1989.8
KCG 11	0--13	1.0	0.0	4.8	242.6	8.8	76.6	2511.5
Average		1.1	0.1	6.4	164.6	12	80	1498.8

0.5 M HCl extraction targets exchangeable Mo on labile SRO Fe- (oxyhydr)oxides
H₂O₂ extraction targets Mo associated with oxidizable organic matter
% of total Fe and % of total C_{org} calculated by measured the bulk soil and extraction residue

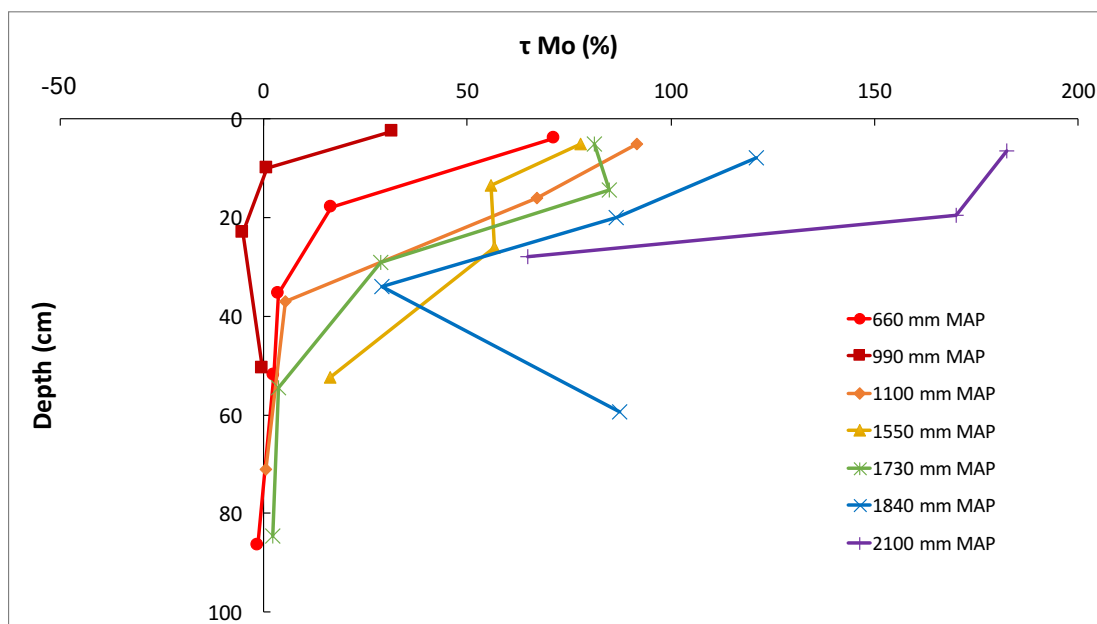


Figure 3.1: τ Mo depth profiles across the KCG

τ Mo depth profiles across the KCG represent the mass gain or loss of Mo relative to parent material inputs. Values greater 0% indicate net gain of Mo and values less than 0% indicate net loss of Mo from the soil. As MAP increases, surface soils exhibit greater net gain. Nb is used as the immobile element for τ calculations. Error bars represent $\pm 10\%$ uncertainty.

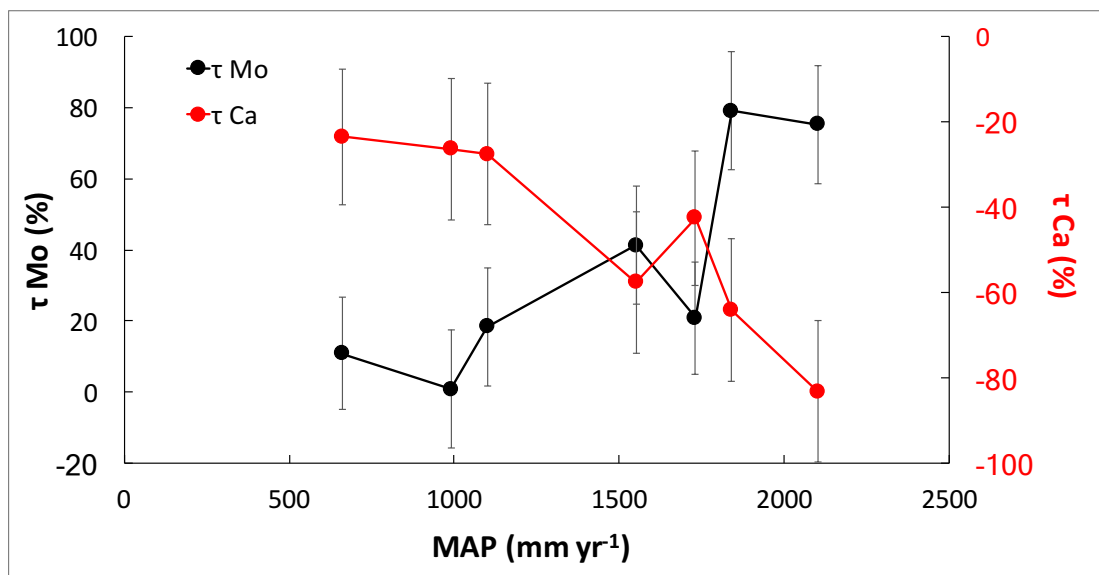


Figure 3.2: Mass-weighted, profile-integrated τ Mo and τ Ca calculations versus MAP.

Positive τ values indicate net gain and negative τ values indicate net loss relative to parent material. Error bars represent $\pm 10\%$ uncertainty.

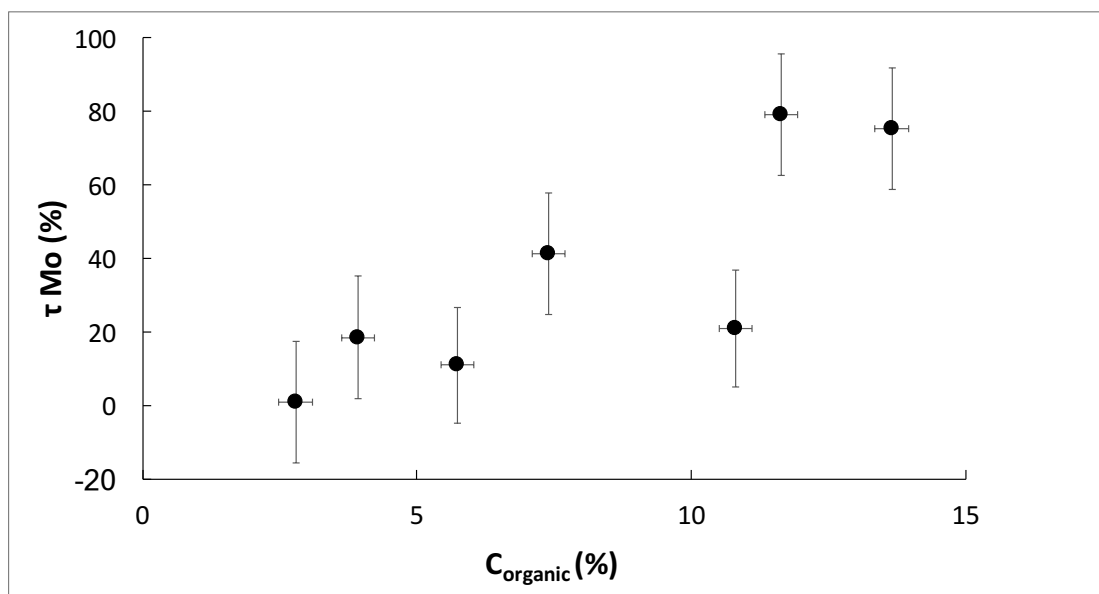


Figure 3.3: Mass-weighted, profile-integrated τ Mo plotted against % C_{org} . As % C_{org} increases, there is an increase in the net gain of Mo. All τ Mo are greater than 0%, indicating net increase across all sites along the KCG. Nb is used as the immobile element for τ calculations. Error bars represent $\pm 10\%$ uncertainty.

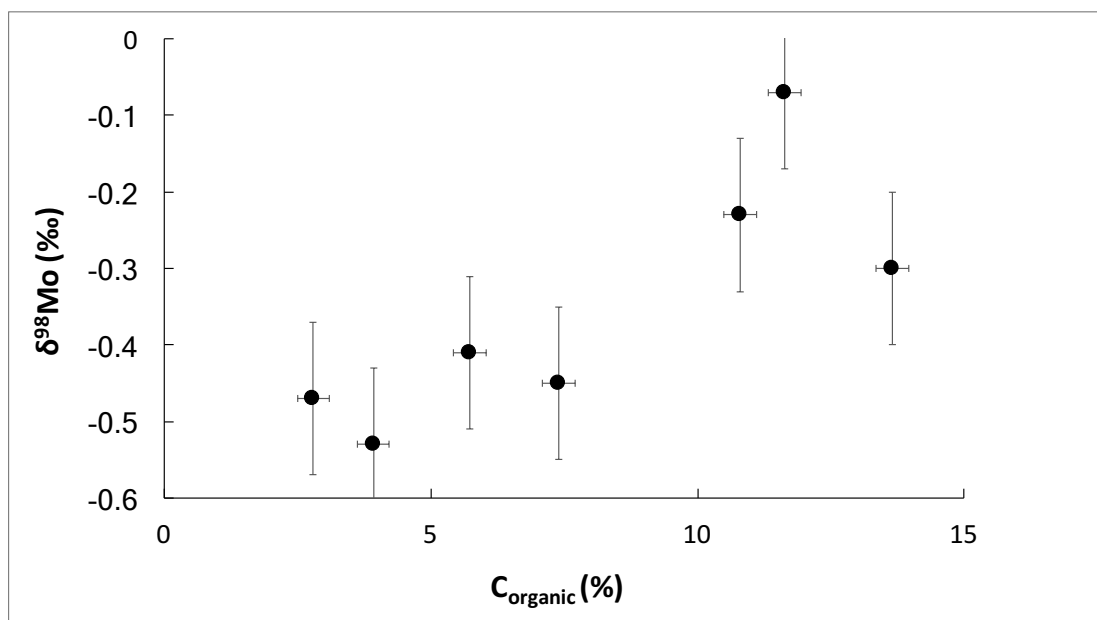


Figure 3.4: Mass-weighted, profile-integrated $\delta^{98}\text{Mo}$ plotted against % C_{org} . As % C_{org} increases, $\delta^{98}\text{Mo}$ values increase, indicating the retention of heavy Mo isotopes. Error bars represent 2σ uncertainty.

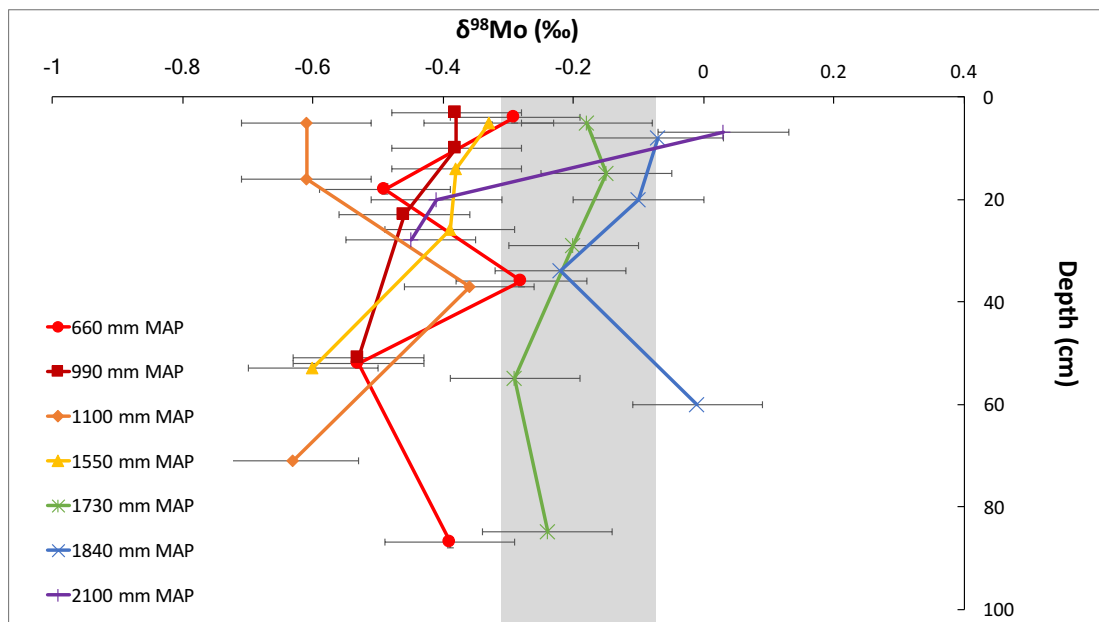


Figure 3.5: $\delta^{98}\text{Mo}$ depth profiles across the KCG.

$\delta^{98}\text{Mo}$ of surface soils are lightest at the dry end of the KCG and increase towards PM and heavier values at the wet end of the KCG. PM 3 has a $\delta^{98}\text{Mo}$ value of -0.26‰ and corresponds to the PM of KCG 3,4, and 6. PM 7 has a $\delta^{98}\text{Mo}$ value of -0.11‰ and corresponds to the PM of KCG 7,10, and 11. PM 9 has a $\delta^{98}\text{Mo}$ value of -0.19‰ and corresponds to the PM of KCG 9. Error bars represent 2σ uncertainty.

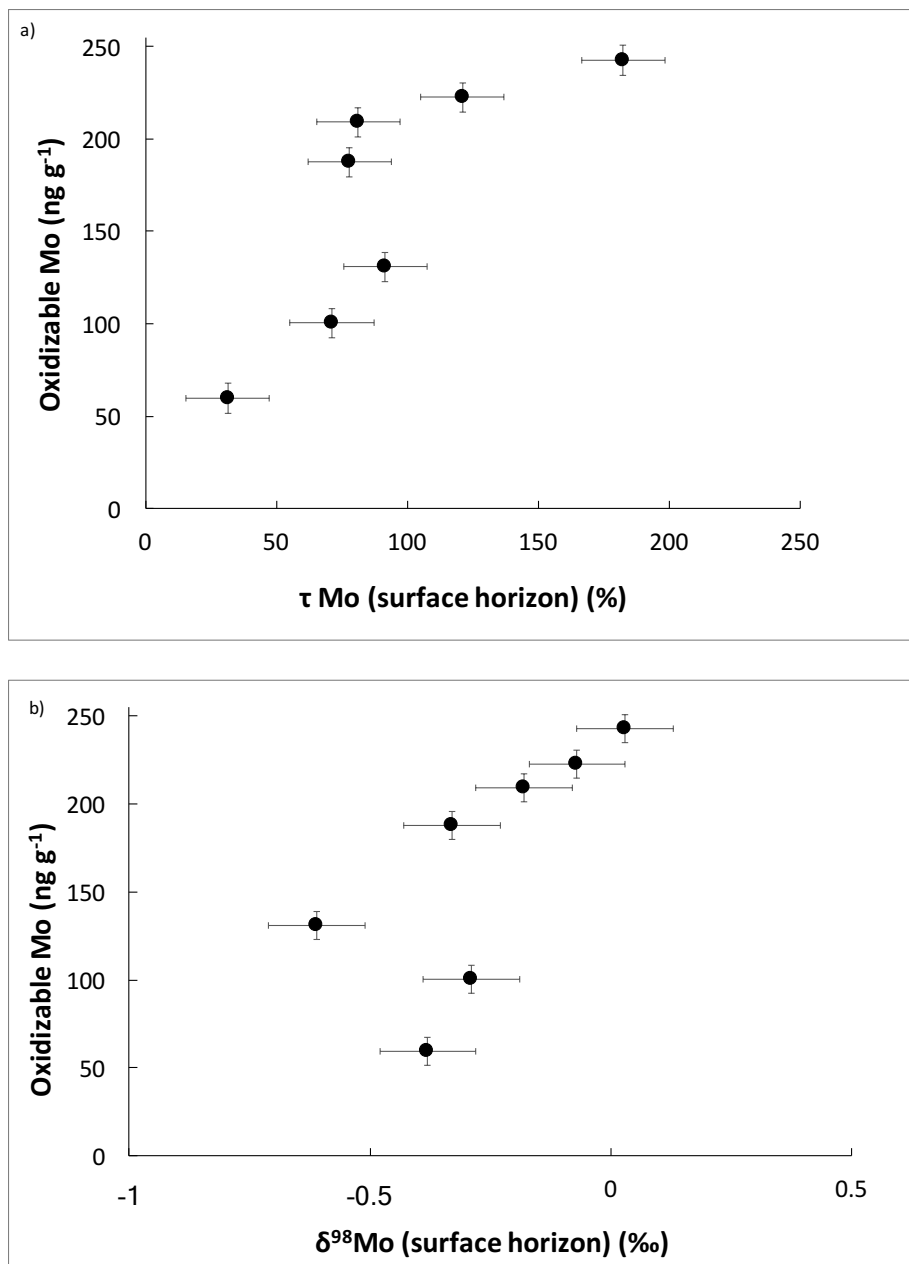


Figure 3.6: Mo released in the H₂O₂ extraction versus mass-weighted, profile-integrated a) τ Mo and b) $\delta^{98}\text{Mo}$.

The H₂O₂ extraction targets Mo in the OM oxidizable pool. As τ Mo increases, there is a concomitant increase in Mo associated with OM. Error bars represent $\pm 10\%$ uncertainty. b) Mo released in the H₂O₂ extractions versus mass-weighted, profile-integrated $\delta^{98}\text{Mo}$. The H₂O₂ extraction targets Mo in the OM oxidizable pool. As $\delta^{98}\text{Mo}$ increases, there is an increase in Mo associated with oxidizable OM. This is likely a result of increasing contribution from atmospheric sources enriched in heavy Mo. Error bars represent $\pm 10\%$ uncertainty for the H₂O₂ extraction and 2σ uncertainty for $\delta^{98}\text{Mo}$.

3.3.4 Selective extractions of Mo in soil

Sequential chemical extractions were performed on surface horizons at all seven KCG sites (Table 3.5). On average, the 0.5 M HCl solution extracted 25% of the oxalate-extractable Fe (Fe_{ox} , i.e., SRO-Fe phases) or 6% of total Fe (Fe_{tot}), and the H_2O_2 solution extracted 80% of total C_{org} . Mo extracted by 0.5 M HCl represent the most labile SRO Fe (oxyhydr)oxides and their concentrations ranged from 0.52 ng g^{-1} to 1.94 ng g^{-1} , accounting for just 0.15% of the total soil Mo for each horizon. Mo concentrations associated with oxidizable OM (H_2O_2 extraction) ranged from 59.6 ng g^{-1} to 242.5 ng g^{-1} and, on average, accounted for 12% of the total soil Mo for each horizon. In the surface soils τ Mo and bulk soil $\delta^{98}\text{Mo}$ were positively correlated with Mo concentration in the H_2O_2 extraction ($r^2 = 0.65$, $p = 0.03$ and $r^2 = 0.50$, $p = 0.07$, respectively) although the bulk soil $\delta^{98}\text{Mo}$ correlation was weak (Figure 3.6a and 3.6b). No significant correlation was found between either τ Mo or $\delta^{98}\text{Mo}$ and Mo concentration in the 0.5 M HCl extractions of the surface soils.

3.4 Discussion

3.4.1 Mo mobility across the KCG

There is a net increase in Mo relative to underlying bedrock in all soil profiles across the KCG based on τ Mo values and absolute Mo mass gain (N_{Mo}) (Tables 3.2 and 3.3). This gain of Mo is surprising considering the large mass loss of base cations (e.g., Ca, Figure 3.2) and the high mass loss rates that have previously been observed across the KCG (Porder et al., 2007). The KCG spans a dry to intermediate precipitation gradient (660 mm to 2,100 mm MAP) where soils are predominantly

oxic. Under oxic conditions, Mo is expected to be mobile as a molybdate ion (MoO_4^{2-}) yielding leaching losses relative to bedrock (negative τ values) (Kabata-Pendias, 2010; Reddy and Gloss, 1993). The fact that KCG τ Mo values are positive indicates that the soils are gaining Mo from a source other than the weathering of bedrock.

One possible explanation for the positive τ Mo values is cycling through vegetation. Deep plant roots transport many rock-derived nutrients, such as phosphorus (P), from lower soil horizons and concentrate them in surface soils, through a process known as biological uplift. This pattern is evident in some Hawaiian soils where subsurface horizons are depleted in P and surface horizons are enriched in P (Porder and Chadwick, 2009; Vitousek and Chadwick, 2013). Mo may also be concentrated in surface horizons through biological uplift, as Mo is a plant micronutrient. However, τ Mo values in the subsurface horizons would then need to be significantly negative to compensate for the large gains of Mo in the surface, which they are not. Biological uplift is most prominent for elements required at concentrations in vegetation that are roughly equal to the concentrations in the soil (e.g., P (Vitousek, 2004b)). In the case of Mo, plant Mo concentrations are an order of magnitude lower than soil concentrations (Tables 3.2 and 3.4), suggesting biological uplift could account for < 10% of the surface enrichment of Mo, and thus is an unlikely candidate for driving the observed τ Mo patterns across the KCG.

3.4.2 *Mo isotopic composition in bulk soil across the KCG*

Across the KCG, open-system Mo cycling leads to the fractionation of Mo relative to bedrock where surface horizons are lightest at the driest sites and become heavier with increasing MAP; while subsurface horizons across all sites contain either heavy or light Mo isotopic values. Unlike τ Mo, $\delta^{98}\text{Mo}$ does not correlate with depth, which suggests that multiple processes fractionate Mo and there is a decoupling between Mo accumulation in the surface and Mo fractionation in the subsurface. Possible drivers of soil Mo isotope variation relative to bedrock include: biocycling, atmospheric inputs of Mo, associations with precipitating secondary minerals (e.g., Fe (oxyhydr)oxides), and Mo complexation by organic matter.

The influence of plant uptake and its decomposition on soil Mo isotope dynamics is not well understood. There is evidence that light Mo isotopes are preferentially taken up by microbes (Voegelin et al., 2012; Zerkle et al., 2011). However, isotopic data from leaf samples across the KCG contain both isotopically heavy and light Mo relative to bedrock (Table 3.4). This may be a function of the depth of the rooting zone. Because biological uplift does not seem to be a mechanism concentrating Mo in these soils, and there is no correlation between the isotopic composition of foliage and that of the soils, it is unlikely that vegetation plays a role in the bulk soil isotopic composition.

Variable precipitation inputs could provide both an additional source of Mo to soil, and explain the variation in bulk soil $\delta^{98}\text{Mo}$ values observed in the KCG (Table

3.2, Figure 3.5). Overall, soil $\delta^{98}\text{Mo}$ values are lighter than bedrock at the dry sites and gradually shift to reflect bedrock or heavier isotopic values at high MAP (Figure 3.5). Mo isotopic values in precipitation are heavier than both the soil and bedrock ($\delta^{98}\text{Mo} = +1.11\text{‰}$) (Table 3.4), which is consistent with soil Mo isotopic data trending heavier with increasing MAP. Interestingly, the Mo isotopic composition of precipitation is not equal to the isotopic composition of seawater ($\delta^{98}\text{Mo} = +2.1\text{‰}$), a possible result of the intrusion of anthropogenic ($\delta^{98}\text{Mo}$ values range from -0.18‰ to $+0.94\text{‰}$) (Chappaz et al., 2012; Lane et al., 2013) or volcanic sources of Mo in precipitation that dilute the marine signal. Nevertheless, the absolute values of bulk soil $\delta^{98}\text{Mo}$ are in most cases lighter than any combination of the effects of weathering losses and precipitation inputs on $\delta^{98}\text{Mo}$. In the absence of a large input of light Mo to soils, in order for soils to have lighter isotopic signatures than both precipitation and bedrock, there must be both a fractionation mechanism and an accompanying removal of heavier Mo isotopes from within the soil profile.

Possible Mo fractionation mechanisms within the soil profile include adsorption onto Fe (oxyhydr)oxides and complexation by OM. Preferential adsorption of light Mo onto Fe and Mn (oxyhydr)oxides has been observed in laboratory studies (Barling et al., 2001; Barling and Anbar, 2004; Wasylenko et al., 2011) and soil horizons with an abundance of Fe (oxyhydr)oxides would thus be expected to retain isotopically light Mo via adsorption. Yet we found no correlation between soil $\delta^{98}\text{Mo}$ and Fe (oxyhydr)oxide content (Fe_{ox} or Fe_d), and our extraction data indicates that the majority of extractable Mo is associated with oxidizable OM

phases (Table 3.5). Thus, Mo-associated with OM likely governs the short-term dynamics of solid-aqueous partitioning of Mo in these soils, while the majority of bulk soil Mo, and long-term soil dynamics may be tied up in more stable phases that are not targeted by our extractions. Our findings agree with other studies investigating Mo availability in soils from Maui, Puerto Rico, Iceland, and the Oregon Coast Range, in which, the fraction of Mo in the OM pool was on the same order of magnitude as what we observe across the KCG (King et al., 2014; Marks et al., 2015; Siebert et al., 2015). The change in the structure of Mo from tetrahedral to octahedral coordination during complexation onto OM, including insoluble tannins (Wichard et al., 2009), likely induces isotopic fractionation within the soil, yet the degree and direction of isotopic fractionation onto OM is not known. As the C_{org} content increases, surface bulk soil $\delta^{98}\text{Mo}$ becomes heavier (Figure 3.4), which suggests that OM preferentially retains heavy Mo in soils. However, increasing C_{org} content corresponds with a concomitant increase in MAP (Table 3.2), and this correlation could be a result of the input of heavy Mo isotopes in precipitation. This is supported by the fact that Mo associated with oxidizable OM only accounts for 12% of the total Mo pool in surface soils so any fractionation signal associated with Mo-OM interactions could easily be dampened by additional inputs of Mo.

3.4.3 Mo isotopic mass balance

Despite their isolation, Hawaiian soils have accumulated both global and local atmospheric inputs (Chadwick et al., 1999; Kurtz et al., 2001; Porder et al., 2007; Vitousek et al., 1999). In addition to precipitation, which scavenges local sea

spray, the main sources of these exogenous inputs are continental dust derived from Asia; volcanic fog (vog) from active volcanic eruptions; and anthropogenic aerosols (Chadwick et al., 2009; Kurtz et al., 2001; Mather et al., 2012; Sansone et al., 2002). Comparing Mo flux calculations from precipitation over 10 kyr (5.2 to $16.0 \mu\text{g Mo cm}^{-2}$) to the absolute gain of Mo relative to bedrock (N_{Mo}) for that same period (8.7 to $20 \mu\text{g Mo cm}^{-2}$) (Table 3.6) reveals that there must be additional atmospheric sources of Mo to the soils besides precipitation to account for the positive N_{Mo} . Continental dust inputs to the Hawaiian Islands are well quantified, but do not become a significant flux relative to bedrock fluxes until the soils are 20 kyr or older (Kurtz et al., 2001; Porder et al., 2007). Vog deposition and anthropogenic inputs are poorly constrained for the Hawaiian Islands but are likely contributors to the atmospheric Mo flux. Although we were not able to measure the vog and anthropogenic fluxes directly, we can use our analyses of Mo mobility and Mo isotopic compositions to model the importance and influence of these atmospheric inputs to the soil.

We use simple elemental and isotopic mass balance models, accounting for both the gain of Mo in surface soils and the isotopic pattern across the KCG to characterize the additional atmospheric Mo sources (Table 3.6, Figure 3.7). Soil profiles across the KCG extend down to unweathered rock (Porder et al., 2007) such that our modeled soil column incorporates the entire chemical weathering zone, allowing us to compare atmospheric inputs to in situ bedrock inputs. The contribution of vog to the KCG can be estimated by scaling Mo concentrations in vog

to deposition across the KCG. Sansone et al. (2002) modeled a $72 \text{ ng cm}^{-2} \text{ yr}^{-1} \text{ Mo}$ deposition rate from volcanic aerosol plumes at Kilauea Volcano. We assume that Nb added to the KCG from vog is negligible, and that the enrichment of Mo we see in τ Mo calculations is not an artifact of concomitant Nb deposition. Because Nb is a lithophile element, it is largely carried in the ash and tephra fraction of volcanic plumes and not volatilized like Mo (Crowe et al., 1987; Mather et al., 2012). In order to estimate the Mo deposition flux we would expect in Kona, the Mo deposition flux of the plume was scaled by the ratio of SO_2 concentrations measured at the Pahala monitoring site adjacent to Kilauea to mean SO_2 concentrations measured at a monitoring site in Kona between the years 2010 to 2015. This yields an estimated depositional flux of Mo to KCG soils of $7 \text{ ng Mo cm}^{-2} \text{ yr}^{-1}$. Multiplying the vog flux by the age of the soils (10 kyr) we estimate a vog contribution of $71 \text{ } \mu\text{g Mo cm}^{-2}$ to the KCG. While small variations in the age of the lava flows exist, we chose to use 10 kyr as the age of our sites, consistent with previous studies of the KCG (Chadwick et al., 2009; Porder et al., 2007; Porder and Chadwick, 2009). High temperature processes do not appear to significantly fractionate Mo isotopes (J. Yang et al., 2015), and we therefore assume vog has a Mo isotopic composition similar to bedrock ($\delta^{98}\text{Mo} \sim -0.19\text{‰}$). This calculation is intended to provide a rough estimate of the contribution vog has had on the KCG soils over the course of their development and this flux will surely change with the history of volcanic emissions and wind patterns (Heath and Huebert, 1999).

The absolute Mo mass gain of our soils relative to what bedrock has contributed over 10 kyr (N_{Mo}) is equal to the difference in exogenous inputs and outputs to the soil. Given that leaching is the dominant Mo output from soils, and that the isotopic composition of the leaching flux has a $\delta^{98}\text{Mo}$ value of +0.14‰, (based on the measured average Mo isotopic composition of groundwater) we can solve for the leaching and vog flux by rearranging and substituting known values in Equations (6) and (7):

$$\frac{dM_{o_{soil}}}{dt} = N_{Mo} = (F_{precip} + F_{vog}) - F_{leach} \quad (6)$$

$$(N_{Mo} \cdot \delta^{98}Mo_N) = ((F_{precip} \cdot \delta^{98}Mo_{precip}) + (F_{vog} \cdot \delta^{98}Mo_{vog})) - (F_{leach} \cdot \delta^{98}Mo_{leach}) \quad (7)$$

Where N_{Mo} is the absolute mass gain of Mo, $\delta^{98}Mo_N$ is the isotopic composition of the absolute mass gain of Mo and is equal to the difference between the bulk soil composition and bedrock (Table 3.3) and should reflect the isotopic offset between soils and bedrock as a function of atmospheric inputs and leaching loss, F_x is the flux of the respective inputs and outputs over 10 kyr, and $\delta^{98}Mo_x$ are the isotopic compositions of the respective fluxes. In this scenario, the vog flux and the leaching flux increase with MAP across the KCG (Figure 3.7). The increase in vog flux with increasing precipitation seems plausible given that wet deposition is a likely scavenging mechanism that removes vog aerosols from the atmosphere. Given the slightly heavy isotopic signal of total atmospheric inputs, and given the increase in

total atmospheric flux across the KCG, the pattern of increasingly heavy soil Mo isotopes across the KCG with increasing MAP can be seen as reflecting this signal of combined rain and vog inputs.

The relative importance of the vog flux for Mo (and other elements) has been observed for the Hawaiian Islands. Elevated Mo concentrations were observed in near-source volcanic aerosols from Kilauea Volcano and hypothesized to be deposited via water molecules on the surfaces of sulfur and other oxides leading to their adsorption onto soil minerals (Mather et al., 2012). Furthermore, the importance of atmospheric deposition of sulfur (S) has been studied by Bern et al. (2015a). They estimate that volcanic emissions can account for up to 48% of the S in Hawaiian soils and high vog deposition rates can equal S soil stocks from weathering of bedrock in as little as 150 to 300 years (Bern et al., 2015a). Mo deposition rates from vog and precipitation are much lower than S deposition rates but can still supply enough Mo to the KCG soil profiles to match bedrock weathering contributions in 5 to 15 kyr based on total atmospheric Mo deposition rates (Table 3.6). Our results show that atmospheric inputs of Mo (and likely other trace metals) are similar in magnitude to the bedrock inputs across the KCG and suggest that the atmosphere has a major control on the dissolved Mo leaching flux, and ultimately the dissolved flux of Mo to the ocean, especially on young, volcanic islands.

Table 3.6: Mo isotopic mass balance

Bulk Soil Mo	N_{Mo}	F_{Rock}	F_{Precip}	F_{Vog}	$F_{Atmospheric\ total}$	F_{leach}	$\delta^{98} Mo_{Leach}$	$\delta^{98} Mo_{Atmosph}$
$\mu g\ Mo\ cm^{-2}$	$\mu g\ Mo\ cm^{-2}$	$\mu g\ Mo\ cm^{-2}$	$\mu g\ Mo\ cm^{-2}$	$\mu g\ Mo\ cm^{-2}$	$\mu g\ Mo\ cm^{-2}$	$\mu g\ Mo\ cm^{-2}$	%	eric total ‰
38.9	8.7	34.9	5.2	23.0	28.2	19.5	0.14	0.05
30.1	0.6	31.9	7.6	15.6	23.1	20.0	0.14	0.13
51.4	17.0	38.2	8.4	46.4	54.8	37.8	0.14	0.01
64.8	9.0	38.5	11.8	48.8	60.6	51.6	0.14	0.06
104.5	14.5	72.9	13.2	47.1	60.4	45.9	0.14	0.10
153.5	19.3	69.2	14.1	48.4	62.4	43.1	0.14	0.10
101.5	20.0	43.1	16.0	67.5	83.5	63.5	0.14	0.06

N_{Mo} is the bulk soil pool after 10 kyr
 F_x is the contribution of each flux to the bulk soil pool after 10 kyr

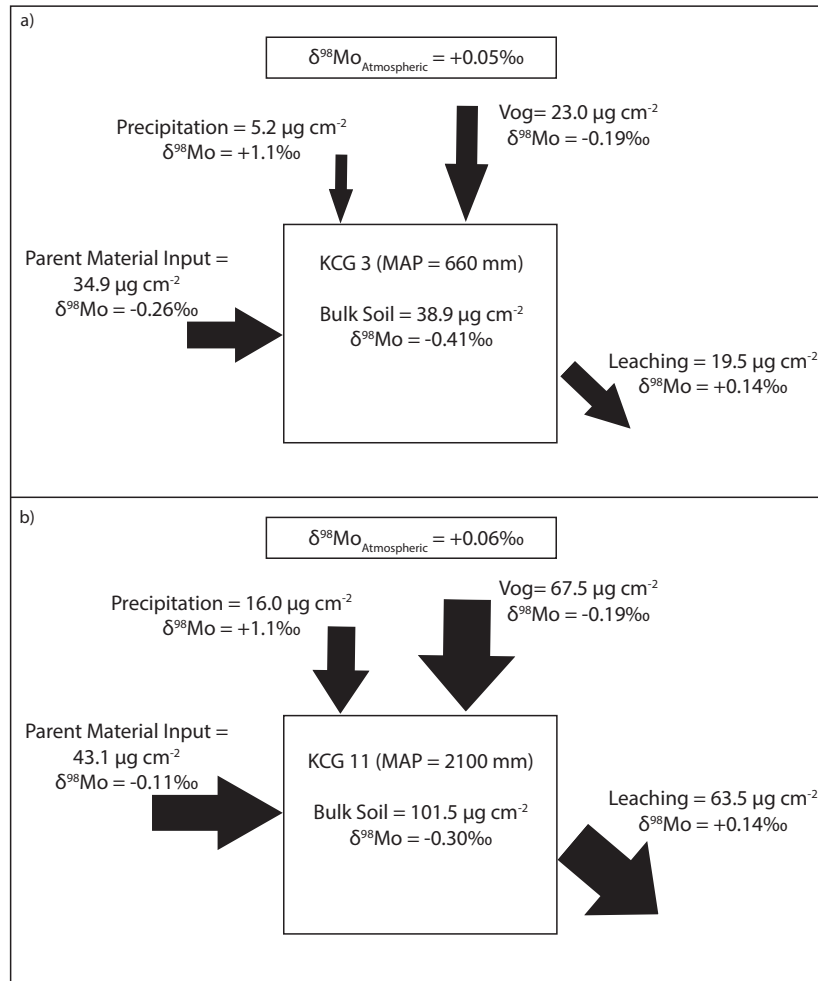


Figure 3.7: Box model of Mo inputs to the driest site along the KCG (MAP = 660 mm) (a) and the wettest site along the KCG (MAP = 2,100 mm) (b).

As MAP increases, the proportion of the atmospheric flux from precipitation relative to vog increases, and the $\delta^{98}\text{Mo}$ signature from atmospheric sources increases. The leaching flux increases with increasing MAP and is enriched in heavy Mo isotopes ($\delta^{98}\text{Mo} = +0.14\text{‰}$). The bulk soil is residually enriched in light Mo isotopes (KCG 3 $\delta^{98}\text{Mo} = -0.41\text{‰}$, KCG 11 $\delta^{98}\text{Mo} = -0.30\text{‰}$)

3.4.4 Terrestrial Mo cycling: Comparison with older soils

The data collected for this study can be compared to a recently published dataset from the island of Maui that investigates soil Mo isotope dynamics on an older (410 kyr), redox influenced, basaltic climate gradient (Siebert et al., 2015). The Maui Climate Gradient (MCG) is wetter than the KCG (850 mm yr⁻¹ to 5,050 mm yr⁻¹, versus 660 mm yr⁻¹ to 2,100 mm yr⁻¹) and experiences fluctuating redox conditions that control soil dynamics (Miller et al., 2001; Schuur and Matson, 2001). Generally, τ Mo for soil profiles along both the MCG and the KCG show the same relative pattern of more positive values in the surface and more negative values in the subsurface. However, integrated soil profile τ Mo along the MCG show moderate losses (τ Mo values range from -2% to -41%), in contrast to overall gains seen in the KCG. One possible explanation for the differences in τ Mo between the two gradients is that redox processes in the MCG that deplete Fe and Mn (oxyhydr)oxides and lead to the destabilization of mineral-OM interactions cause greater Mo losses (King et al., 2014; Thompson et al., 2011). Further, the long timescale of intense weathering conditions in MCG soils likely allow leaching losses of both bedrock and atmospheric-derived Mo to outweigh gains from atmospheric inputs.

The Mo isotopic composition of the MCG is similar in both magnitude (when re-normalized to NIST SRM 3134) and direction of fractionation compared to the KCG. Similar to most KCG soils, the MCG surface soil horizons have heavier $\delta^{98}\text{Mo}$

values ($\delta^{98}\text{Mo}$ values range from -0.10‰ to -0.02‰) than the deep soil horizons ($\delta^{98}\text{Mo}$ values range from -0.36‰ to -0.53‰) and there is a large amount of variability through the soil profile. Additionally, horizons that exhibit less Mo loss (more positive τ Mo) have heavier $\delta^{98}\text{Mo}$ values, similar to the KCG. Siebert et al. (Siebert et al., 2015) attribute the variability of the Mo isotopic composition to multiple fractionation mechanisms, which involve Mo-OM interactions, the influence of SRO Fe (oxyhydr)oxides, and redox oscillations. They also suggest that the addition of atmospheric Mo—via Asian dust deposition and marine-influenced precipitation—are a possible source of heavy Mo to surface horizons, though these isotopic signatures may be dampened over time as a function of soil processes and redox status. Although not well constrained, vog input has also been suggested as a significant source of material to Maui soils, contributing between 30-48% of the current soil sulfur pool (Bern et al., 2015a).

3.4.5 Implications for global Mo cycling

Mo isotope behavior is of great interest because of its potential utility as a proxy from biogeochemical processes including redox (Anbar et al., 2001; Barling and Anbar, 2004; Siebert et al., 2003). If Mo isotopes are fractionated during rock weathering or during soil processes, then it is useful to know if they are fractionated in predictable ways, for example, as a function of soil age, lithology, or climate. A predicted retention of light Mo isotopes in the soil profile or onto particulates in aqueous environments has been used to explain the heavy global riverine dissolved load but there have only been limited soil Mo isotope data (Archer and Vance, 2008;

Siebert et al., 2015; Voegelin et al., 2012). This is the first study to measure the Mo isotopic composition of the soil solid and the dissolved groundwater phase simultaneously providing evidence that light Mo isotopes are retained in the soil while heavy isotopes are leached (Figure 3.7).

A general conceptual model of a soil mixing zone (Table 3.6, Figure 3.7) can be further distilled to a reservoir where inputs to soils are separated into different pools based on their chemical properties. Mo is partitioned into pools based on its adsorptive affinity to OM and secondary minerals, with the adsorption being very sensitive to changes in pH. Stronger Mo adsorption is expected under more acidic conditions (Kabata-Pendias, 2010; Wichard et al., 2009). As soil mineral and OM composition evolve, or as soils become more acidic from a number of processes including OM decomposition, vog input, and the weathering and leaching of base cations, the retention of Mo in soil is altered, which likely changes Mo leaching loss or redistribution in soil as well. In this sense, soil patterns of Mo loss, gain, and isotopic fractionation are a function of the integrated history of the soil as well as the relative fluxes of different inputs into the profile.

Many studies have quantified inputs of metals to soil from the atmosphere (Hernandez et al., 2003; Nicholson et al., 2003), but only a handful of those studies have been able to put those fluxes in the context of rock weathering input fluxes because few soils have well-constrained age and well-characterized bedrock (Bern et al., 2015a; Clergue et al., 2015; Kraepiel et al., 2015; Monastera et al., 2004). Evidence from the KCG that atmospheric inputs strongly influence soil Mo isotopic

compositions has important implications for the predictive ability of the Mo isotopic signatures. The open system cycling of Mo between the atmosphere, soils, and the oceans can buffer the Mo isotopic signature of riverine fluxes because the loss of heavy soil Mo isotopes is dampened by the addition of heavy Mo from atmospheric inputs. A similar conclusion of the buffering effect of open system cycling was made for Fe isotopes based on the analysis of lateritic profiles in Cameroon (Poitrasson et al., 2008). Over long timescales, the dissolved flux of Mo to the ocean does not change simply as a function of the residual enrichment of light Mo in the soil and the loss of heavy Mo into the dissolved phase, but instead is modulated by replenishment of Mo from atmospheric sources.

In the case of Hawaii, atmospheric inputs appear to be dominated by vog and precipitation, but the source of atmospheric inputs can vary by location. In older soils or soils less isolated from centers of fossil fuel combustion, dust and anthropogenic inputs of Mo may become a significant exogenous source (i.e. Chappaz et al., 2012; Lane et al., 2013; Miller et al., 2011; Siebert et al., 2015). This implies that the riverine input of Mo to the oceans represents a balance between weathering processes and atmospheric inputs, which has important implications for the Mo isotopic proxy.

3.5 Conclusion

Globally, the dissolved riverine Mo flux is isotopically heavy; suggesting that isotopically light Mo must be retained in soils or in the riverine particulate load. In this study, the isotopic composition of soil Mo deviates from bedrock values,

consistent with expectations for retention of lighter Mo in soils. Additionally, groundwater is enriched in heavy Mo isotopes (average $\delta^{98}\text{Mo} = +0.14\text{‰}$), providing evidence that pedogenic processes fractionate Mo isotopes. We find that 12% of total Mo is associated with C_{org} and that Mo-OM interactions likely play a larger role in driving the short-term cycling of Mo compared to Fe (oxyhydr)oxides. Net accumulation of Mo across all sites along the KCG correlated with increasing OM content and a concomitant increase in MAP. We propose that the gains in Mo relative to bedrock are attributed to atmospheric inputs of Mo and the preservation of these inputs depends strongly on Mo-OM interactions.

The significance of atmospheric inputs has been previously unaccounted for but our calculations suggest that they can equal bedrock contributions on 5-15 kyr timescales. Furthermore, atmospheric inputs of Mo are enriched in isotopically heavy Mo isotopes and change the net isotopic composition of soils. Our isotopic mass balance shows that large precipitation and vog inputs exist, and that the absolute gains of Mo expressed in current soil data reflect multiple exogenous sources. The observed correlations of Mo and OM and the influence of atmospheric inputs suggest that the atmospheric input of Mo to soils should not be underestimated, nor should the isotopic composition of dissolved Mo in transit from bedrock to soil to the ocean be regarded as a simple function of age and weathering status.

3.6 Acknowledgements

We thank Daniel Swanson of Greenwell Farms and Ric Lopez of the U.S. Forest Service in Hilo, for volunteering to collect precipitation samples. Amanda McCutcheon of the National Parks Service, Charles Dawrs of the Hualalai Resort, and Rick Strojny of Napu'u Water are thanked for their assistance in collecting groundwater. Allen Wall is thanked for sharing historical precipitation records. Nina Bingham is thanked for her help in collection of soil. Andy Ungerer and YanPing Qian are thanked for their analytical assistance. NSF award 1053470 supported this work.

Chapter 4: Molybdenum isotope fractionation during adsorption onto organic matter

Elizabeth King, Steven Perakis, and Julie Pett-Ridge

ABSTRACT

Molybdenum (Mo) isotope fractionation during adsorption onto organic matter (OM) is an unconstrained factor of Mo geochemistry. In this study, Mo isotope fractionation was investigated during adsorption onto insolubilized humic acid (IHA), a surrogate for OM, as a function of time (2 – 170 h) and pH (2 – 7). For the time series experiment, performed at pH 4.2, a steady-state was reached between Mo adsorbed onto IHA and dissolved Mo after 26 hours. We found the average Mo isotope fractionation between the solution and the IHA ($\Delta^{98}\text{Mo}_{\text{solution-IHA}}$) to be 1.39‰ ($\pm 0.16\text{‰}$, 2σ , based on $^{98}\text{Mo}/^{95}\text{Mo}$ relative to the NIST 3134 standard). For the pH series experiment, as pH increased from 2.0 to 6.9, Mo adsorption decreased from 47% to 26% and $\Delta^{98}\text{Mo}_{\text{solution-IHA}}$ increased from 0.82‰ to 1.79‰. We also evaluated natural Mo isotope patterns in precipitation, foliage, organic horizon, surface mineral soil, and bedrock from 12 forested sites in the Oregon Coast Range; the average Mo isotope fractionation factor observed between precipitation inputs and organic horizon soil was 2‰. Fractionation during adsorption to OM is similar in magnitude and direction to prior observations of Mo fractionation during adsorption onto Fe- and Mn- (oxyhydr)oxides. Mineral soil Mo accumulation and isotope signatures were positively correlated with soil carbon and negatively correlated with soil pH. This suggests that increasing OM content at low pH leads to greater Mo adsorption from the dissolved phase, and is consistent with IHA experiment results indicating that lower pH soils have greater Mo adsorption. A lack of Mo isotopic offset observed between mineral soil and foliage further suggests

little or no fractionation during plant uptake. Our finding that OM influences Mo isotope composition by preferentially adsorbing light Mo has important implications for the role of OM as a driver of trace metal retention and isotope fractionation patterns in soils, as well as implications for the interpretation of the sedimentary Mo record and its use as a paleoredox tracer.

4.1 Introduction

Molybdenum (Mo) is an essential micronutrient and a redox sensitive trace metal. Because of its biological importance and unique behavior coupled to redox state, many studies have investigated the isotopic fractionation of Mo to determine its utility as a tracer of biogeochemical processes (Anbar, 2004; Wiederhold, 2015). In terrestrial environments Mo can limit biological N₂ fixation (Barron et al., 2008; Rousk et al., 2016; Silvester, 1989; Wurzbürger et al., 2012), and Mo isotopes may fractionate during uptake by N₂ fixing bacteria (Liermann et al., 2011; Wasylenko et al., 2007; Zerkle et al., 2011). In marine environments, the accumulation of isotopically distinct Mo in sediments under varying redox conditions has been used to determine patterns of ocean oxygenation throughout Earth history (Kendall et al., 2015; Pearce et al., 2008; Siebert et al., 2003). Interpretations of Mo isotopes as a tracer of redox state rely on assumptions that Mo isotope fractionation is a function of adsorption onto iron (Fe)- and manganese (Mn)- (oxyhydr)oxides (Anbar, 2004; Arnold, 2004; Siebert et al., 2003) and that riverine input to the ocean is well-constrained (Archer and Vance, 2008; Neubert et al., 2011; Pearce et al., 2010). However, there is growing evidence that Mo adsorption onto organic matter (OM) is

a driver of Mo biogeochemistry in both soils (King et al., 2016, 2014; Marks et al., 2015; Siebert et al., 2015; Wichard et al., 2009) and marine environments (Algeo and Lyons, 2006; McManus et al., 2006; Wagner et al., 2017). Thus, the controls on Mo adsorption onto OM and the potential resulting fractionation of Mo isotopes need to be determined.

Molybdenum adsorbs onto crystalline and non-crystalline oxides, clays, and organic substances. In oxic conditions, the dominant aqueous species of Mo is the tetrahedrally configured molybdate (Mo(VI)O_4^{2-}) oxyanion at circumneutral pH. With decreasing pH, Mo(VI)O_4^{2-} protonates forming octahedrally configured species (H_2MoO_4 and HMoO_4^-) that persist in solutions when $\text{pH} < 5$ (Oyerinde et al., 2008; Tkac and Paulenova, 2008). Adsorption of dissolved Mo onto clays, crystalline and non-crystalline aluminum (Al), and Fe- and Mn- (oxyhydr)oxides is well-documented in laboratory studies, and is thought to be controlled by ligand exchange with surface hydroxyl ions (Goldberg et al., 1996). Mo adsorption onto these oxide phases is greatest at low pH (3 – 5) and decreases with increasing pH (Bibak and Borggaard, 1994; Goldberg et al., 1996; Karimian and Cox, 1978). The accumulation of Mo in organic-rich soils has been attributed to the adsorption of Mo onto tannins and tannic-like substances (Bellenger et al., 2007; Wichard et al., 2009). Similar to adsorption onto clays and oxides, Mo adsorption in organic-rich soils is pH-dependent, with maximum adsorption between pH 4 – 5 and decreasing adsorption up to pH 9 (Bibak and Borggaard, 1994; Karimian and Cox, 1978; Wichard et al., 2009).

Existing evidence for Mo fractionation during adsorption comes from studies of Fe- and Mn- (oxyhydr)oxides, where light Mo isotopes are preferentially adsorbed, resulting in the enrichment of heavy Mo in the dissolved phase ranging from 0.8‰ to 2.9‰ (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011, 2008). Isotope fractionation has been attributed to the aforementioned changes in coordination in the dissolved phase from tetrahedral to octahedral, with adsorption of the octahedral species (Barling and Anbar, 2004; Goldberg et al., 2009; Siebert et al., 2003; Tossell, 2005; Wasylenki et al., 2011, 2008). Heavy Mo isotopes are fractionated into the stronger-bonded tetrahedral species and light isotopes are fractionated into the weaker-bonded octahedral species; octahedral Mo species are more particle-reactive compared to tetrahedral Mo species (Siebert et al., 2003). Thus, scavenging of Mo during adsorption preferentially acts on the lighter Mo isotope pool, consistent with observations of lighter Mo isotope ratios associated with Fe- and Mn- (oxyhydr)oxides (Siebert et al., 2003; Tossell, 2005).

Despite progress in understanding how Mo isotopes fractionate during adsorption to Fe- and Mn- (oxyhydr)oxides, it remains unknown whether and how Mo isotopes may fractionate during adsorption onto OM. In natural samples, OM often forms intimate associations with minerals, and pure OM is difficult to extract without generating artificial isotope effects. Results of X-ray adsorption spectroscopy (XAS) from organic-rich soils show that Mo binds to OM through ligand exchange as an octahedrally-coordinated complex, comparable to Mo adsorption onto Fe- and Mn- (oxyhydr)oxides (Bellenger et al., 2007; Dahl et al., 2010; Wichard

et al., 2009). In addition, data from humid, montane, and OM-rich soils indicate that the Mo isotopic composition of mineral soil is more strongly correlated with OM content than Fe- and Mn- (oxyhydr)oxide content, suggesting that Mo isotope fractionation may be occurring during adsorption onto OM in soils (King et al., 2016; Siebert et al., 2015).

The goal of this study is to assess whether Mo isotopes are fractionated during adsorption onto OM. We chose to focus on measuring isotope fractionation that arises in the terrestrial environment to better constrain the mechanisms fractionating Mo in soils, potentially influencing riverine Mo fluxes to the marine environment. To avoid the artificial isotope effects of extracting OM from natural soil samples where there may be mixing of minerals and OM, we measured Mo isotopic fractionation using a purified form of OM, insolubilized humic acid (IHA) (Bigalke et al., 2010; Chen et al., 2009; Khalili and Al-Banna, 2015; Seki and Suzuki, 1995; Weber et al., 2006). We also characterized the Mo isotopic composition of OM from the organic (O) horizon of 12 temperate forest sites. To more broadly evaluate effects of open-system cycling of Mo, we measured the Mo isotopic composition in a vertical cross-section of atmospheric deposition, foliage, mineral soil, and bedrock. In choosing to first quantify Mo fractionation during adsorption to IHA, the goal was to directly test whether Mo adsorption onto OM produced a reservoir of isotopically-light Mo, and then use those results to understand fractionation patterns in natural environments.

4.2 Methods

4.2.1 *Insolubilization of humic acid and preparation of Mo stock solution*

We formed insolubilized humic acid (IHA) using Sigma Aldrich humic acid based on the methods of Seki and Suzuki (1995) and Bigalke et al., (2010). During insolubilization, 5 g of humic acid was pretreated with 2 M CaCl_2 to convert it to a Ca salt to prevent the rapid dehydration of acidic groups, and was then heated for 2 hours in a muffle furnace at 330 °C. The IHA was then ground using an agate mortar and pestle, and washed two times with 18.2 MΩ ultrapure water. It was further purified by rinsing: once in a 1 M HNO_3 solution, once in a concentrated HF:HCl solution (2:1), and twice in a concentrated HCl solution. All rinses were performed at 70°C with ultrapure acid. The IHA was shaken for 20 minutes per rinse cycle before centrifugation at 3800 rpm for 10 minutes. Following the final rinse with concentrated HCl, the 5 g IHA pellet was dried down, powdered, and stored in an acid-washed plastic bottle until subsampling. Though insolubilization of humic acid can decrease the number of reactive of reactive sites due to condensation reactions, particularly phenolic-type groups (Seki and Suzuki, 1995; Weber et al., 2006), it does not alter the complexing properties of those functional groups (Bigalke, 2010). Therefore, Mo adsorption onto IHA is a proxy for Mo adsorption onto natural OM samples. IHA blanks were $< 1 \text{ ng Mo mg}^{-1} \text{ IHA}$ (compared to upwards of $2 \text{ } \mu\text{g Mo g}^{-1} \text{ IHA}$ in the Mo adsorption experiments). Stock solutions of Mo were prepared in acid-washed Teflon by dissolving reagent grade sodium molybdate dihydrate ($\text{Na}_2\text{MoO}_4 \bullet 2\text{H}_2\text{O}$) in 0.1 M KNO_3 .

4.2.2 Sorption experiments

To determine appropriate proportions for the experimental setup, a matrix of 12 samples with a range of IHA mass (3.4 to 18.4 mg IHA) and Mo concentrations (2, 5, 10, and 20 $\mu\text{g mL}^{-1}$) was measured over a seven-day period. The goal of this experiment was to identify a Mo:IHA ratio that would not result in the complete removal of Mo from solution, to ensure a measurable fractionation between solid and solution. For each Mo:IHA combination, duplicate samples comprised of 10 mL of Mo stock solution and IHA were weighed into acid-washed 15 mL polypropylene centrifuge tubes and put on a rotary shaker under ambient temperature and light conditions. After seven days, samples were centrifuged at 3800 rpm for 30 minutes and the supernatant was collected, filtered through a 0.45- μm syringe top filter, evaporated to dryness, and re-suspended in 0.5 M HNO_3 for elemental analysis. The IHA residue was rinsed with 18.2 M Ω ultrapure water, centrifuged at 3800 rpm for 10 minutes, digested on a hot plate using 8 mL of concentrated HNO_3 and 2 mL of H_2O_2 , and re-suspended in 0.5 M HNO_3 . Samples were diluted for Mo concentration analysis on a Thermo X-Series II inductively couple plasma mass spectrometer (ICP-MS). Mixed element standards were prepared as calibration standards and the USGS BCR-2 rock standard was monitored as an external standard and agreed within 5% of published concentrations. Concentrations and standard deviations were recorded for each sample point. Based on these results, we choose a Mo:IHA mass ratio for the adsorption experiments of 15:1 ($\mu\text{g Mo:mg IHA}$), which captured an intermediate range of Mo adsorption (40-70%) onto the IHA (Figure B.1).

For the time and pH series experiments, 3.5 mg of IHA was weighed into 15 mL polypropylene centrifuge tubes and 10 mL of a $5 \mu\text{g mL}^{-1}$ Mo stock solution in 0.1M KNO_3 was added. Preliminary experiments suggested that acid leaching from polypropylene centrifuge tubes could influence solution pH. Therefore, centrifuge tubes were not acid-washed and instead were rinsed with 18.2 M Ω ultrapure water and pre-conditioned with 0.1 M KNO_3 . All the solutions in the time series were adjusted to pH 4.2 using 0.1 M HNO_3 . The solutions in the pH experiments ranged from pH 2 to pH 7 (Table 4.1). The initial pH of each solution was adjusted to the desired concentration using 0.1 M HNO_3 or 0.1 M NaOH . The pH experiment was not extended to values greater than pH 7 because: 1) a wide range of natural environments fall between pH 2 to pH 7 and 2) in alkaline solutions IHA solubilizes, compromising the integrity of the adsorption experiment (Bigalke et al., 2010; Seki and Suzuki, 1995). In order to avoid artificial Mo speciation and isotope fractionation effects, no buffer was added to the solutions. For the time series experiment, samples were collected at eight time steps between two hours and seven days. For the pH experiment, samples were removed from the rotary shaker after five days. The solutions and IHA residue were isolated and prepared for elemental analysis following the procedures described above for the Mo-IHA matrix experiment. Samples were diluted for trace element concentration analysis by ICP-MS. On average, the final pH was 0.2 units lower than the initial pH for both experiments. Procedural blanks for Mo were less than 0.05% of the Mo stock solution. Dissolved organic carbon was also measured in solutions after the IHA experiment on a

Shimadzu TOC-V CSH Analyzer to ensure that IHA was not solubilized during the sorption experiment (Table B.1).

4.2.3 Oregon Coast Range samples

We examined natural patterns of Mo isotope variation across 12 forested sites in the Oregon Coast Range. The sites span both basaltic and sedimentary bedrock—seven sites were basaltic, three were sedimentary, and two were mixed basaltic and sedimentary. Basaltic sites were formed on Siletz River Volcanics, Tillamook Volcanics, and Lee’s Falls Formations; sedimentary sites were formed on Nestucca, Yamhill, and Tyee formations and include sandstone, siltstone, and mudstone units (Hynicka et al., 2016; Marks et al., 2015). The Oregon Coast Range is characterized by a Mediterranean climate regime where nearly all precipitation occurs in the fall, winter, and spring. Mean annual precipitation (MAP) ranges from 1,930 mm year⁻¹ to 3,230 mm year⁻¹ and temperatures range from a minimum of 4 to 6°C to a maximum of 13 to 17°C. All of the study sites are single species plantations of the native conifer tree Douglas-fir (*Pseudotsuga menziesii*) ranging in age from 22 years to 37 years old (Hynicka et al., 2016; Marks et al., 2015). Sites were chosen to span a range of mineral soil carbon (C) (from 49 mg C g⁻¹ to 167 mg C g⁻¹, 0-10 cm) concomitant with a wide range of soil pH_(H2O) (from 3.9 to 6.5, 0-10 cm) (Table 4.2). A full description of the Oregon Coast Range sites can be found in Marks et al., (2015) and Hynicka et al., (2016).

In the summer of 2012, first-year foliage was collected from the upper one-third of three different trees per site. Foliage was separated by age class, and

combined into one sample per site. Organic (O) horizon soil was collected as grab samples from five locations per site and combined into one sample. Samples were homogenized in the laboratory and sorted by hand to remove any mineral soil, rocks, or living moss. The average C content for the O horizon samples was 518 mg C g^{-1} and the average Fe content was 1.8 mg Fe g^{-1} , which confirms there is no mineral soil in these O horizon samples, making them a good field test of Mo-OM interactions (Table B.2). Mineral soil (0 – 10 cm depth) was collected using a 6.8 cm diameter corer. Three replicate cores were collected per site and pooled into a single composite sample, homogenized, and sieved to 2 mm. Bedrock from sites 19 (basaltic), NFT (basaltic), GV1 (sedimentary), and Trask (mixed) were collected in the summer of 2013 using a portable drill (Hynicka et al., 2016; Marks et al., 2015). O horizon and mineral soil pH was measured on field moist samples following a 30-minute equilibration period in a 10:1 and 2:1 soil-water mixture, respectively. Organic matter fractions in O horizon soil were previously reported in Perakis et al., (2017) based on the van Soest extraction protocol (van Soest and Wine, 1967) (Table B.2). Event-based sampling of precipitation occurred in the winter and spring of 2013 using 1.0 L acid-washed bottles affixed with a 16-cm polypropylene funnel and a 2-mm mesh screen at sites GV1 and 143. Precipitation samples were acidified with 1% HNO_3 , evaporated on a hotplate, refluxed in concentrated HNO_3 , dried down, and re-suspended in 10 mL of 0.5 M HNO_3 (Hynicka et al., 2016; Marks et al., 2015). Following elemental analysis, precipitation was combined into a composite sample to allow for Mo isotopic analysis.

Foliage, O horizon, and mineral soil were oven dried for 48 hours, powdered in an agate ball mill, and microwave digested. Foliage was digested in 8 mL of ultrapure HNO₃ and 2 mL H₂O₂. Samples of O horizon, mineral soil, and bedrock were digested in 6 mL of ultrapure HNO₃, 2 mL of ultrapure HCl, and 2 mL of ultrapure HF. Sites were previously analyzed for C and N concentrations with a Costech ECS 4019 at the USGS Forest and Rangeland Ecosystem Science Center in Corvallis, OR and by ICP-OES (Fe, Al) and ICP-MS (Mo, Nb) at Oregon State University (Marks et al., 2015).

Marks et al., (2015) used mineral soil and bedrock data for Mo and the immobile element niobium (Nb) to calculate Mo mobility via the mass transfer function:

$$\tau_{Mo} = \left[\frac{C_{Mo,w} C_{Nb,p}}{C_{Nb,w} C_{Mo,p}} - 1 \right]$$

where C is the concentration of Mo or Nb and w and p refer to the weathered soil and parent material (bedrock), respectively (Brimhall and Dietrich, 1987; Chadwick et al., 1990). A negative τ_{Mo} in mineral soil samples represents Mo loss and a positive τ_{Mo} represents Mo gain relative to bedrock.

4.2.4 Mo isotopic composition

Isotopic measurements were performed on a Nu Plasma multicollector ICP-MS (MC-ICP-MS) at Oregon State University using a double spike procedure (King et al., 2016; Siebert et al., 2001). A ⁹⁷Mo – ¹⁰⁰Mo double spike was added to an aliquot

of each sample (samples ~600 ng Mo) targeting a $^{97}\text{Mo}/^{98}\text{Mo}$ ratio of 3, though results were stable across a $^{97}\text{Mo}/^{98}\text{Mo}$ range of 1 to 10. To allow for homogenization between sample and double spike, samples were refluxed overnight in 0.5 M HNO_3 , dried down, and re-suspended in a 6 mL 1 M HF – 0.5 M HCl solution with 200 μL of H_2O_2 to ensure complete oxidation. Column chromatography methods are outlined in King et al., (2016), and modified from Pearce et al., (2009). Briefly, clean Bio-Rad AG1-X8 anion resin is used to separate Mo from possible elemental interferences including iron (Fe), manganese (Mn), and zirconium (Zn). Mo is eluted in 1 M HCl, dried down, and re-suspended in 0.5 M HNO_3 for isotopic analysis. Column chromatography was repeated to ensure complete separation of Mo from the IHA or soil matrix.

Isotope measurements are made relative to NIST SRM 3134 (Lot No.: 891307) (Goldberg et al., 2013; Greber et al., 2012) and are reported in delta notation ($\delta^{98}\text{Mo}$) for $^{98}\text{Mo}/^{95}\text{Mo}$ ratios:

$$\delta^{98}\text{Mo} = \left[\frac{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{sample}}}{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{NIST SRM 3134}}} - 1 \right] \cdot 1000$$

Repeated measurements of an in-house standard (Alfa Aesar Specpure® Product No.: 35758 (Lot No.: 23-16504a)) and USGS rock standards BCR-2, BHVO-2, and SDO-1, over eighteen months yielded $\delta^{98}\text{Mo}$ values of -0.15‰, 0.00‰, -0.04‰, and +0.80‰. External reproducibility of the Alfa Aesar in-house standard was $\pm 0.11\text{‰}$.

(2σ). When sample volume allowed for it, duplicate analyses were measured and agreed within external reproducibility. Reported uncertainties reflect the long-term external reproducibility of the Alfa Aesar in-house standard.

4.2.5 Data analysis

Relationships among Mo concentrations, Mo isotopic composition, and soil chemical parameters were determined with least-squares linear regression for both the IHA laboratory experiments and the Oregon Coast Range field data. For the laboratory data, we used linear regression of adsorption concentrations versus time, starting initially with the complete time series, with stepwise removal of the earliest time steps to determine the time step after which there was no significant temporal change in Mo adsorption (time steps listed in Table 4.1). The $\delta^{98}\text{Mo}$ of the IHA and solution was used with the measured Mo concentrations to determine the isotopic composition of the initial Mo stock solution, which was compared to the measured $\delta^{98}\text{Mo}$ of the initial Mo stock solution. This comparison was used to calculate that an average of 11% Mo was lost from the solution during the filtration and purification steps, which was incorporated into the error propagation for the calculation of Mo adsorption values. The potential Mo loss has no effect on the isotopic composition of the samples or on the calculation of Mo fractionation factors. For the field data, we determined significant differences between the $\delta^{98}\text{Mo}$ of foliage, O horizon, and mineral soil using Analysis of Variance (ANOVA), blocked by site, with Tukey post-hoc comparison tests. Regression analyses and statistical significances between Mo and soil parameters (organic matter content, pH, Fe- (oxyhydr)oxide content) were

determined using a p -value < 0.10 . All statistics were run using Systat Software, Inc. (Version 13.1).

4.3 Results

4.3.1 Insolubilized humic acid experiment: Mo adsorption and isotopic composition

In the time series experiment, performed at pH 4.2, the adsorption of Mo onto IHA increased from $1.8 \mu\text{g Mo mg}^{-1} \text{IHA}$ to $8.2 \mu\text{g Mo mg}^{-1} \text{IHA}$ between 2 and 26 hours and remained broadly constant throughout the rest of the seven-day sampling period (Figure 4.1a). Statistically, there was a significant temporal trend in Mo adsorption from the 2-hour time step to the end of the experiment on Day 7 ($p = 0.007$). With the stepwise removal of the 2-hour time step, the remaining time steps showed no significant change in Mo adsorption from 26 hours to the end of experiment on Day 7 ($p = 0.13$). Therefore, Mo adsorption did not change significantly from 26 hours onwards. In the pH series experiment, the adsorption of Mo onto IHA decreased from a maximum of $13.3 \mu\text{g Mo mg}^{-1} \text{IHA}$ to a minimum of $2.7 \mu\text{g Mo mg}^{-1} \text{IHA}$ with increasing pH between pH 2 – 7 (Figure 4.1b) ($r^2 = 0.56$, $p = 0.012$). For consistency, results refer to the final pH of the experiment (Table 4.1).

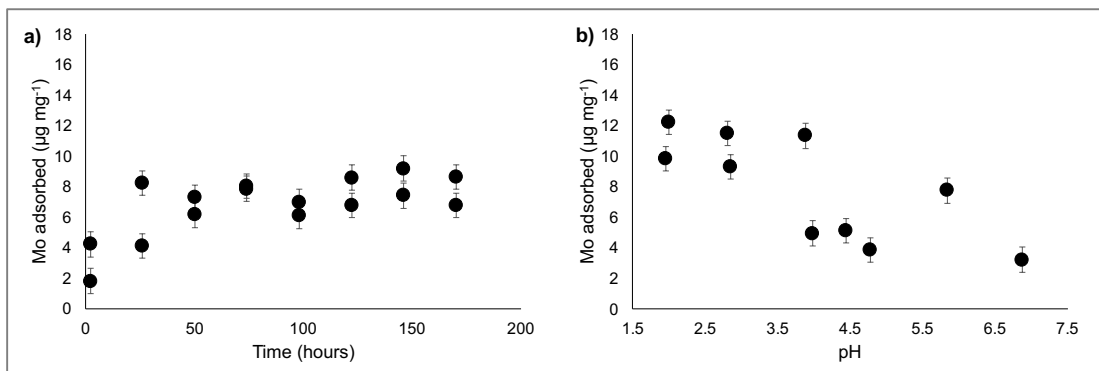


Figure 4.1: Mo adsorption onto insolubilized humic acid (IHA) as a function of (a) time (hours) and (b) pH.

Error bars represent the error propagation assuming a 5% error during measurement of Mo concentrations and an average 11% error associated with Mo loss during filtration of Mo solution from IHA.

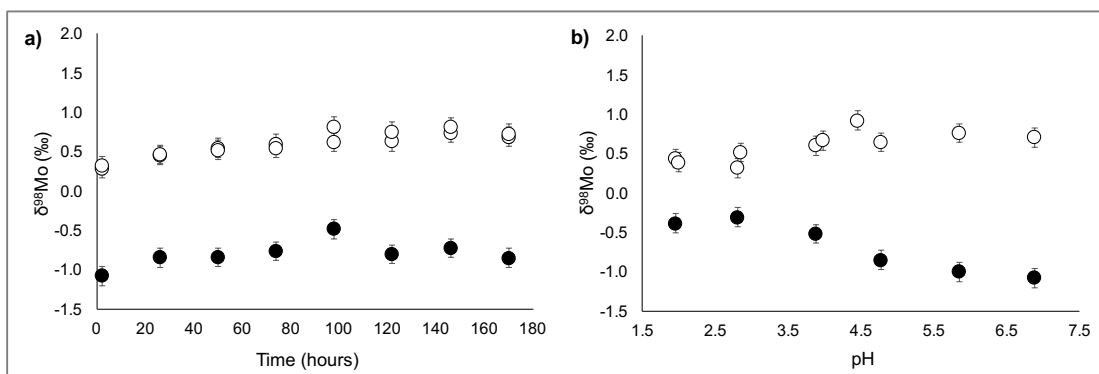


Figure 4.2: Mo isotopic composition ($\delta^{98}\text{Mo}$) of solution (open circles) and IHA (closed circles) versus (a) time (hours) and (b) pH.

Light Mo is preferentially adsorbed onto the IHA complex and heavy Mo remained in solution. Error bars represent $\pm 2\sigma$ of the external reproducibility ($\pm 0.11\text{‰}$). Initial Mo stock solution $\delta^{98}\text{Mo} = +0.20\text{‰}$.

Table 4.1: IHA experiment: Duration, pH, Mo adsorbed onto insolubilized humic acid (IHA) and fractionation of Mo isotopes

Sample	Duration (hours)	Initial pH	Final pH	Mo in solution μg	Mo adsorbed %	Mo adsorbed $\mu\text{g mg}^{-1}$	$\delta^{98}\text{Mo}_{\text{solution}}$ ‰	$\delta^{98}\text{Mo}_{\text{IHA}}$ ^a ‰	$\Delta^{98}\text{Mo}_{\text{solution-IHA}}$ ‰
<i>Initial</i>				51.8			0.20		
<i>Time Series</i>									
D0	2	4.4	4.4	46.2	10.8	1.8	0.28	-1.08	1.36
	2	4.1	4.1	35.4	31.7	4.2	0.32	--	--
D1	26	4.4	4.1	23.9	53.9	8.2	0.45	-0.85	1.30
	26	4.3	4.2	40.0	22.8	4.1	0.46	--	--
D2	50	4.2	4.2	29.9	42.2	7.3	0.54	-0.84	1.39
	50	4.3	4.2	32.2	37.9	6.1	0.52	--	--
D3	74	4.2	4.1	26.7	48.5	7.9	0.59	-0.76	1.36
	74	4.3	4.2	27.8	46.4	8.0	0.54	--	--
D4	98	4.1	3.9	23.9	53.9	7.0	0.82	-0.49	1.30
	98	4.3	4.2	34.8	32.8	6.1	0.62	--	--
D5	122	4.1	4.3	31.5	39.2	6.8	0.62	-0.80	1.43
	122	4.3	4.1	26.1	49.7	8.6	0.75	--	--
D6	146	4.1	4.1	20.6	60.2	9.2	0.74	-0.73	1.46
	146	4.1	4.1	26.7	48.5	7.4	0.81	--	--
D7	170	4.4	4.2	30.9	40.3	6.7	0.69	-0.85	1.54
	170	4.3	4.2	28.6	44.8	8.6	0.73	--	--
Average		4.2	4.2	30.3	41.5	6.7	0.59	-0.80	1.39
<i>pH Series</i>									
pH 2	74	2.0	2.0	26.3	47.0	9.0	0.43	-0.39	0.82
	74	2.1	2.0	21.3	57.0	11.3	0.39	--	--
pH 3	74	2.9	2.8	11.7	76.5	10.9	0.31	-0.31	0.63
	74	2.9	2.8	26.7	46.2	8.5	0.51	--	--
pH 4	74	4.0	3.9	12.3	75.2	13.3	0.60	-0.52	1.12
	74	4.0	4.0	25.2	49.2	4.5	0.66	--	--
pH 5	74	5.2	4.8	31.8	35.9	3.4	0.64	-0.86	1.50
	74	4.8	4.4	21.3	57.1	4.7	0.92	--	--
pH 6	74	6.0	5.8	31.7	36.1	6.9	0.76	-1.01	1.76
	--	--	--	--	--	--	--	--	--
pH 7	74	7.5	6.9	36.8	25.9	2.7	0.70	-1.09	1.79
	--	--	--	--	--	--	--	--	--

^a Mo isotopic composition of IHA ($\delta^{98}\text{Mo}_{\text{IHA}}$) measured on samples during one analytical session. All isotope data was measured in duplicate and agreed within the 2σ external reproducibility on the in-house standard ($\pm 0.11\text{‰}$)

Adsorption of Mo onto IHA led to isotope fractionation where light Mo isotopes were preferentially adsorbed and heavy isotopes remained in solution (Table 4.1, Figure 4.2a). The initial isotopic composition ($\delta^{98}\text{Mo}$) of the Mo stock solution was +0.20‰ ($\pm 0.12\text{‰}$, 2σ , $n=6$). For the time series experiment, the $\delta^{98}\text{Mo}$ of the solution ranged from +0.28‰ at the 2-hour mark to +0.69‰ on Day 7 (maximum $\delta^{98}\text{Mo}$ of +82‰ on Day 4). The corresponding $\delta^{98}\text{Mo}$ of the IHA ranged from -1.08 ‰ at the 2-hour mark to -0.85‰ on Day 7. For the pH series experiment, the $\delta^{98}\text{Mo}$ of the Mo solution ranged from +0.31‰ at pH 2.8 to +0.92‰ at pH 4.4 and the $\delta^{98}\text{Mo}$ of IHA ranged from -0.31‰ at pH 2.8 to -1.09‰ at pH 6.9. The $\delta^{98}\text{Mo}$ of the IHA was only measured for one of the duplicates for each sample point and is recorded in Table 4.1.

On average, the Mo isotopic fractionation between the solution and the IHA ($\Delta^{98}\text{Mo}_{\text{A-B}} = \delta^{98}\text{Mo}_{\text{A}} - \delta^{98}\text{Mo}_{\text{B}}$) was 1.39‰ ($\pm 0.16\text{‰}$, 2σ) for the time series, corresponding to an average fractionation factor ($\alpha = (^{98}\text{Mo}/^{95}\text{Mo})_{\text{solution}} / (^{98}\text{Mo}/^{95}\text{Mo})_{\text{IHA}}$) of 1.0014. Closed-system equilibrium and Rayleigh fractionation models were developed using the experimentally determined fractionation factor ($\alpha_{\text{solution-IHA}} = 1.0014$) (Figure B.2). For the pH series experiment the $\Delta^{98}\text{Mo}_{\text{solution-IHA}}$ ranged from 0.63‰ to 1.79‰. Fractionation increased with increasing pH, with the highest $\Delta^{98}\text{Mo}_{\text{solution-IHA}}$ (1.79‰) occurring at pH 6.9 ($r^2 = 0.88$, $p = 0.049$).

4.3.2 Mo dynamics in the Oregon Coast Range

Major and minor element concentrations and site chemistry previously reported in Marks et al., (2015) and Perakis et al., (2017) for the Oregon Coast Range sites are summarized in Table 4.2 and can be paired with the Mo isotope data (Table 4.3). Foliage, O horizon, and mineral soil are all lighter than precipitation ($\delta^{98}\text{Mo}_{\text{precipitation}} = +1.15\text{‰}$) (Figure 4.3). The $\delta^{98}\text{Mo}$ of the foliage and the mineral soil appeared to be indistinguishable at 10 of 12 sites, and when assessed statistically across all sites, there was no significant difference between foliage and mineral soil ($p = 0.68$) (Figure 4.3). In contrast, when evaluated across all sites, the $\delta^{98}\text{Mo}$ of the O horizon was significantly lighter than both the foliage ($p = 0.04$) and the mineral soil ($p = 0.006$) (Figure 4.3).

We observed several important relationships between O horizon, mineral soil, and Mo geochemistry. Molybdenum concentrations in the O horizon were not significantly correlated to the amount of soluble C ($r^2 = 0.13$, $p = 0.24$) nor total C ($r^2 = 0.001$, $p = 0.91$), but did increase with lignin content ($r^2 = 0.43$, $p = 0.03$, Table B.3). As both O horizon pH increased and as the amount of soluble C extracted from the O horizon increased, the Mo isotopic composition becomes significantly lighter (pH: $r^2 = 0.43$, $p = 0.02$; soluble C: $r^2 = 0.39$, $p = 0.03$) (Table B.3). However, there were no significant correlations between Mo concentrations, isotopic composition, and other O horizon OM fractions (Tables B.2 and B.3). In the mineral soil τ Mo becomes more positive (net gain of Mo relative to bedrock) with increasing C content ($r^2 = 0.86$, $p = 0.002$) (Figure 4.4a) and $\delta^{98}\text{Mo}$ becomes heavier ($r^2 = 0.41$, $p = 0.02$) (Figure 4.4b).

Additionally, τ Mo and $\delta^{98}\text{Mo}$ of the mineral soil are negatively correlated with mineral soil pH; as soils become more acidic (lower pH), τ Mo increases ($r^2 = 0.46$, $p = 0.02$) (Figure 4.5a) and $\delta^{98}\text{Mo}$ values become heavier ($r^2 = 0.76$, $p < 0.001$) (Figure 4.5b). No significant correlations between τ Mo and Fe, or $\delta^{98}\text{Mo}$ and Fe (either total Fe or extractable Fe in the mineral soil or total Fe in the O horizon) were observed (all p values ≥ 0.10 , not shown).

4.4 Discussion

4.4.1 Mechanisms of Mo isotope fractionation on organic matter

Our laboratory experiments demonstrate that Mo isotopes fractionate during adsorption onto insolubilized humic acid (IHA), a proxy for natural OM. For the time series experiment, the $\Delta^{98}\text{Mo}_{\text{solution-IHA}}$ between Mo in solution and Mo adsorbed onto the IHA is 1.39‰ (Table 4.1), and after 26 hours the Mo adsorbed showed no significant change, suggesting a steady-state was reached between Mo in solution and adsorbed Mo (Figure 4.1a). When plotted as a potential Rayleigh fractionation, we find that the relationship between % Mo adsorbed and the isotopic offset between adsorbed Mo and Mo in solution fall on roughly parallel lines, which suggests closed-system equilibrium exchange (Figure B.2). Previous studies of both Mo adsorption processes onto mineral surfaces (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011) and adsorption processes of other metals onto IHA (Bigalke et al., 2010; Chen et al., 2009; Khalili and Al-Banna, 2015; Weber et al., 2006) all observe that equilibrium between the exchange complex and solution are

reached within the first 24-48 hours, aligning well with our results for the Mo-IHA complex.

The results of our pH experiment provide insight into the dissolved Mo species that may be most important for fractionation during adsorption onto OM. As solution pH increases from 2 to 7, we observe decreasing Mo adsorption (Figure 4.1b) and increasing $\Delta^{98}\text{Mo}_{\text{solution-IHA}}$ ranging from 0.82‰ to 1.79‰ (Figure 4.2b, Table 4.1). Because adsorption of oxyanions occurs via the protonation of either the adsorbing surface or the oxyanion (Balistrieri and Chao, 1990), at more acidic pH there will be a greater proportion of Mo adsorbed or protonated, and thus a smaller fractionation between adsorbed and dissolved Mo. Conversely, at high pH, a smaller proportion of total Mo becomes protonated. The Mo that does protonate to H_2MoO_4 and HMoO_4^- —and subsequently dissociates to MoO_3 and $\text{MoO}_3(\text{H}_2\text{O})_3$ —is preferentially comprised of light Mo isotopes since heavy Mo isotopes are fractionated into the stronger-bonded tetrahedral molybdate species (Figure 4.2b) (Goldberg et al., 2009; Oyerinde et al., 2008; Tossell, 2005).

Possible fractionation mechanisms during Mo adsorption on to OM include changes in coordination from tetrahedral to octahedral, equilibrium effects based on differences in bond strength, and kinetic effects of metal-ligand interactions (Goldberg et al., 2009; Kashiwabara et al., 2009; Malinovsky et al., 2007). Previous studies of Mo adsorption onto OM have used X-ray absorption fine structure spectroscopy (EXAFS) to determine the structure of Mo-OM complexation (Bellenger et al., 2007; Wagner et al., 2017; Wichard et al., 2009). In all of these studies,

octahedrally-coordinated Mo ligands form inner-sphere complexes with phenolic and catechol functional groups in tannin-like compounds or with α -hydroxy functional groups in malic acid, leading to Mo accumulation in OM rich reservoirs (Bellenger et al., 2007; Knobler et al., 1983; Wagner et al., 2017; Wichard et al., 2009). Although our dataset provides no evidence that adsorption of a minor Mo species is the mechanism leading to isotope fractionation, based on what is known about Mo isotope partitioning in other systems it is reasonable that light Mo is preferentially incorporated into an octahedrally-coordinated molybdic acid and/or as an organic ligand that is then able to bind to OM structures.

A compelling result of this study is that patterns of Mo adsorption and fractionation onto IHA were similar to the patterns observed in studies of Mo adsorption onto Fe- and Mn- (oxyhydr)oxides. The observation that adsorption onto both OM (this study) and Fe- and Mn- (oxyhydr)oxides (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011, 2008) leads to comparable isotope effects suggests that adsorption mechanisms are similar between the two substrates. This is significant for environments where there is potential for Mo to be adsorbed to either Fe- and Mn- (oxyhydr)oxides or OM because the two mechanisms could mask each other.

Table 4.2: Site properties for foliage, O horizon, and 0 – 10 cm mineral soils in the Oregon Coast Range

Site Name	Bedrock	MAP	Mo Concentrations					τ Mo
			Precipitation	Foliage	O horizon	Mineral Soil	O horizon excess	
		mm	pg g ⁻¹	ng g ⁻¹	ng g ⁻¹	ng g ⁻¹	ng g ⁻¹	
8	Igneous	2503	--	2	19	451	350	0.73
14	Igneous	2737	--	3	78	391	2480	-0.52
19	Igneous	2804	--	17	55	1002	2420	-0.68
BC1	Igneous	2476	--	16	23	928	350	2.93
Jensen	Igneous	1927	--	15	56	1189	1640	-0.52
NFT	Igneous	2160	--	16	62	978	1100	-0.55
Stein	Igneous	2275	--	3	25	579	260	0.46
GV1	Mixed	2866	5.80	12	64	1866	1130	0.75
54	Mixed	3227	--	3	66	1073	600	1.09
56	Sedimentary	2038	--	22	683	1116	1150	0.18
143	Sedimentary	2014	6.53	82	26	2993	970	2.11
Trask	Sedimentary	2712	--	8	147	1702	2590	1.18

Table 4.2. (continued)

Site Name	Mineral Soil pH	Mineral Soil C mg C g ⁻¹	Mineral Soil Fe mg Fe g ⁻¹	Reducible Fe mg Fe g ⁻¹	Mo Flux ^a		Mo residence time ^b	
					Litterfall g ha ⁻¹ year ⁻¹	Precipitation g ha ⁻¹ year ⁻¹	O horizon yrs	Mineral Soil yrs
8	5.4	108	91	10	0.01	0.19	1	295
14	5.1	63	89	10	0.01	0.21	5	871
19	5.3	61	99	7	0.04	0.22	3	458
BC1	4.6	167	66	10	0.04	0.19	2	767
Jensen	6.5	67	119	6	0.04	0.15	5	984
NFT	5.4	49	68	5	0.04	0.17	5	769
Stein	5.8	71	93	8	0.01	0.18	2	415
GV1	4.3	110	56	11	0.03	0.22	1	1675
54	5.1	139	79	7	0.01	0.25	0	472
56	5.4	57	35	5	0.05	0.16	56	1186
143	3.9	157	51	6	0.20	0.16	2	1813
Trask	4.6	98	60	8	0.02	0.21	9	1031

Table 4.3: Mo isotopic composition of precipitation, foliage, O horizon, mineral soil (0-10 cm) and bedrock in the Oregon Coast Range

Site Name	$\delta^{98}\text{Mo}^a$					$\Delta^{98}\text{Mo}^b$
	Precipitation ^c ‰	Foliage ‰	O-Horizon ‰	Mineral Soil ‰	Bedrock ‰	Precipitation - Excess ‰
8	--	-0.45	-0.86	-0.36	--	2.07
14	--	-0.03	-0.15	-0.15	--	1.31
19	--	-0.36	-0.25	-0.39	0.07	1.35
BC1	--	-0.11	-0.98	-0.16	--	4.05
Jensen	--	-0.38	-2.21	-0.55	--	4.05
NFT	--	-0.99	-1.47	-0.26	0.01	2.80
Stein	--	-1.21	-0.72	-0.67	--	1.80
GV1	1.15	0.08	-0.32	0.26	0.09	1.56
54	--	0.01	0.00	0.03	--	1.15
56	--	-0.42	-0.94	-0.51	--	1.55
143	1.15	-0.10	-0.16	0.25	--	1.22
Trask	--	-0.04	-0.26	-0.07	-0.10	1.43

^a Mo isotopic composition ($\delta^{98}\text{Mo}$) measured on samples in duplicate during one analytical session. Reproducibility was between $\pm 0.03\text{‰}$ to $\pm 0.10\text{‰}$, however error bars are reported as the 2σ external reproducibility on the in-house standard ($\pm 0.11\text{‰}$)

^b $\Delta^{98}\text{Mo}$ was calculated assuming constant precipitation $\delta^{98}\text{Mo}$ value of 1.15‰ across all sites

^c Precipitation is composite sample of site GV1 and 143

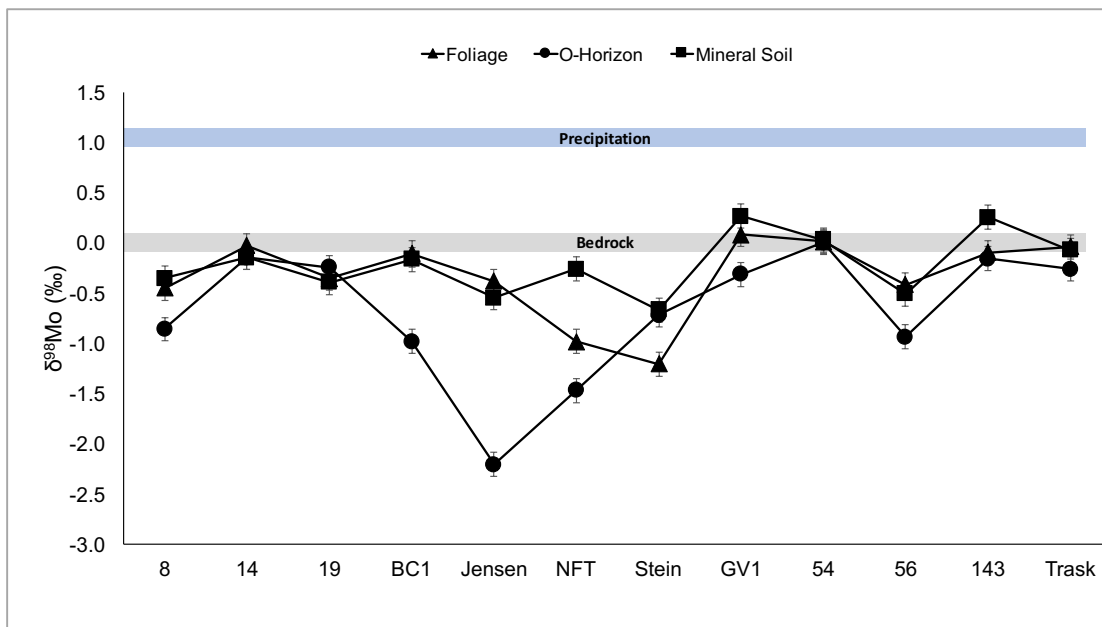


Figure 4.3: Mo isotopic composition ($\delta^{98}\text{Mo}$) of foliage (triangles), O horizon (circles), and mineral soil samples (squares) for the Oregon Coast Range. Horizontal bars signify the average $\delta^{98}\text{Mo}$ of precipitation (blue bar) and bedrock (gray bar). Error bars for $\delta^{98}\text{Mo}$ represent $\pm 2\sigma$ of the external reproducibility. O horizon $\delta^{98}\text{Mo}$ is significantly lighter than foliage $\delta^{98}\text{Mo}$ ($p = 0.04$) and mineral soil $\delta^{98}\text{Mo}$ ($p = 0.006$). Foliage $\delta^{98}\text{Mo}$ and mineral soil $\delta^{98}\text{Mo}$ are not significantly different ($p = 0.68$).

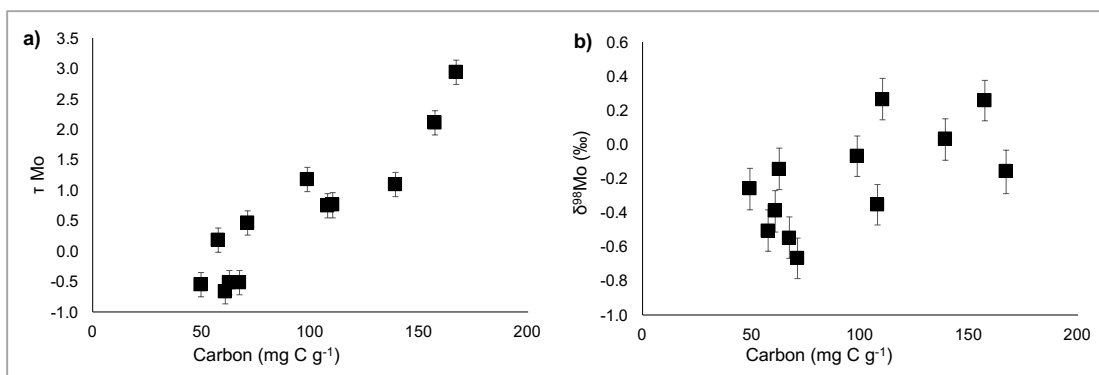


Figure 4.4: Elemental mass transfer of Mo (τ_{Mo}) (a) and Mo isotopic composition ($\delta^{98}\text{Mo}$) (b) versus carbon content for mineral soil samples (0-10 cm) along the Oregon Coast Range.

As organic carbon content increases, Mo accumulates in mineral soils ($r^2 = 0.86$, $p = 0.002$) and $\delta^{98}\text{Mo}$ becomes heavy ($r^2 = 0.41$, $p = 0.02$). Error bars for τ_{Mo} represent a $\pm 20\%$ error and error bars for $\delta^{98}\text{Mo}$ represent $\pm 2\sigma$ of the external reproducibility.

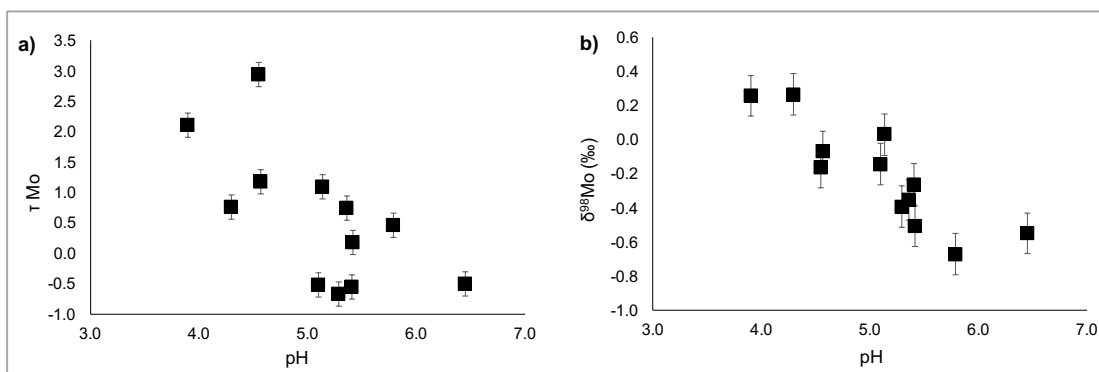


Figure 4.5: Elemental mass transfer of Mo (τ_{Mo}) (a) and Mo isotopic composition ($\delta^{98}\text{Mo}$) (b) versus pH for mineral soil samples along the Oregon Coast Range (OCR). As pH increases, Mo accumulation decreases ($r^2 = 0.46$, $p = 0.02$) and $\delta^{98}\text{Mo}$ becomes lighter ($r^2 = 0.76$, $p < 0.001$). Error bars for τ_{Mo} represent a $\pm 20\%$ error and error bars for $\delta^{98}\text{Mo}$ represent $\pm 2\sigma$ of the external reproducibility.

4.4.2 Mo isotope fractionation during adsorption onto natural organic matter

The vertical cross section of data from the Oregon Coast Range provides a snapshot of Mo dynamics during terrestrial biogeochemical cycling. The net result of Mo cycling between precipitation, foliage, O horizon, and mineral soil is the overall retention of light Mo in surface soil relative to both bedrock and precipitation (Figure 4.3). Specifically, the observation that the isotopic composition of the O horizon does not reflect that of the foliage, and tends to be isotopically lighter, implies a fractionation mechanism occurring as Mo cycles from plants and back into soils (Table 4.3 and Figure 4.3). Fractionation of Mo during adsorption onto OM is consistent with other studies looking at terrestrial Mo isotope signatures, where Mo abundance is positively correlated with OM content and light isotopes are preferentially retained in soils (King et al., 2016; Siebert et al., 2015). These results highlight a potential alternative mechanism for isotopically heavy river waters draining from soils by which light Mo is adsorbed onto OM rather than Fe- and Mn-(oxyhydr)oxides (Archer and Vance, 2008; Pearce et al., 2010; Voegelin et al., 2012), and may even explain the isotopically light Mo signature of riverine colloids (Pearce et al., 2010; Rahaman et al., 2014; Wang et al., 2015).

To compare the results from the IHA experiment to Mo adsorption onto natural OM, the open-system cycling of Mo in natural settings needs to be considered. Mo concentrations increase during litter decomposition in soil O horizons, even when normalized to mass loss through mineralization (Brun et al., 2008; Kraepiel et al., 2015; Pourhassan et al., 2016). In the Oregon Coast Range

specifically, Mo concentrations are eleven times higher in the O horizon than in the Douglas-fir needles from which the O horizon formed (Table 4.2), and atmospheric inputs are likely responsible for this elevated Mo content in the O horizon (Marks et al., 2015). The average Mo flux from precipitation ($0.19 \text{ g Mo ha}^{-1} \text{ yr}^{-1}$) is five times larger than the average Mo flux from litterfall ($0.04 \text{ g Mo ha}^{-1} \text{ yr}^{-1}$) at these sites (Table 4.2) (Marks et al., 2015), similar to observations elsewhere (Campbell et al., 2010; Gardner et al., 2014; King et al., 2016; Kraepiel et al., 2015; Siebert et al., 2015; Tsukuda et al., 2005). Presumably, as OM begins to decompose in the O horizon, charged functional groups are exposed on the OM surface and the adsorption of atmospherically-derived Mo can lead to increasing Mo content.

An estimated natural fractionation factor for Mo isotopes adsorbing onto OM can be calculated based on the offset between atmospherically-derived Mo and excess Mo in the O horizon. In this scenario, the “excess Mo” supplied by atmospheric inputs is assumed to be the difference between the concentration of Mo in the O horizon and the concentration of Mo in foliage (Table 4.2). Using an isotopic mass balance model, the isotopic composition of the “excess Mo” in the O horizon can be calculated as:

$$\delta^{98}\text{Mo}_{\text{O horizon,excess}} = \frac{((\delta^{98}\text{Mo}_{\text{O horizon}} \times [\text{Mo}_{\text{O horizon}}]) - (\delta^{98}\text{Mo}_{\text{foliage}} \times [\text{Mo}_{\text{foliage}}]))}{[\text{Mo}_{\text{excess}}]}$$

where $[\text{Mo}_{\text{excess}}]$ is the Mo supplied by atmospheric inputs and

$\delta^{98}\text{Mo}_{\text{O horizon,excess}}$ is the isotopic composition of the O horizon contributed by

atmospheric inputs. The fractionation factor ($\Delta^{98}\text{Mo}_{\text{precipitation-excess}}$) can be calculated by subtracting the isotopic composition of $\delta^{98}\text{Mo}_{\text{O horizon,excess}}$ from precipitation ($\delta^{98}\text{Mo}_{\text{precipitation}} = +1.15\text{‰}$) (Table 4.3). Using this approach, we find that the average $\Delta^{98}\text{Mo}_{\text{precipitation-excess}}$ among the Oregon Coast Range sites was 2‰. This average field-based value fits with the direction and magnitude of the IHA pH experiment results in the range of O horizon pH (pH 5.1 – 6.1), which should yield a Mo fractionation between 1.50‰ and 1.76‰ (Tables 4.1 – 4.3).

Although the average fractionation between “excess Mo” in the O horizon and atmospheric inputs was 2‰, the range in $\Delta^{98}\text{Mo}_{\text{precipitation-excess}}$ varied from 1.15‰ to 4.05‰ (Table 4.3). This is likely a result of the assumptions made while calculating $\Delta^{98}\text{Mo}_{\text{precipitation-excess}}$. One source of variability arises from the assumption that there are no changes to Mo concentrations in foliage prior to litterfall, though there is some evidence that Mo may become enriched in foliage with increasing age (Lang and Kaupenjohann, 2000). Additionally, the loss of Mo during OM decomposition is difficult to measure as it can be released and re-adsorbed many times before leaching below the O horizon, and each cycle of adsorption may increase the cumulative isotope fractionation. However, the observed strong retention of Mo onto OM in other studies suggests that the assumption of no Mo loss from the O horizon is a valid first-order approximation (Bellenger et al., 2007; Wichard et al., 2009). Our calculation also assumes that precipitation sampling reflects total atmospheric Mo inputs, but trace metal inputs can vary with time and space as a function of sea salt, dust, and anthropogenic contributions (Bern et al.,

2015a; Clergue et al., 2015; King et al., 2016; Monastra et al., 2004). Finally, Mo isotope fractionation during OM adsorption likely varies as a function of O horizon chemistry. As the pH of the O horizon increases, the Mo isotopic composition of the O horizon becomes lighter and the $\Delta^{98}\text{Mo}_{\text{precipitation-excess}}$ increases (Tables 4.2 and 4.3), which aligns with the pH-Mo relationship reported in the IHA experiment, suggesting that the pH of the O horizon determines the extent of Mo fractionation (Figure B.3b). The significant negative correlation we observed between O horizon Mo isotopic composition and soluble OM content may also reflect the higher exchange capacity of more soluble forms of OM (Berg and Laskowski, 2006), resulting in greater opportunity for accumulation of light Mo. This relationship suggests that Mo isotope dynamics in the O horizon may also be driven by sorptive processes and OM quality (Table B.3). In contrast to the Mo isotopic composition, there is no relationship between O horizon pH and Mo concentrations, which may be because the field range of O horizon pH is too narrow to shape quantitative Mo retention compared to the Mo isotopic composition, or because rates of Mo deposition differ in unmeasured ways across our sites.

4.4.3 Effect of plant uptake on the Mo isotopic composition

Molybdenum is a cofactor for enzymes involved in both nitrogen and sulfur metabolism and is especially important during N_2 -fixation, where it can become a limiting micronutrient (Barron et al., 2008; Perakis et al., 2017; Rousk et al., 2016; Silvester, 1989; Wichard et al., 2009; Wurzbürger et al., 2012). Thus, it is important to understand the patterns of Mo uptake via biological cycling and whether this

leads to additional Mo fractionation. There is evidence of bacterial fractionation of Mo isotopes from solution ($\Delta^{98}\text{Mo}_{\text{cell-solution}} = -0.2\text{‰}$ to -1.0‰) though it was unresolved whether fractionation was a function of kinetic effects during Mo assimilation or adsorption on cellular surfaces, and the importance of this in soils or non- N_2 fixers is unknown (Wasylenki et al., 2007; Zerkle et al., 2011). Mo supply often limits heterotrophic N_2 fixation in the O horizon soils we studied, but the Mo demands and uptake rates for Douglas-fir trees are unknown. The nitrate reductase enzyme used by plants requires Mo, but soil nitrate production and availability to plants are consistently high in these forests (Perakis and Sinkhorn, 2011), making it unclear whether plant Mo uptake is active or passive in the transpiration stream (Cornish and Page, 2000; Liermann et al., 2005; Marks et al., 2015; Maynard et al., 1994; Silvester, 1989). For 10 of the 12 sites measured in this study, the isotopic composition of Mo in foliage is within uncertainty (2σ) of the isotopic composition of Mo in mineral soil (Table 4.3, Figure 4.3), suggesting plants may not appreciably fractionate Mo during uptake from mineral soil. This dataset highlights an interesting area of Mo biogeochemical cycling regarding Mo bioavailability and associated isotope fractionation that requires further development.

4.4.4 Relationship between soil Mo, carbon content, and pH

Patterns in Mo mobility and mineral soil chemistry can further elucidate the mechanisms governing Mo isotope dynamics. The mineral soil data presented here span a range of positive and negative τ Mo values, which means that the relative balance of atmospheric inputs versus leaching losses is variable across the sites.

Both the mobility of Mo based on losses or gains relative to underlying parent material (τ Mo) and the Mo isotopic composition of surface mineral soil (0 – 10 cm) are positively correlated with carbon concentrations, used here as a proxy for OM content (Figure 4.4a), and are also negatively correlated with pH (Figure 4.5a). In this study, as OM increases, τ Mo becomes positive relative to underlying parent material, signifying retention and accumulation of Mo via adsorption, and the mineral soil Mo isotopic composition becomes heavier. This can be explained by the top-down control of atmospherically derived Mo, which has a heavy isotope signature ($\delta^{98}\text{Mo}_{\text{precipitation}} = +1.15\text{‰}$). As precipitation adds Mo to soils, light Mo is adsorbed onto decomposing OM in the O horizon (Figure 4.3) and the Mo isotopic composition of percolating soil porewater will become even heavier. This porewater will then be exposed to surfaces in mineral soil, generating a soil Mo isotopic composition that is fractionated from a heavier porewater source, and soils with higher OM content will have a greater proportion of surface sites available for Mo to adsorb leading to positive τ Mo values, and adsorption of progressively heavier Mo (Figures 4.4 and 4.5). Additionally, as the soils in the Oregon Coast Range increase in OM content across sites, pH decreases from 6.5 to 3.9, due to the release of organic acids through increased mineralization and nitric acid production via nitrification (Binkley and Sollins, 1990, Perakis and Sinkhorn 2011). Thus, soils with high OM content and low pH may have a higher adsorptive capacity for Mo leading to greater retention of Mo from isotopically-heavy porewater. Conversely, soils with less OM decomposition would have a higher pH, and less Mo adsorption (Figure 4.5a). At

high pH there may be a greater preference for non-protonated minor Mo species (Hiemstra and Van Riemsdijk, 1996) that are the most isotopically-depleted (e.g. MoO_3) (Figures 4.2b and 4.5b) (Tossell, 2005). This feature that has also been observed during Mo adsorption onto Fe- (oxyhydr)oxides (Goldberg et al., 2009).

The relationships between Mo, OM content, and pH that we observed in the Oregon Coast Range parallel prior studies of Mo mobility in soils where Mo concentrations are elevated in the O horizon and surface mineral soils (King et al., 2016; Kraepiel et al., 2015; Siebert et al., 2015; Wichard et al., 2009). Similar to the Oregon Coast Range, these studies attribute Mo accumulation to atmospheric deposition and subsequent retention via complexation with OM (Wichard et al., 2009; Wurzbarger et al., 2012). Our results showing less Mo retention (τ Mo) at high pH (Figure 4.3a) also agree with prior reports of Mo-pH relationships. For example, Kraepiel et al., (2015) attributed Mo retention in the organic and mineral soils of temperate forest soils in the Susquehanna Shale Hills Critical Zone Observatory to artifacts of anthropogenic Mo deposition, amplified by the fact that these soils have low pH (pH $\sim$ 4, Jin et al., (2010)), and thus higher adsorption capacity for oxyanions. In soils from Iceland and Maui, Siebert et al., (2015) observe decreasing τ Mo with decreasing $\delta^{98}\text{Mo}$ with increasing pH. Similarly, on the Big Island of Hawaii, King et al., (2016) postulated that positive τ Mo and heavy $\delta^{98}\text{Mo}$ in surface mineral soils are a result of atmospheric inputs and subsequent adsorption onto OM. Comparing the Mo parameters to mineral soil pH reported in Table 3.2, it is clear that Mo concentrations and τ Mo decrease with increasing pH and that the lightest $\delta^{98}\text{Mo}$

correspond to horizons with higher pH (up to pH ~ 8). Likewise, assuming the input of Mo to surface soils is atmospherically derived, the $\Delta^{98}\text{Mo}_{\text{soil-atmosphere}}$ for these soils is ~ 1.5‰ between pH 5.5 to 7.0, comparable to the IHA experimental results from this study (Table 4.1). Thus, the results from the Oregon Coast Range and IHA experiment highlight the potential processes controlling Mo isotopic signatures in the terrestrial weathering environment to be adsorption of Mo onto OM with accompanying isotope fractionation, mediated by pH and atmospheric inputs.

More work needs to be done to understand the evolution of Mo isotope signatures as OM decomposes and Mo is released and re-adsorbed. For example, with respect to the precipitation flux, Mo is only stored in the O horizon on decadal time scales while Mo is stored in minerals soils on 1 – 10 kyr timescales (Table 4.2). Thus, the isotopic composition of mineral soils will reflect the integrated input of chemical weathering, atmospheric inputs, and subsequent fractionation. Because interactions with soils leads to the retention of light Mo in soils (King et al., 2016; Siebert et al., 2015) there is potential for Mo to be a tracer of pedogenic processes. However, because the overall Mo budget for soil (including OM accumulation) is strongly influenced by atmospheric inputs—and these inputs are enriched in heavy Mo isotopes—the effects of pedogenesis and atmospheric inputs may overprint one other. Similar conclusions regarding the buffering effect of atmospheric inputs have been previously discussed for other metal systems including Li and Fe (Clergue et al., 2015; Poitrasson et al., 2008) and a study of Mo isotope dynamics across a climate gradient in Hawaii illustrates this challenge, as the most pedogenically well-

developed soils (high precipitation, high OM content) are the least fractionated relative to bedrock (King et al., 2016).

4.5 Conclusions and broader implications

The results of this study show that light Mo is preferentially adsorbed onto OM and that fractionation between the dissolved and adsorbed phase varies with pH. Adsorption onto OM is thus a potentially important mechanism for how Mo cycles through terrestrial environments, leaches into rivers and groundwater, and is eventually deposited in ocean sediments. The isotopic composition of dissolved Mo entering oceans from rivers may vary as a function of OM content in terrestrial and riverine systems as well. In the few riverine Mo studies that analyze particulates, colloids, and the truly dissolved phases, adsorbed Mo is isotopically lighter than dissolved Mo (Pearce et al., 2010; Rahaman et al., 2014; Wang et al., 2015), which may be a function of Mo adsorption onto OM solid phases. The Mo isotopic composition of soils and sediments is therefore a function of several factors including OM, Fe- and Mn- (oxyhydr)oxide, and sulfide content. Recognizing the interactions driving Mo fractionation will help to advance the understanding of how both terrestrial and marine systems reflect changing environments.

In addition to understanding trace metal behavior in terrestrial environments, Mo isotopic fractionation during adsorption onto OM has important implications for interpreting the Mo dynamics in marine sediments. Based on the results presented here and recent studies in euxinic environments (Dahl et al., 2016; Wagner et al., 2017), Mo-OM associations have the potential to skew paleo-ocean

oxygenation calculations based on Mo isotope records. In marine sediments, Mo is associated with OM in addition to Fe- and Mn- (oxyhydr)oxides, Fe-Mo-S complexes, and thiomolybdates (Algeo and Lyons, 2006; Ardakani et al., 2016; Chappaz et al., 2014; Dahl et al., 2016, 2013; Kerl et al., 2017). The adsorption of Mo onto OM in the water column (McManus et al., 2006) has the potential to deliver light Mo to sediments. Additionally, the decomposition of OM in the top few centimeters of sediment could release light Mo to sediment porewaters. This light Mo could then diffuse into bottom water and sediment porewater where it could be re-adsorbed. In anoxic and euxinic environments, the persistence of OM means that the isotopic composition of sediments may be isotopically-lighter than expected based on Fe-Mo-S and thiomolybdate Mo sequestration. Future studies are needed to examine Mo fractionation during adsorption to OM as a function of O₂ fugacity, pH, ionic strength, and hydrogen sulfide concentrations.

4.6 Acknowledgements

We thank Jade Marks, Justin Hynicka, and Chris Catricala for collection and elemental analyses of Oregon Coast Range samples. Andy Ungerer and Brian Haley are thanked for their analytical assistance and advice on experimental design. NSF award EAR-1053470 to Pett-Ridge supported this work. Any use of trade names does not imply endorsement by the U.S. Government.

Chapter 5: Interactions between lithology and redox cycling in controlling trace metal mobilization and Mo isotope dynamics in soils

Elizabeth King, Aaron Thompson, and Julie Pett-Ridge

ABSTRACT

In soils subjected to fluctuating reduction-oxidation (redox) cycles, the reductive dissolution of iron (Fe)- (oxyhydr)oxide minerals, colloidal dispersion, and associated shifts in pH have been shown to drive the mobilization of trace metals. For this reason, trace metal distributions, abundances, and isotopic fractionation patterns may be powerful tracers of the redox history of an environment, but this requires constraining trace metal behavior during fluctuating redox conditions via direct measurement of mobilization. In this study, we sampled surface soils from intensely weathered profiles formed on contrasting lithologies, and subjected those soils to two consecutive, 8-day redox cycles in the laboratory. Mössbauer spectroscopy was used to quantify the composition, crystallinity and abundance of Fe phases in the soils. A suite of metals (Al, Mn, Fe, Ti, Rb, Zr, Nb, Mo, REEs, Pb, Th, U) were quantified in aqueous (< 10 nm) and colloidal (< 415 nm) fractions of the solution. Mo isotopes were also measured to investigate their potential as a soil redox tracer. In soils formed on volcanoclastic bedrock—characterized by high clay content, low permeability, and a high abundance of short-range-ordered (SRO) Fe-(oxyhydr)oxides phases—reducing conditions and colloidal dynamics drove trace metal mobility. Conversely, in soils formed on granodiorite bedrock—characterized by low clay content, high permeability, and a high abundance of crystalline Fe-(oxyhydr)oxides phases—trace metal mobilization was driven by the aqueous phase independent of redox state and colloidal dynamics. This study provides evidence that lithology remains an overarching factor governing the characteristics of metal

mobility in soils, even after prolonged intense weathering. Ultimately, the Mo isotopic composition of the colloids and the aqueous phase were not adequate predictors of the redox history of the soils, suggesting that additional fractionation mechanisms must be constrained to understand the redox behavior of Mo.

5.1 Introduction

Soils evolve in response to the accumulation, transformation, and loss of minerals, nutrients, and organic matter, and are a central component of the Critical Zone—the region of Earth’s surface where the lithosphere, hydrosphere, atmosphere, and biosphere intersect (Amundson et al., 2007; Anderson et al., 2007; Brantley et al., 2007; Chorover et al., 2007). The interaction of these soil constituents has the potential to affect the trajectory of Earth’s surface biogeochemistry, and many of these interactions are reflected in the abundance and mobility of trace metals. Trace metals are a suite of elements that can serve as micronutrients, contaminants, or benign ancillary soil components depending on their concentrations. Many trace metals are becoming anthropogenically-enriched through fossil fuel combustion and smelting operations, and therefore understanding their geochemical behavior is important (Pacyna and Pacyna, 2001). Additionally, soil trace metal mobilization patterns may serve as a useful tracer for understanding fundamental soil processes. Trace metal mobility is often a function of the surface charge of soil particles, which in turn is a function of the degree of weathering, bedrock and soil mineralogy, pH, and redox state (Sposito, 2004; Thompson et al., 2006a).

Within a soil profile, the translocation of trace metals occurs via two main pathways: colloid mobilization and aqueous transport (Bern et al., 2015b; Kretzschmar et al., 1999; Thompson et al., 2006a; Viers et al., 2000). Colloid mobilization is defined as the transport of soil constituents adsorbed to particles that remain suspended in solution for extended periods of time (Kretzschmar et al., 1999; Lead and Wilkinson, 2007). Because of their small size (< 415 nm) and abundance of reactive SRO Fe and Al minerals and organic matter, colloids often have high surface areas ($> 10 \text{ m}^2 \text{ g}^{-1}$) and highly reactive sorption sites (Bunn et al., 2002; Heil and Sposito, 1993; Thompson et al., 2006a) that can facilitate the redistribution of trace metals, contaminants, organics, and low-solubility soil constituents (Ti, Zr, Al) in terrestrial and aquatic environments (Amrhein et al., 1993; Bern et al., 2015b; Dai et al., 1995; Kretzschmar and Sticher, 1997; Thompson et al., 2006a). Aqueous transport, on the other hand, is defined as mobilization in the truly dissolved phase (Lead and Wilkinson, 2007), and is typically driven by mineral dissolution or organic matter decomposition, which release chemical species into the dissolved phase. Both colloid mobilization and aqueous transport are affected by changes in particle surface charge and can be influenced by the redox status of a soil (Thompson et al., 2006a). Yet, differences in trace metal mobilization between these two pathways are poorly understood because of the ephemeral nature of these transfers and challenges in measuring mobilization *in situ*.

Reduction-oxidation (redox) oscillations mobilize soil constituents by altering the stability of solid phase Fe- (oxyhydr)oxides and organic matter, and by producing

and consuming hydrogen ions (causing pH shifts) (Grybos et al., 2007; Henderson et al., 2012; Sposito, 2004; Thompson et al., 2006a). This has a profound effect on the mass transfer of trace metals, secondary mineral formation, nutrient cycling, and microbial activity (Ginn et al., 2017; Henderson et al., 2012; Thompson et al., 2006a). The inherent heterogeneity of soils makes it difficult to predict redox status as the availability of oxidants (O_2 , NO_3^- , Mn(IV), Fe(III), etc.) and reductants (organic matter) is largely a function of moisture and biological activity, which are temporally and spatially variable. In surface soils where there is an ample supply of both organic matter and Fe- (oxyhydr)oxides, reducing conditions can persist at the microsite spatial scale despite the proximity of these soils to atmospheric O_2 (Hall et al., 2016). The development of reducing conditions in microsites is a function of the mineral grain size, porosity and permeability, secondary mineral, and clay formation—factors that are all governed by the lithology of soil parent material (Brantley and White, 2009; Buss et al., 2017). Thus, to understand the effects of redox cycling on colloid and aqueous transport, it is important to understand the role of lithology.

Mo is a redox-sensitive trace metal that partitions itself between Fe- (oxyhydr)oxides, organic matter, and the aqueous solution—where it is predominately found as the molybdate oxyanion (MoO_4^{2-}) (Anbar, 2004). Molybdenum (Mo) isotopes may be a powerful tool for understanding aqueous and colloidal transport driven by redox oscillations provided the Mo isotopic fractionation between solid, particulate, and aqueous phases change predictably as

a function of redox state. In marine sediments, variations in Mo isotope signatures have been used extensively to model the extent of global euxinic (anoxic and sulfidic) conditions throughout Earth's history (Anbar et al., 2007; Kendall et al., 2015; Wille et al., 2007). In terrestrial systems, the Mo isotope system is less understood, but the interplay between Fe- (oxyhydr)oxides and organic matter provides a dynamic environment for Mo adsorption between anoxic and oxic soils (King et al., 2016; Siebert et al., 2015). Under oxic conditions, light Mo isotopes are preferentially adsorbed onto Fe- (oxyhydr)oxides and organic matter, leading to the retention of isotopically light Mo on soil solids, and the loss of isotopically heavy Mo via leaching (King et al., 2016; Siebert et al., 2015). However, under reducing conditions, the dissolution of Fe- and Mn- (oxyhydr)oxides and the redistribution/mineralization of organic matter leads to the release light Mo to the aqueous phase (McManus et al., 2002).

The purpose of this study was twofold: 1) to quantify trace metal mobilization in the total solution (colloidal plus dissolved phase) and the aqueous (dissolved only) phase in soils developed on volcaniclastic and quartz diorite bedrock within the Luquillo Critical Zone Observatory, and 2) to focus on Mo to investigate whether the isotopic composition of soil or mobilized Mo differs between lithologies, and if it is indicative of the redox history of the environment. The chosen lithologies give rise to differences in soil permeability and mineralogy that may control redox-mediated mobilization of trace metals. We expect that under oxic conditions, isotopically light Mo should adsorb onto colloids and soils, generating a

heavy aqueous phase that can be leached from the soil profile. Under reducing conditions, the reductive dissolution of Fe- (oxyhydr)oxides should release light Mo to the aqueous phase. We expect subsequent oxidizing conditions should then re-adsorb Mo from an isotopically light pool such that the cumulative response of soils to extensive redox oscillations is the preservation of light Mo onto soils and colloids and the loss of heavy Mo in the aqueous phase. By exposing natural samples to controlled redox fluctuations, this study will test the utility of Mo isotopes as an integrated tracer of soil redox history. Together, these results will improve our understanding of how lithology and fluctuating redox conditions interact to control soil geochemical behavior.

5.2 Methods

5.2.1 *Study sites and sample collection*

Soil samples were collected from the Luquillo Critical Zone Observatory (LCZO), a subtropical wet forest ecosystem located in the Luquillo Mountains of northeastern Puerto Rico. The mean annual temperature is 22°C and mean annual precipitation ranges from 3,500 mm yr⁻¹ to 4,200 mm yr⁻¹ (McDowell et al., 2012; White et al., 1998). High amounts of precipitation in the LCZO creates periodic soil saturation events, fluctuating oxygen concentrations, and anoxic conditions on the scale of days to weeks (Chacon et al., 2006; Hall et al., 2016, 2013; Hall and Silver, 2013; Heartsill-Scalley et al., 2007; Liptzin et al., 2011).

The LCZO comprises a natural laboratory where soil-forming factors—climate, relief, and vegetation—can remain roughly constant and the isolated effect

of lithology can be studied. Both lithologies in the LCZO are covered by a thick layer of highly weathered saprolite and soil. The Bisley site is located within the Rio Mamayes watershed underlain by the Fajardo Formation, a 100 Ma basaltic to andesitic, volcanoclastic bedrock (Jolly et al., 1998; Schellekens, 1998). Bisley soils are moderately well-drained, very-fine, parasesquic, isohyperthermic Typic Haplohumults (Soil Survey Staff, 2002). Ridgetop sites ($< 10^\circ$ slope) are comprised of 1 m thick bioturbated soil on top of thick (9 – 15 m), highly cohesive saprolite showing a near complete loss of inorganic nutrients (e.g. Ca, Mg, K, Na) and primary minerals down to 9 m (Buss et al., 2017, 2013). Soils are considered fine-grained with low porosity, low sand content (8%), and high clay content (39%) (Hall and Silver, 2015). Biomass is dominated by Tabonuco trees (*Dacryodes excelsa*) (Chinea et al., 1993; Scatena, 1990). On the other hand, Guaba Ridge is located within the Rio Icacos watershed underlain by the Rio Blanco Formation, a 49 Ma quartz diorite (Smith et al., 1998). Soils are well-drained, kaolinitic isothermic Aquic Dystrudepts (Soil Survey Staff, 2002). Ridgetops sites are comprised of 1 m thick bioturbated soil on top of 7 m of saprolite, with near-complete loss of primary minerals down to 5 m (Buss et al., 2017, 2008; Pett-Ridge et al., 2009; White et al., 1998). Soils are medium-grained with high porosity, high sand content (56%), and low clay content (19%) (Hall and Silver, 2015). Biomass is dominated by Palo Colorado trees (*Cyrilla racemiflora*) (Scatena, 1990).

Surface soil samples (0 – 10 cm) were collected from ridgetop sites at both Bisley and Guaba Ridge (Table 5.1). The leaf litter layer was carefully removed prior

to sampling, and two 1 m x 1 m sampling plots were extracted to 10 cm depth and divided into polypropylene Ziploc[®] bags at each site. All samples were transported at field moisture and temperature to the University of Georgia where they were air dried at 30°C for 48 hours prior to dry sieving (< 2 mm) and homogenizing. Previous work has concluded that air-drying tropical soils preserves their Fe reducing capability—and likely stimulates organic matter release—although it may alter microbial populations (Ginn et al., 2014).

5.2.2 Redox experiment

Artificial reduction experiments were performed at the University of Georgia's Environmental Soil Chemistry Lab. Samples were collected for two full redox cycles following each half-cycle (oxic half-cycle I, reducing half-cycle I, oxic half-cycle II, reducing half-cycling II) (Figure C.1). The duration of each redox half-cycle and the appropriate sample volumes were determined to make sure that enough Mo would be collected in the supernatant to measure the Mo isotopic composition (100 ng Mo). These parameters were based on preliminary results measuring Mo release in tropical surface soils in Maui, HI where < 1% of soil Mo was released after being subjected to reducing conditions for 48 hours (King et al., 2014). To prepare the soil slurry, approximately 400 g of soil was added to 800 mL of 18.2 MΩ ultrapure water adjusted to pH 4.5 using 0.1 M HNO₃ in acid-washed, 1-L Nalgene bottles. This pH was chosen to approximate the native soil pH to ensure the trace metals released during the redox oscillations would reflect the most easily leachable and bioavailable phases (Peretyazhko and Sposito, 2005; Tishchenko et al.,

2015). The soil slurries were agitated on a variable speed reciprocal shaker. Oxic half-cycle I was prepared in 21% O₂ lab atmosphere and collected after 48-hours. The rest of the experimental points were prepared in an anoxic glovebox with a 95%:5% N₂:H₂ atmosphere modeled after the experimental setup of Thompson et al., (2006a). The 18.2 MΩ ultrapure water (adjusted to pH 4.5) was deoxygenated by bubbling the solutions with N₂ gas for 2 hours, and then exposed to the glovebox atmosphere for 72 hours. The soil slurries were agitated on a variable speed reciprocal shaker in the dark. After 6 days, a set of samples was collected (reducing half-cycle I). The rest of the samples were also removed from the glove box and exposed to ambient lab atmosphere (21% O₂) for 24 hours, with intermittent physical shaking. After 24 hours, samples were capped and put on a shaker outside of the glovebox for another 24 hours, then removed from the shaker and either collected (oxic half-cycle II) or brought back into the anoxic glove box (reducing half-cycle II). The final set of samples, which had now been exposed to a full redox cycle, were exposed to anoxic conditions for 6 more days, and thus two complete redox oscillations (oxic half-cycle I (48 hours)–reducing half-cycle I (6 days)–oxic half-cycle II (48 hours)–reducing half-cycle II (6 days)). The pH was monitored throughout the sampling scheme and recorded for each lithology at each sampling point. To ensure that Fe redox cycling was occurring, Fe(II) concentrations were qualitatively determined using the ferrozine-assay protocol (Thompson et al., 2006b) by monitoring the color changes between oxic half-cycles and reducing half-cycles,

whereby darkening of the sample color during reducing half-cycles was caused by increasing Fe(II) concentrations.

Samples were particle-size fractionated using differential centrifugation into the solution (colloidal and dissolved) the aqueous (dissolved) phase. Centrifugation was performed using a Thermo Scientific Sorvall centrifuge with an F14S-6X250y rotor into < 415 nm (3-min, 11,000 RCF) and < 10 nm (15-min, 26,000 RCF) size fractions. We recognize that defining the aqueous phase as < 10 nm may lead to the inclusion of small colloids (Bauer and Blodau, 2009), however this experimental design should effectively separate the majority of Fe- (oxyhydr)oxides and organic matter aggregates (Lead and Wilkinson, 2007). Centrifugation parameters were calculated using Stokes Law, accounting for the low angle (23°) of the fixed rotor (Bern et al., 2015b; Henderson et al., 2012). After centrifugation, the supernatant (800 mL per sample) was collected and acidified to pH 2 using ultrapure 0.1 M HNO₃. The soil residue was rinsed with 18.2 MΩ ultrapure water, centrifuged, and then shipped to Oregon State University where it was oven-dried.

Duplicate samples for each time point were individually analyzed for major and minor element concentrations and then combined into one sample for Mo isotopic measurements. Because of the large volume required for each isotopic measurement (1600 mL), subsampling of one bottle at multiple time points throughout the entire redox experiment was not possible, thus each sample proceeded through the experiment in parallel. In total, each redox half-cycle had two bottles dedicated to the solution (colloidal and dissolved) and two bottles

dedicated to the aqueous (dissolved) phase, for a total of four, 1-L bottles per treatment at each collection point (Figure C.1). Despite homogenization of soils prior to preparation of a soil slurry, the heterogeneous nature of these soils and the low concentrations of Mo and other metals leads to the propagation of large uncertainties when calculating the elemental concentrations associated with colloids as the difference between the solution and the aqueous phase. Thus, we chose to present the total solution and aqueous phase, and infer colloidal dynamics.

5.2.3 Chemical analyses

Following the artificial redox experiment, samples were shipped to the W.M. Keck Collaboratory at Oregon State University for chemical analyses. Supernatants were dried down on a hot plate, refluxed once in concentrated HNO_3 , dried-down, and re-suspended in 0.5 M HNO_3 . Bulk soil and soil residues from the artificial redox experiment were oven-dried for 48 hours, powdered in an agate ball mill, and microwave digested in 6 mL of ultrapure HNO_3 , 2 mL of ultrapure HCl , and 2 mL of ultrapure HF . Digested samples were refluxed twice on a hotplate in concentrated HNO_3 , dried down, and re-suspended in 0.5 M HNO_3 . For all samples, trace metal (Mo, Rb, Nb, REE, Pb, Th, U) concentrations were measured on a Thermo X-Series II Inductively Couple Plasma Mass Spectrometer (ICP-MS) and major elements (Al, Mn, Fe, Ti) were measured on a Teledyne Leeman Prodigy ICP-OES. A mixed-element solution standard was used for instrument calibration, and a USGS reference material (BCR-2) was monitored as an external standard and agreed with published concentrations within 5% (Li et al., 2014). Procedural blanks for Mo (< 2 ng) during

the artificial redox experiment were < 2% of the average Mo concentrations collected in the supernatant. Soil samples were analyzed for C and N content on a ThermoQuest NC 2500.

Molybdenum isotope measurements were performed on a Nu Plasma multi-collector ICP-MS (MC-ICP-MS) at Oregon State University. Following trace metal analyses, duplicate samples were combined and dried down. An aliquot of ^{97}Mo - ^{100}Mo double spike targeted to yield a $^{97}\text{Mo}/^{98}\text{Mo}$ ratio of 3 was added to the artificial redox samples, soil digestions, and residue. Samples were dissolved in a 1 M HF – 0.5 M HCl solution and 200 μL of H_2O_2 was added to each sample to ensure complete oxidation prior column chromatography. The procedures for the double-spike and column chromatography are outlined in King et al., (2016), whereby Bio-Rad AG1-X8 anion resin is used to separate Mo from possible elemental interferences including iron (Fe), manganese (Mn), and zirconium (Zr). Mo is eluted in 1 M HCl, dried down, and re-suspended in 0.5 M HNO_3 for isotopic analysis.

Isotope measurements are made relative to NIST SRM 3134 (Lot No.: 891307) (Goldberg et al., 2013; Greber et al., 2012) and are reported in delta notation ($\delta^{98}\text{Mo}$) for $^{98}\text{Mo}/^{95}\text{Mo}$ ratios:

$$\delta^{98}\text{Mo} = \left[\frac{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{sample}}}{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{NIST SRM 3134}}} - 1 \right] \cdot 1000$$

Repeated measurements of an in-house standard (Alfa Aesar Specpure® Product No.: 35758 (Lot No.: 23-16504a)) and USGS rock standards BCR-2, BHVO 2, and SDO 1, over two years yielded $\delta^{98}\text{Mo}$ values of -0.13‰, -0.01‰, -0.03‰, and +0.81‰. External reproducibility of the Alfa-Aesar in-house standard is $\pm 0.12\text{‰}$ (2σ). When sample volume allowed for it, duplicate analyses were measured and agreed within the external reproducibility.

Mössbauer spectroscopy (MBS) was performed on bulk soil samples for Bisley and Guaba Ridge to determine the quantitative speciation of soil solid-phase Fe based on the methods of Thompson et al., (2011). Once samples were oven-dried and powdered, subsamples were shipped to the University of Georgia's Soil Chemistry Lab for MBS analysis. Analyses were performed at 295 K, 77 K, and 5 K. A full description of MBS methodology can be found in the Appendix C (Figures C.2 and C.3).

5.3 Results

Surface soil chemistry including pH, C content, and a suite of major and trace metal concentrations (Al, Ti, Mn, Fe, Rb, Zr, Nb, Mo, REE, Pb, Th, U) were measured for the two soil types (Tables 5.1 and C.1). Briefly, soil pH was similar between the two sites (4.63 for Bisley and 4.72 for Guaba Ridge) while the C content for Bisley (29.4 mg g^{-1}) was double that of Guaba Ridge (14.1 mg g^{-1}) (Table 5.1). On average, Bisley bedrock and bulk soil had two times higher trace metal concentrations compared to Guaba Ridge bedrock and bulk soil (Table C.1). Bulk soil and bedrock Mo concentrations were 410 ng g^{-1} and 320 ng g^{-1} for Bisley, and 314 ng g^{-1} and 420

ng g⁻¹ for Guaba Ridge. This corresponded to bulk soil and bedrock Mo isotopic compositions ($\delta^{98}\text{Mo}$) of +0.21‰ and -0.07‰ for Bisley and +0.49‰ and +0.13‰ for Guaba Ridge, respectively (Table 5.1).

Iron minerals at Bisley were 3.5 times more abundant, but less crystalline than Fe minerals at Guaba Ridge (Table 5.2). In both Bisley and Guaba Ridge soils, Fe phases exist along a continuum of crystallinity (Figure 5.1). At the most ordered end of the Fe spectrum, Fe in silicates (although this could also represent organic-bound Fe) make up 17.5% of the total abundance in Bisley and 5.3% of the total abundance in Guaba Ridge (Figure 5.1, Table 5.2). The majority of Fe at Bisley is found in the intermediate range of crystallinity (short-range-ordered (SRO) phases) as a nano-goethite (nGt)-like phase (69.4%). In the intermediate range at Guaba Ridge, we identified both lepidocrocite (Lp)-like and nGt-like phases (32.5% and 52.8%, respectively). At the most disordered end of the crystallinity continuum, are SRO Fe-(oxyhydr)oxides that are too disordered to be assigned a phase and make up 10.8% of Fe in Bisley and 9.5% of Fe in Guaba Ridge. When converted to Fe concentrations, 70.6 mg g⁻¹ of Fe is characterized as SRO or nGt-like phases at Bisley and 23.3 mg g⁻¹ of Fe is characterized as highly-disordered, Lp-like, or nGt-like phases at Guaba Ridge (Figure 5.1, Table 5.2).

Table 5.1: Luquillo CZO site chemistry

	Bisley	Guaba Ridge
<i>Latitude</i>	18.31508	18.28155
<i>Longitude</i>	-65.79101	-65.79101
<i>Bulk Soil (0-10 cm)</i>		
<i>pH</i>	4.63	4.72
<i>C (mg g⁻¹)</i>	29.4	14.1
<i>Al (mg g⁻¹)</i>	10.6	8.9
<i>Ti (mg g⁻¹)</i>	4.6	2.5
<i>Fe (mg g⁻¹)</i>	88.1	24.6
<i>Mo (ng g⁻¹)</i>	410	314
$\delta^{98}\text{Mo}$ (‰)	0.21	0.49
<i>Bedrock</i>	<i>Volcaniclastic</i>	<i>Diorite</i>
<i>Al (mg g⁻¹)</i>	88.9	90
<i>Ti (mg g⁻¹)</i>	3.9	3.5
<i>Fe (mg g⁻¹)</i>	60.2	59.5
<i>Mo (ng g⁻¹)</i>	320	420
$\delta^{98}\text{Mo}$ (‰)	-0.07	0.13

^a2 σ uncertainties for $\delta^{98}\text{Mo}$ are $\pm 0.12\text{‰}$

Table 5.2: Soil Fe phases based on Mössbauer spectroscopy

	Bisley		Guaba Ridge	
<i>Fe</i> (mg g ⁻¹)	88.1		24.6	
Mössbauer Fe Assignments ^a	mg g ⁻¹	%	mg g ⁻¹	%
<i>Fe</i> ^{III} -silicate/organic	15.4	17.5	1.3	5.3
<i>Fe</i> ^{II} -clay	2.1	2.4	--	--
<i>nGt-like</i> ^b	61.1	69.4	13.0	52.8
<i>Lp-like</i> ^c	--	--	8.0	32.5
<i>disordered Fe</i> ^{III} - (oxyhydr)oxide	9.5	10.8	2.3	9.5

^a Calculated as the ratio between nGt-like phases at 77 K and 295 K versus 5 K (see Table C.2)

^b based on spectrum distributions at 5 K (see Appendix C)

^c best fit to nano-goethite (nGt)-like phases

^d best fit to lepidocrocite (Lp)-like phases

^e short-range-ordered (SRO), highly disordered

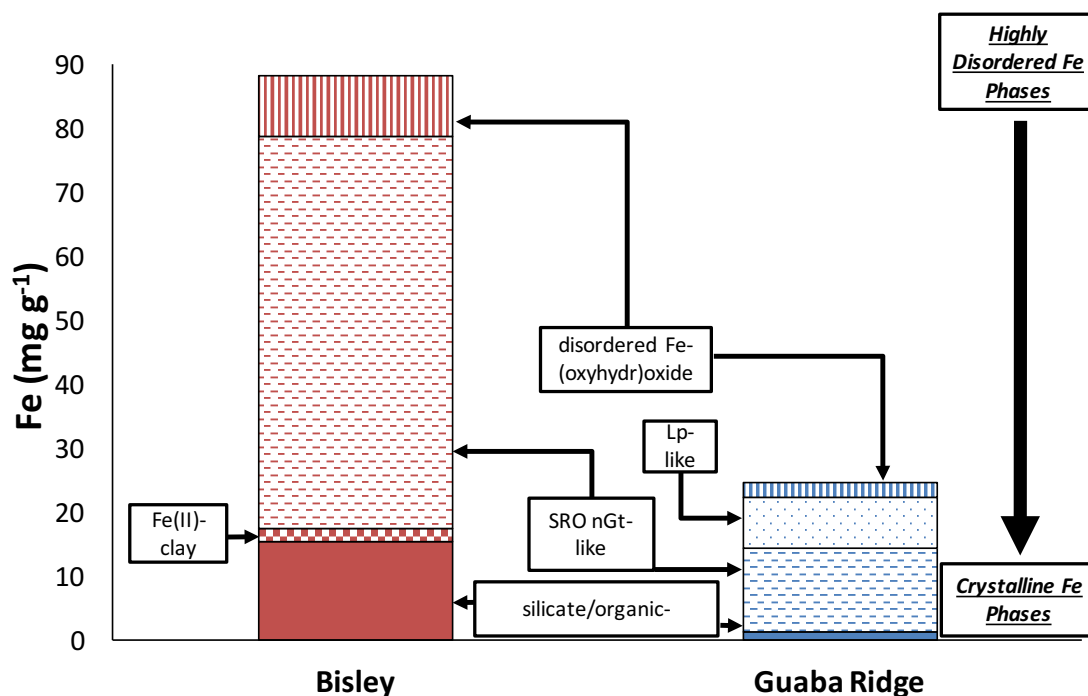


Figure 5.1: Mössbauer spectroscopy Fe phase abundances.

Crystallinity increases downward in the order: highly disordered SRO Fe phases (vertical-striped bars) < Lp-like (lepidocrocite) phases (dotted bar) (Guaba Ridge only) $\leq$ nGt-like phases (nano-goethite) (horizontal dashed lines) < Fe(II)-clay phases (checkered) (Bisley only) < Fe-silicate and organic-bound phases (*organic-bound Fe would not be considered crystalline) (solid bars).

During the artificial reduction experiment, greater mobilization of Al, Ti, and Fe was apparent at the Bisley site (Table 5.3 and Figure 5.2). For Bisley, the pH of the solution increased by > 1 unit per redox half-cycle, and reducing half-cycles always had a higher pH than oxic half-cycles (Table 5.3). Aluminum, Ti, and Fe doubled in solution (colloid and dissolved) during reducing half-cycles (Table 5.3 and Figure 5.2, left panel) while concentrations in the aqueous phase remained low and slightly increased as a function of time (Table 5.3 and Figure 5.2, left panel). For Guaba Ridge, reducing half-cycles also always had a higher pH than oxic half-cycles, though the pH shifts were < 1 pH unit (Table 5.3). Compared to Bisley, the Al, Ti, and Fe concentrations at Guaba Ridge remained lower and did not consistently change in either the solution and aqueous phase throughout the artificial redox experiment (Table 5.3 and Figure 5.2, right panel). Based on qualitative ferrozine method observations, both soils exhibited more Fe(II) in solution during the reducing half-cycles compared to the oxidizing half-cycles (data not shown). However, because Fe(II) adsorption onto the soil solid and colloid particles prevents the release of Fe(II) in the aqueous phase when the Fe shift is below 20 – 30 mmol kg⁻¹ (1120 – 1180 µg g⁻¹) in Luquillo soils (Tishchenko et al., 2015; Wilmoth, 2016), we do not expect to see a significant shift in aqueous phase Fe concentrations during reducing half-cycles.

Table 5.3: Artificial redox experiment chemistry

	Oxic Half-Cycle I				Reducing Half-Cycle I			
	Bisley		Guaba Ridge		Bisley		Guaba Ridge	
	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous
<i>pH</i>	4.6	--	4.6	--	5.7	--	5.5	--
<i>Al</i> ($\mu\text{g g}^{-1}$)	32.9	10.5	21.9	12.6	90.6	10.9	12.6	8.1
<i>Ti</i> ($\mu\text{g g}^{-1}$)	0.3	0.1	0.2	0.1	1.4	0.2	0.2	0.1
<i>Fe</i> ($\mu\text{g g}^{-1}$)	38.2	16.0	24.0	19.6	94.2	19.5	23.0	19.8
<i>Mo</i> (ng g^{-1})	0.3	0.2	0.3	0.2	0.7	0.1	0.1	0.1
$\delta^{98}\text{Mo}$ (‰)	-0.1	0.2	0.6	-0.3	-0.3	-0.3	0.4	0.3

	Oxic Half-Cycle II				Reducing Half-Cycle II			
	Bisley		Guaba Ridge		Bisley		Guaba Ridge	
	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous
<i>pH</i>	4.5	--	4.9	--	5.9	--	5.7	--
<i>Al</i> ($\mu\text{g g}^{-1}$)	23.2	17.1	37.4	8.0	64.3	10.9	7.1	24.9
<i>Ti</i> ($\mu\text{g g}^{-1}$)	0.4	0.3	0.3	0.2	1.5	0.5	0.2	0.1
<i>Fe</i> ($\mu\text{g g}^{-1}$)	40.7	25.7	47.9	18.0	96.9	47.1	50.7	38.7
<i>Mo</i> (ng g^{-1})	0.3	0.3	0.3	0.1	0.4	0.2	0.2	0.1
$\delta^{98}\text{Mo}$ (‰)	-0.4	-0.6	0.4	0.2	-0.4	0.0	0.7	0.8

Solution is defined as < 415 nm size fraction and consists of colloidal and dissolved phase

Aqueous is defined as < 10 nm size fraction and consists of truly dissolved phase

2 σ uncertainties for $\delta^{98}\text{Mo}$ are $\pm 0.12\%$

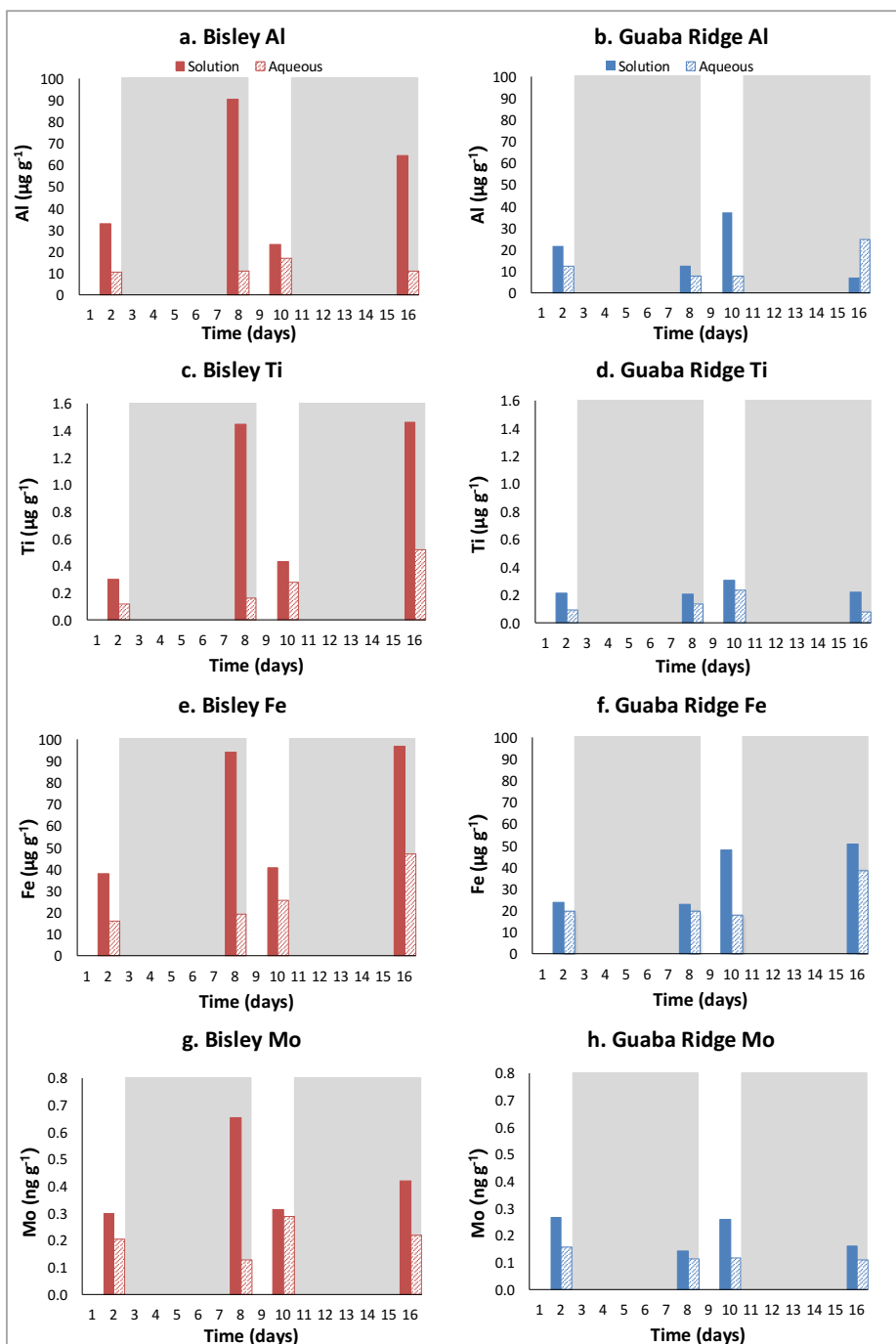


Figure 5.2: Al ($\mu\text{g g}^{-1}$ dry soil), Ti ($\mu\text{g g}^{-1}$ dry soil), Fe ($\mu\text{g g}^{-1}$ dry soil), and Mo (ng g^{-1} dry soil) concentrations during artificial redox experiment: Bisley (red) and Guaba Ridge (blue) solution (colloidal and dissolved) phases are represented as solid bars and aqueous (dissolved) phases are represented by striped bars. White shading represents oxic half-cycles and gray shading represents reducing half-cycles. Analytical error for element concentrations is 5%.

On average, 7x more trace metals were released to the solution during redox oscillations from the Bisley soils relative to the Guaba Ridge soils, despite bulk soil trace metal concentrations being only 2x more abundant in Bisley soils (Tables C.3 and C.4). Since we were not able to directly quantify colloid mobilization and abundances at these sites, we can use the ratio between metals at Bisley and metals at Guaba Ridge ($[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$) as a proxy for colloid presence (Figure 5.3). As such, if the two lithologies behave similarly under oxic and reducing conditions, then the ratio of trace metals ($[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$) in the solution (aqueous and particles < 415nm) and/or the aqueous phase should be consistent with the $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ of bulk soil (~ 2). In cases where there is greater mobilization of trace metals at Bisley, the $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratio of the phase of interest will be greater than the $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ of bulk soil, and vice versa for Guaba Ridge. The ratios of $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ for the aqueous phase are elevated about bulk soil levels during oxic-half cycles (Figures 5.3a and 5.3c). During reducing half-cycles the $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ of the aqueous phase decreases and the solution increases (Table C.4). On average, the solution of reducing half-cycle I has a $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratio of 11 and reducing half-cycle II has a $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratio of 7 (Figures 5.3b and 5.3d). Additionally, except for Nb, the correlations between Fe and trace metals in the solution (comprising aqueous constituents and particles < 415nm) normalized to soil concentrations of the respective elements, were always stronger for Bisley (R^2 range from 0.22 to 0.88) compared to Guaba Ridge (R^2 range from 0.00 to 0.53) (Figure 5.4, Table C.5).

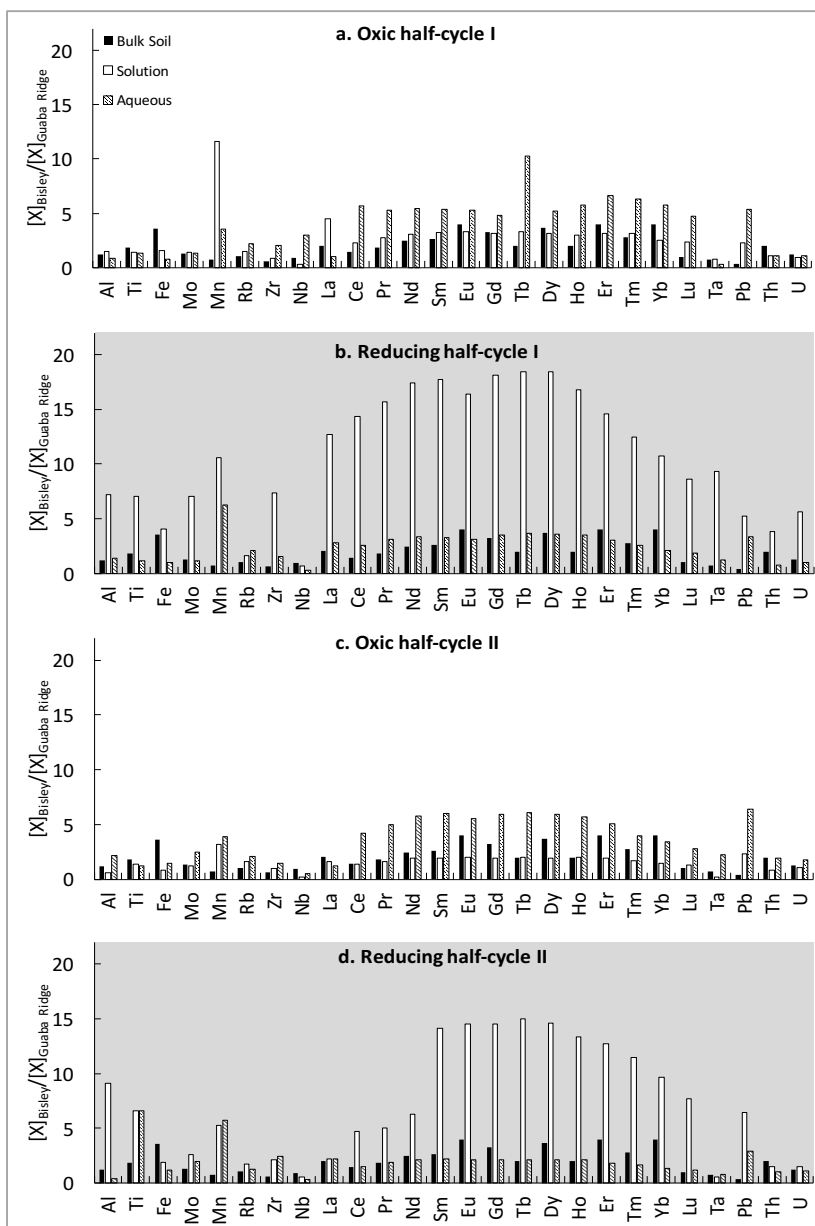


Figure 5.3: Ratio of the trace metal concentrations ($[X]$) at Bisley to Guaba Ridge during oxidic half-cycle I (a), reducing half-cycle I (b), oxidic half-cycle II (c), and reducing half-cycle II (d).

Bulk soil concentrations are represented as black bars while solution (colloid and dissolved) and the aqueous phase (dissolved only) are represented by white bars and striped bars, respectively. Relative to the differences in natural soil abundances of the two lithologies (bulk soil, black bar), Bisley trace metals are more readily mobilized during reducing half-cycles (b and d). Given that the solution ratio increases, while the aqueous solution reflects bulk soil, this can be interpreted as colloid activity playing a larger role in trace metal mobilization for Bisley.

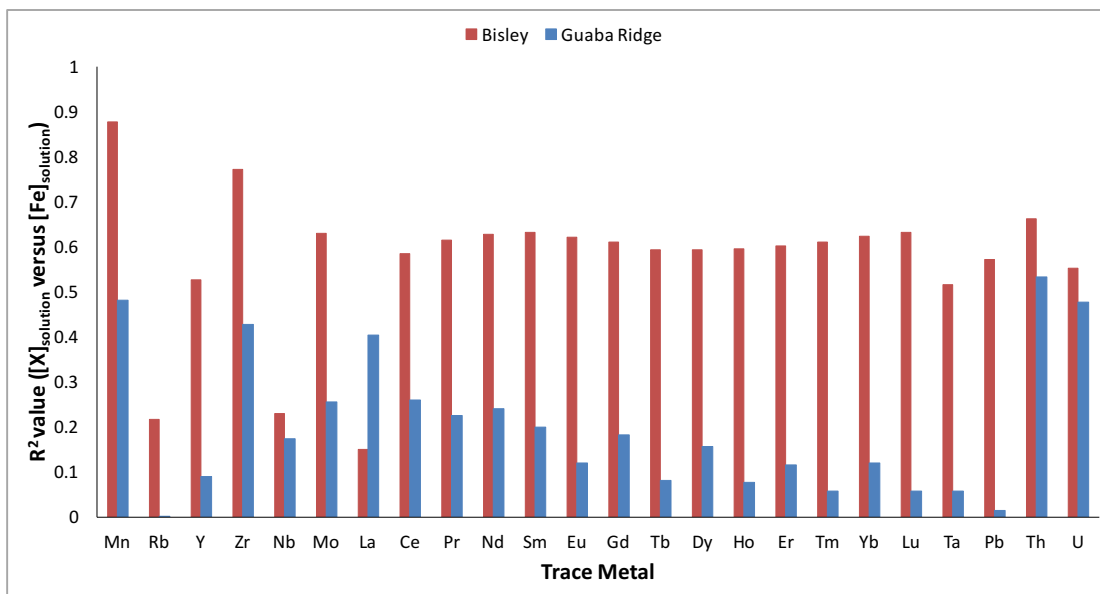


Figure 5.4: Coefficient of determination (R^2) based on linear regression analyses for trace metal solution concentrations versus Fe solution concentrations. Bisley (red) and Guaba Ridge (blue). Both oxic half-cycles and reducing half-cycles are considered in the linear regression analyses. R^2 values closer to 1 suggest that Fe is a strong predictor of trace metal redox dynamics.

Molybdenum mobilization behaved similarly to Al, Ti, and Fe mobilization (Figure 5.2). For Bisley soils, solution Mo concentrations increased during reducing half-cycles (Figure 5.2g). For Guaba Ridge soils, solution Mo concentrations remained low during reducing half-cycles (Figure 5.2h). In both soils, the Mo released into solution during the redox oscillations is < 1% of the total bulk soil pool. Similar to results for the full suite of trace metals, the solution $[\text{Mo}]_{\text{Bisley}}/[\text{Mo}]_{\text{Guaba Ridge}}$ ratio increased by a factor of 7 during reducing half-cycle I and a factor of 3 during reducing half-cycle II. The solution $[\text{Mo}]_{\text{Bisley}}/[\text{Mo}]_{\text{Guaba Ridge}}$ ratios during oxic half-cycles were similar to that of the bulk soil (1.3) (Table C.4).

Isotopically, at Bisley, the solution Mo isotopic composition ($\delta^{98}\text{Mo}$, $\pm 0.12\text{‰}$ 2σ) becomes progressively lighter (-0.06‰ to -0.42‰) over the course of the redox experiment. In the aqueous phase, the $\delta^{98}\text{Mo}$ becomes lighter ($+0.23\text{‰}$ to -0.61‰) from oxic half-cycle I to oxic half-cycle II, and then returns to a heavier value ($+0.03\text{‰}$) in reducing half-cycle II (Table 5.3, Figure 5.5a-b). At Guaba Ridge, the solution $\delta^{98}\text{Mo}$ ($\pm 0.12\text{‰}$ 2σ) becomes lighter ($+0.58\text{‰}$ to $+0.36\text{‰}$) through oxic half-cycle II, and then becomes heavier ($+0.70\text{‰}$) in reducing half-cycle II, but is within error of the bulk soil ($+0.49\text{‰}$). In the aqueous phase, the $\delta^{98}\text{Mo}$ becomes heavier (-0.34‰ to $+0.32\text{‰}$) between oxic half-cycle I and reducing half-cycle I, lighter ($+0.32\text{‰}$ to $+0.17\text{‰}$) between reducing half-cycle I and oxic half-cycle II, and then heavier between oxic half-cycle II and reducing half-cycle II ($+0.17\text{‰}$ to $+0.81\text{‰}$) (Table 5.3, Figure 5.5c-d).

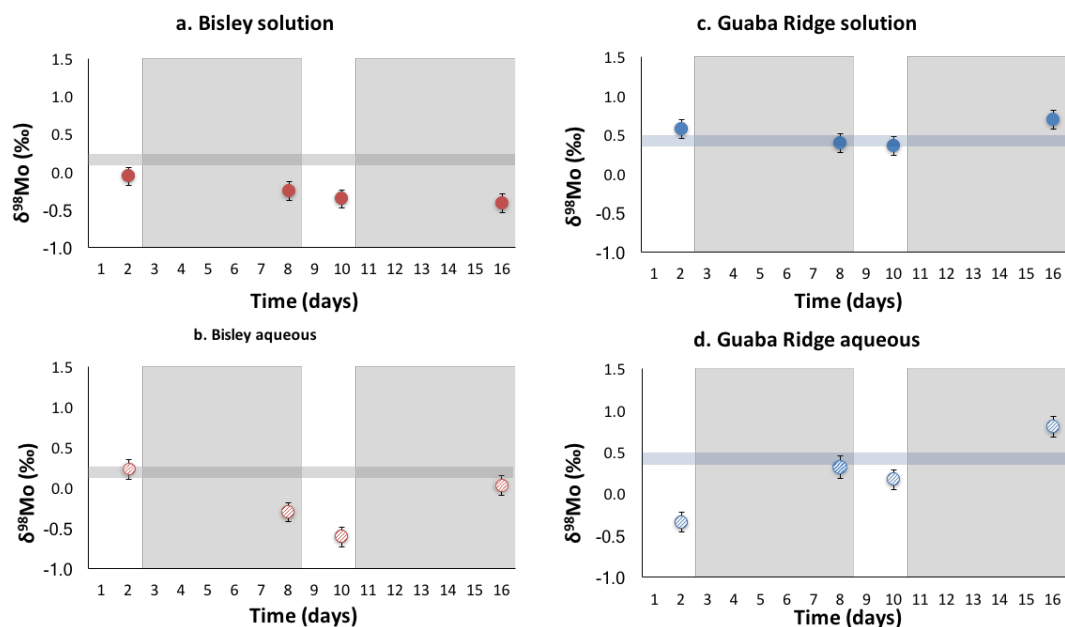


Figure 5.5: Mo isotopic composition ($\delta^{98}\text{Mo}$) during redox oscillations (a) Bisley solution (colloidal and dissolved) phase (red circles), (b) Bisley aqueous (dissolved) phase (red striped circles), (c) Guaba Ridge solution (colloidal and dissolved) phase (blue circles), and (d) Guaba Ridge aqueous (dissolved) phase (striped blue circles). Symbols represent the average concentration of duplicate samples. Error bars represent $\pm 2\sigma$ external reproducibility of an in-house standard ($\pm 0.12\text{‰}$). Horizontal bars represent bulk soil $\delta^{98}\text{Mo}$. Bedrock $\delta^{98}\text{Mo}$ for Bisley (-0.07‰) and Guaba Ridge ($+0.13\text{‰}$) are not shown.

5.4 Discussion

5.4.1 *Importance of lithology on Fe mineralogy and redox*

Results from the artificial redox experiment are consistent with the expected redox dynamics and colloid mobilization that vary as a function of site lithology. The lithological differences between Bisley and Guaba Ridge set up a cascade of features that ultimately determine the biogeochemical response to redox oscillations. The Bisley soils are developed on a volcanoclastic bedrock where Fe-rich minerals weather rapidly and the regolith is largely devoid of primary minerals (Buss et al., 2017). Chemical weathering at Bisley creates fine-grained soils with a silty clay loam texture (Hall et al., 2013). The higher clay content leads to a low water permeability and high fluid residence time (Chacon et al., 2006; Silver et al., 2013; W. H. Yang et al., 2015). In contrast, Guaba Ridge soils are developed on a granitic quartz diorite bedrock with higher silica content and quartz minerals that are resistant to weathering (Johnson and Hao, 2012; Schulz and White, 1999; Wang, 2011). These soils are coarse—56% sand at Guaba Ridge compared to 8% sand at Bisley (Hall and Silver, 2015)—and have lower specific surface area which leads to high permeability and short fluid residence times (White et al., 1998). While both tropical soils have experienced > 50 kyr of intense weathering conditions, with similar climate, topography, vegetation, and landscape position, the legacy of the underlying rock type remains an overarching control on their chemical behavior.

The contrasting hydrologic regimes that develop at Bisley and Guaba Ridge as a function of lithologically-determined pore structure, and permeability influence

the susceptibility of soils to redox oscillations, Fe mineral composition, and ultimately colloid mobilization. When soils are oxic or exposed to infrequent reducing conditions, the sorption of Fe(II) onto Fe(III) solid-phases (“atom exchange”) has been shown to accelerate the crystallization of Fe- (oxyhydr)oxides (Pedersen et al., 2005). Conversely, when soils are exposed to highly fluctuating redox conditions, the crystallization of SRO Fe- (oxyhydr)oxides is limited due to the leaching of Fe(II) (Thompson et al., 2011). This is especially true in organic matter rich surface soils, where SRO-organic matter complexes can form. The fine texture and higher fluid residence time mean that Bisley soils are prone to highly fluctuating redox conditions on the timescale of days to weeks (Liptzin et al., 2011; Silver et al., 2013). Thus, a potential explanation for the high abundance of nano-particulate Fe phases in Bisley is because these soils experience frequent reducing conditions and have a high C content, creating an environment where SRO Fe- (oxyhydr)oxides can persist (Figure 5.1, Table 5.2). These SRO and nano-particulate Fe- (oxyhydr)oxides are then more apt to form colloids capable of adsorbing trace metals because of their high surface charge site densities and small size (Kretzschmar et al., 1999). On the other hand, the high permeability and low water residence time of Guaba Ridge soils suggest that these soils experience fewer redox oscillations. For example, during an eight-year study of surface soils, ridgetop sites on the quartz diorite rarely experienced O_2 levels < 3% (Silver et al., 2013). Comparatively, in a similar study over an 82-week period, Bisley surface soils remained at O_2 levels < 3% for 25 consecutive weeks (nearly 30% of the study period) (Silver et al., 1999). Infrequent reducing

conditions means Guaba Ridge soils are likely exposed to crystallization processes through Ostwald ripening sequences and atom exchange via Fe(II) adsorption onto solid phases (Ostwald, 1900; Pedersen et al., 2005; Thompson et al., 2011). Our MBS data aligns well with these interpretations as Bisley has a much higher SRO Fe-(oxyhydr)oxide phase. Assuming reducible Fe is best defined as the nGt-like, Lp-like, and highly-disordered Fe phases, there is 33% more reducible Fe available at Bisley (70.6 mg g⁻¹ Fe) compared to Guaba Ridge (23.3 mg g⁻¹ Fe), suggesting that Bisley soils are more prone to reductive dissolution and colloid mobilization than Guaba Ridge soils (Figure 5.1, Table 5.2).

During our experimental redox oscillations, the pH of the soil slurries increased during reducing half-cycles indicating Fe reduction was occurring for both soils. However, the magnitude of the pH shift was larger for Bisley compared to Guaba Ridge, indicating stronger redox dynamics (Table 5.3). Although we were unable to measure the colloids directly, the consistent redox patterns between trace metals and the strong differences between sites allow us to confidently interpret the different colloidal dynamics. As such, the larger response of Fe in the solution for Bisley soil is evident in the $[\text{Fe}]_{\text{Bisley}}/[\text{Fe}]_{\text{Guaba Ridge}}$ solution ratio, which increased to 4.1 and 2.0 during reducing half-cycles I and II. Comparatively, $[\text{Fe}]_{\text{Bisley}}/[\text{Fe}]_{\text{Guaba Ridge}}$ aqueous ratio decreases during reducing half-cycles compared to bulk soil, suggesting that at Guaba Ridge, more Fe enters the aqueous phase while at Bisley more Fe is mobilized by colloids (Figure 5.3), confirming that colloidal particles drive redox dynamics in Bisley. Since Al and Ti are insoluble and mobile primarily as

suspended colloids (Bern et al., 2015b; Thompson et al., 2006a), this observation is further supported by the $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratios, which increase to values > 2 during reducing half-cycles.

5.4.2 Trace metal cycling during redox oscillations

During oxic conditions, Bisley has proportionally more trace metals in the aqueous phase relative to Guaba Ridge (relative to their abundances in bulk soil), suggesting that trace metals are more mobile at Bisley (Figures 5.3a and 5.3c). This is especially true for the rare earth elements (REEs), which have $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratios between 5 and 6 in the aqueous phase for oxic half-cycles. Under typical soil pH conditions, REEs are highly particle reactive, and do not easily dissolve except in the presence of aqueous organic ligands that can complex with REEs (Shan et al., 2002; Viers and Wasserburg, 2004). Therefore, high $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratios in the aqueous phase during oxic half-cycles (Figures 5.3a and 5.3c) combined with higher carbon contents at Bisley relative to Guaba Ridge (Table 5.1) may suggest that trace metals are readily mobilized during oxic conditions, likely because of complexation with organic ligands.

Furthermore, during reducing half-cycles, Bisley soils mobilized on average 7x more trace metals than Guaba Ridge soils. Trace metal mobilization at Bisley was detected via elevated $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratios in the solution, compared to the aqueous phase, suggesting that colloid mobilization increases during reducing half-cycles for Bisley (Figures 5.3b and 5.3d). Additionally, trace metal mobilization in Bisley soil is better-correlated with Fe in solution than it is at Guaba Ridge (Figure

5.4), which suggests that in soils with abundances of SRO Fe- (oxyhydr)oxides, reduction events are important for trace metal mobility. Comparatively, trace metal concentrations are significantly lower at Guaba Ridge, though they also increase in the aqueous phase during reducing half-cycles (Table C.3). The observation that the $[X]_{\text{Bisley}}/[X]_{\text{Guaba Ridge}}$ ratios in the aqueous phase are lower than bulk soil ratios, implies that Guaba Ridge soils do experience trace metal mobilization during redox fluctuations and that these soils preferentially release trace metals into the aqueous phase (Figures 5.3b and 5.3d).

The lack of colloid trace metal mobilization at Guaba Ridge is somewhat unexpected because the reductive dissolution of Fe- (oxyhydr)oxides and increasing pH has been previously shown to disperse colloids into solution (Thompson et al., 2006a). It is possible that because Guaba Ridge soils contain less total Fe, and the Fe that is present is more crystalline than at Bisley, colloids are more responsive to ionic strength or pH changes to particle surface charge rather than redox state. In this scenario, the artificial redox experiment may have reduced enough of the SRO Fe- (oxyhydr)oxides to account for the observed pH shifts between 4.6 to 5.7 during reducing cycles (Table 5.3). This would have led to a concurrent increase in ionic strength. If ionic strength drives colloidal behavior at Guaba Ridge, then coagulation of colloids and/or weak adsorption of trace metals at high ionic strength could explain the lack of colloidal dynamics during reducing half-cycles (Figure 5.3b) (Bunn et al., 2002; Kowalski et al., 2013; Kretzschmar and Sticher, 1997). Bisley soils would also experience the same changes to particle surface charge; yet they may not be

detectable within this dataset because the greater abundance of reducible SRO Fe-(oxyhydr)oxides at Bisley, and the tendency for these SRO phases to become colloids during redox oscillations is the dominant process controlling trace metal mobilization. The different patterns between these two soil types support the idea that lithology remains an important control on trace metal mobilization and redox dynamics via its influence on hydrologic regimes and the identity of secondary Fe minerals.

5.4.3 Mo partitioning during redox oscillations

Our focus on the mobilization and isotopic composition of Mo during redox oscillations was aimed at determining whether soil Mo isotope signatures are indicative of the redox history of the environment. Our initial hypothesis was that redox oscillations would lead to fractionation of Mo between the soil, colloidal, and aqueous phases such that soils and colloids would preferentially adsorb light Mo isotopes, and heavy Mo isotopes would preferentially enter the aqueous phase. The reductive dissolution of Fe-(oxyhydr)oxides during reducing conditions should release light Mo to the aqueous phase, and subsequent oxidizing conditions would lead to the re-adsorption of Mo onto soils from an isotopically light pool, leading to the cumulative retention of isotopically lighter Mo in soils. This mechanism could explain the light Mo observed in reducing soils in Maui (Siebert et al., 2015). However, the results from this study suggest that our expectation of using Mo isotopes as a redox tracer in soils is complicated by additional fractionation mechanisms and overprinted by the influence of lithology on redox behavior.

In the Bisley soils, Mo concentrations track Al, Ti, and Fe, whereby under reducing conditions Mo concentrations increase in solution, with a significant colloid component, and under oxic conditions Mo concentrations decrease (Figure 5.2, left panel). The isotopically light Mo signatures of the solution during reducing cycles are consistent with processes of colloid dispersion and/or reductive dissolution of Fe minerals, based on previous work determining that light Mo preferentially adsorbs onto Fe-(oxy)hydroxides (Goldberg et al., 2009) and organic matter (Figure 5.5a-b). However, the Mo isotope mobilization during redox oscillations also reveals unexpected patterns of Mo fractionation. Initially, Mo behaves as predicted because the aqueous pool is slightly heavier than the solution pool, implying that colloids must be lighter than aqueous Mo (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011, 2008). This is followed by the release of light Mo into the aqueous phase during reducing half-cycle I (Figure 5.5a-b). However, the persistence of light Mo in the aqueous phase between reducing half-cycle I and oxic half-cycle II is unexpected because oxic conditions should promote Fe- (oxyhydr)oxide precipitation and colloid coagulation (Thompson et al., 2006a); providing conditions for adsorption of isotopically light Mo, and enrichment of heavy Mo in the aqueous phase. One possible explanation for light Mo during oxic half-cycles could be stimulation of organic matter decomposition. As Fe(II) in solution is re-oxidized, it has been observed in tropical soils that organic matter decomposition also increases because of increased reactive oxygen species (e.g. H_2O_2) and increased availability of dissolved organic carbon during the transition to oxic conditions (Hall and Silver,

2013). Because organic matter is a strong complexing agent for Mo (Wichard et al., 2009), as it oxidizes isotopically light adsorbed Mo may be released into the aqueous phase, increasing Mo concentrations and shifting the $\delta^{98}\text{Mo}$ signature towards lighter values. Finally, the observation of increasingly heavy Mo in the aqueous phase during reducing half-cycle II does not align with the expected trend of releasing light Mo isotopes and further suggests that additional fractionation mechanisms are acting on Mo that cannot be discerned from this dataset.

In Guaba Ridge soils, Mo also tracks Al, Ti, and Fe, whereby concentrations remain low in both the solution and aqueous phases (Figure 5.2, right panel). Isotopically, Mo in the solution phase reflects the isotopic composition of soil throughout the experiment. Molybdenum in the aqueous phase becomes generally becomes isotopically heavier during the redox oscillations. During oxic half-cycle I, light Mo in the aqueous phase implies some initial dissolution of a labile phase enriched in light Mo isotopes. However, Mo isotopic signatures in the aqueous phase do not follow any of the predicted trends, since during reducing half-cycles Mo tends to be isotopically heavier than the preceding oxic half-cycles. Instead, pH effects may contribute to the $\delta^{98}\text{Mo}$, where at higher pH (reducing half-cycles), the fractionation between aqueous and adsorbed Mo increases via adsorption of a more isotopically-depleted pool (Figure 5.5d) (Goldberg et al., 2009; Tossell, 2005). Overall, the Mo and Fe cycling in Guaba Ridge soils is not clearly driven by redox fluctuations, and the solution $\delta^{98}\text{Mo}$ signature reflects the bulk soil isotopic composition (Figures 5.5c-d).

The fractionation of Mo isotopes during redox fluctuations in soils may influence the flux and isotopic composition of Mo translocated to other soil horizons or Mo delivered to rivers, groundwater, and eventually the oceans. Overall, $\delta^{98}\text{Mo}$ in Bisley and Guaba Ridge surface soils are heavier than their respective bedrock, which conflicts with the expectation that soils are preferentially enriched in light Mo (Archer and Vance, 2008). This suggests that isotopically light Mo is leached out of both soils or that heavy Mo is added via atmospheric inputs (King et al., 2016).

Considering the concentrations of Mo mobilized during the redox oscillations, the net $\delta^{98}\text{Mo}$ of mobilized Mo for Bisley is -0.28‰ while the net $\delta^{98}\text{Mo}$ for Guaba Ridge is +0.50‰. Compared to the $\delta^{98}\text{Mo}$ of the bulk soil, Bisley preferentially releases light Mo isotopes into solution and Guaba Ridge releases Mo that is unfractionated relative to the bulk soil. The net mobilization of light Mo in Bisley seems to result from the preferential adsorption of light Mo onto colloids. However, because the offset between bulk soil (+0.21‰) and bedrock (-0.07‰) is small, the light Mo that is mobilized at Bisley may only be translocated via colloids and reabsorbed within the soil profile while the net leaching loss of light Mo reflects less particle-reactive Mo, which tends to be isotopically heavier. This observation supports $\delta^{98}\text{Mo}$ data across a Hawaiian redox gradient, where the most reducing soil has the isotopically lightest $\delta^{98}\text{Mo}$ signatures (Siebert et al., 2015). Nevertheless, the Mo isotope signature of the bulk soil does not appear to do a good job of reflecting the intensity or frequency of redox cycling given that Bisley and Guaba Ridge have similar offsets relative to their rock, despite Bisley having more active redox chemistry. A possible

explanation for this is the accumulation of Mo from heavy atmospheric sources, fractionation of those inputs within the soil, and variations in the degree to which those inputs are retained in the soil (King et al., 2016), which need to be well-constrained in order to glean any redox signatures from Mo isotope data.

5.5 Conclusions

Our results reveal that lithology plays a large role in determining the effect of redox on trace metals despite intense chemical weathering over long timescales. Soils that have a high clay content, low porosity, and abundant reducible Fe-(oxyhydr)oxides are exposed to redox fluctuations more frequently than soils lacking the confluence of these variables (Buss et al., 2005; Hall et al., 2016; Silver et al., 1999). Bisley soils are characterized by having strong colloidal dynamics that can drive trace metal behavior. Since colloidal dynamics are driven by changes in pH and redox state, and these parameters vary with depth, trace metal enrichment and depletion throughout a soil profile will be a function of colloid mobility and adsorption (Chorover et al., 2004; Chorover and Sposito, 1995; Henderson et al., 2012; Thompson et al., 2006a). Focusing on Mo dynamics, the mobilization of light Mo during redox oscillations may lead to the translocation of light Mo in solution and provides a mechanistic explanation for other studies of Mo isotopes in soils, where the retention of light Mo under reducing conditions is observed (Siebert et al., 2015). In soils that are not frequently exposed to redox oscillations, trace metal fluxes may be driven by shifts in pH when trace metal adsorption onto colloids is lacking. Thus, even in highly weathered soils many meters removed from bedrock,

trace metal mobilization can be considered a function of lithology, which ultimately drives grain size, porosity, Fe mineralogy and the redox state of a soil.

5.6 Acknowledgements

NSF award EAR-1053470 to Pett-Ridge and Thompson supported this work.

We also acknowledge support for the Luquillo Critical Zone Observatory (EAR-1331841), and a NSF SAVI fellowship to E.K. King.

Chapter 6: Reassessing the dissolved molybdenum isotopic composition of ocean inputs: The effect of chemical weathering and groundwater

Elizabeth King and Julie Pett-Ridge

ABSTRACT

The abundance and isotopic composition of molybdenum (Mo) in marine sediments is used to reconstruct redox conditions throughout Earth's history. However, the utility of Mo as a paleoredox tracer relies on quantifying the flux and isotopic composition of Mo delivered to the ocean from the terrestrial environment. We present data from a series of rivers and groundwater sources across the Hawaiian Islands where the magnitude and stage of chemical weathering is well-constrained and varies as a function of lithological age. At the youngest sites, groundwater dominates the chemical weathering flux. These waters have the highest Mo concentrations but are the least isotopically fractionated relative to bedrock. As lithological age increases, rivers draining shallow flowpaths in soils become the main vector for water transport to the oceans, though groundwater flow still contributes to the observed Mo isotopic composition. These waters have Mo concentrations two orders of magnitude lower than groundwater but are more isotopically fractionated relative to bedrock values. River samples enriched in heavy Mo isotopes are hypothesized to reflect the net effect of chemical weathering, atmospheric inputs, and Mo isotope fractionation occurring in soils. In addition, rivers that drain soils experiencing extensive redox fluctuations exhibit the lowest Mo concentrations, and are enriched in light Mo isotopes, indicating that the reductive dissolution of Fe- (oxyhydr)oxides or decomposition of organic matter leads to the leaching of light Mo isotopes. This deviates from the general trend of dissolved $\delta^{98}\text{Mo}$ signatures that are heavier than bedrock. We also present data

from waters draining a variety of sedimentary, metamorphic, and igneous lithologies to characterize the range of Mo isotopic signatures (+0.21‰ to +1.91‰) across diverse landscapes with known denudation rates. The relationship between Mo concentrations and $\delta^{98}\text{Mo}$ signatures aligns well with previous studies of riverine Mo. In locations where the Mo flux is small, the isotopic composition is highly variable. On the other hand, both rivers with high Mo discharge fluxes and groundwater samples are isotopically similar to the average continental crust, suggesting that if high discharge locations dominate the long-term Mo flux, the range of Mo isotopic compositions throughout Earth's history may be constrained by a relatively narrow range close to average crustal values.

6.1 Introduction

Molybdenum (Mo) is the most abundant transition metal in the ocean (~ 100 nM), an essential micronutrient, and a redox-sensitive trace metal that is frequently used to reconstruct past environmental conditions (Algeo and Lyons, 2006; Barling et al., 2001). More specifically, the Mo sedimentary record has the potential to be a powerful paleoredox proxy because Mo accumulation and isotopic fractionation patterns depend on the redox state of the depositional environment, whereby Mo exhibits distinctive accumulation patterns and isotopic signatures in oxic, suboxic, anoxic, and euxinic environments (Anbar et al., 2007; Kendall et al., 2015; Siebert et al., 2003). However, in order to appropriately employ this isotope system as a paleoredox proxy, a knowledge of the flux and isotopic composition of Mo entering oceans from the terrestrial environment is required.

Molybdenum geochemistry is thought to be driven by adsorption onto Fe- and Mn- (oxyhydr)oxides and organic matter (Goldberg et al., 2009; Marks et al., 2015). Specific mechanisms of Mo isotopic fractionation include the preferential adsorption of octahedrally-coordinated Mo species enriched in light isotopes, kinetic effects during metal–ligand complexation, and equilibrium effects due to variations in bond strengths for isotopes with different masses (Goldberg et al., 2009; Malinovsky et al., 2007; Tossell, 2005). Under oxidizing conditions in the oceans, Mo is predominately present as the dissolved molybdate (MoO_4^{2-}) ion, and fractionation occurs as octahedrally-coordinated minor species are preferentially adsorbed onto iron (Fe)- and manganese (Mn)- (oxyhydr)oxides (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011). This results in an isotopically light sedimentary Mo reservoir ($\delta^{98}\text{Mo} = -1.0\text{‰}$) and a heavy seawater Mo reservoir ($\delta^{98}\text{Mo} = +2.1\text{‰}$) (Barling et al., 2001). As oxygen is depleted and reducing conditions persist, MoO_4^{2-} is converted to highly particle-reactive oxythiomolybdate species ($\text{MoO}_{4-x}\text{S}_x^{2-}$) that display a wide range in Mo isotopic compositions (Kerl et al., 2017; Poulson et al., 2006; Tossell, 2005). Under euxinic conditions, where reduced sulfur can accumulate to appreciable levels ($\text{H}_2\text{S} > 11 \mu\text{M}$), the complete conversion of $\text{MoO}_{4-x}\text{S}_x^{2-}$ species to MoS_4^{2-} , and subsequent scavenging of Mo into sediments yields no fractionation between sediments and seawater (Erickson and Helz, 2000; Helz et al., 1996; Tossell, 2005; Vorlicek et al., 2004).

Global ocean paleoredox conditions can be determined using a Mo isotope mass balance model assuming that seawater Mo is at steady-state and the riverine

flux equals the sum of the three sedimentary Mo sinks—oxic, euxinic, and sulfidic at depth sediments (Barling and Anbar, 2004; Kendall et al., 2016). At the outset of Mo paleoredox research, the isotopic composition of rivers was assumed to reflect the isotopic composition of the average continental crust ($\delta^{98}\text{Mo}$ between +0.1‰ and +0.4‰) (Barling et al., 2001; Siebert et al., 2003; Willbold and Elliott, 2017).

However, more recent studies have reported that the modern $\delta^{98}\text{Mo}$ of rivers is heavier than average continental crust values and the $\delta^{98}\text{Mo}$ of rivers may have varied over time (Archer and Vance, 2008; Neubert et al., 2011; Pearce et al., 2010; Voegelin et al., 2012). Not taking into account variations in riverine $\delta^{98}\text{Mo}$ value leads to incorrect estimations of the extent of global euxinia (Archer and Vance, 2008). Thus, understanding the mechanisms that shift dissolved $\delta^{98}\text{Mo}$ fluxes prior to delivery to the oceans and how the oceanic input can be constrained throughout Earth's history is of great importance for the functioning of the Mo isotope mass balance model for ocean paleoredox.

Based on river samples that represent 22% of global discharge to the oceans, the modern average riverine $\delta^{98}\text{Mo}$ value is +0.5‰ (re-normalized to the Mo standard NIST 3134), though values range from -0.4‰ to +2.1‰ (Archer and Vance, 2008). Several mechanisms can explain the isotopic offset between riverine Mo and Mo in the average continental crust. In some cases, the heavy $\delta^{98}\text{Mo}$ signature of rivers can be attributed to the preferential dissolution of mineral phases with heavy $\delta^{98}\text{Mo}$ values (Neubert et al., 2011; Voegelin et al., 2012). This hypothesis is supported by a positive relationship between dissolved sulfate (SO_4^{2-})

concentrations and the $\delta^{98}\text{Mo}$ signature in a series of small catchments, suggesting that rivers enriched in heavy Mo reflect the weathering of isotopically-heavy sulfates and sulfides (Neubert et al., 2011). Other studies attribute heavy $\delta^{98}\text{Mo}$ in rivers to the adsorption of light Mo onto Fe- and Mn- (oxyhydr)oxides and organic matter in soils (King et al., 2016; Pearce et al., 2010; Siebert et al., 2015). Finally, anthropogenic activities (Kelly and Matos, 2014; McBride and Spiers, 2001; Nriagu and Pacyna, 1988) or atmospheric inputs (e.g. dust, marine-derived precipitation, volcanic aerosols) (King et al., 2016) may lead to elevated Mo concentrations in rivers, with a range of $\delta^{98}\text{Mo}$ values. Therefore, it is important to determine the parameters that drive Mo dynamics in waters in order to constrain the riverine flux over timescales relevant to ocean paleoredox studies.

The goal of this study was to investigate the influence of chemical weathering stage on the dissolved Mo flux and isotopic composition. We compare Mo behavior in both rivers and groundwater from the Hawaiian Islands where the effects of bedrock age and climate can be isolated, and the stage of chemical weathering is well known. These results enable us to better understand how the riverine flux of Mo may have changed with weathering stages throughout Earth's history. To extend our analytical framework beyond basaltic islands, we also investigated Mo flux and isotope data from rivers draining catchments spanning a wide range of lithology, climate and chemical weathering stage from the Critical Zone Observatory (CZO) network.

6.2 Study Sites

The Hawaiian Islands make up the southeast segment of the Hawaiian-Emperor Volcanic Chain. Each volcano along the southeast to northwest transect is progressively older with ages ranging from zero years on the island of Hawaii to 4,100 thousand-years (kyr) on Kauai (Chadwick et al., 1999) (Figure 6.1a). The islands have a warm climate, and mean annual precipitation (MAP) ranges from a low of 100 mm yr^{-1} on the dry, leeward side to a high of $6,000 \text{ mm yr}^{-1}$ on the wet, windward side (Vitousek, 2004b). Several studies have used the Hawaiian Islands as a model system for chemical weathering and soil development research because the homogenous lithology, distinct age patterns, and well-constrained climate gradients allow the impact of individual state factors to be assessed (Goodfellow et al., 2014; Porder et al., 2007; Vitousek and Chadwick, 2013). Furthermore, minimal erosion on remnant shield surfaces means that the age of the soil at those sites can be approximated by bedrock age.

To capture initial, intermediate, and final stages of chemical weathering we focus our study on the islands of Hawaii, Maui, and Kauai. The main island of Hawaii ranges in age from zero years at the active Kilauea volcano to 400 kyr on the Kohala volcano (Chadwick et al., 1999; Sherrod et al., 2007) (Figure 6.1a). The leeward side of Hawaii (Kona region) is dry ($\text{MAP} < 2,500 \text{ mm yr}^{-1}$), young (5 – 10 kyr), and chemical weathering is still in its initial stages (Porder et al., 2007; Porder and Chadwick, 2009). Soils are classified as Inceptisols and Andisols, and contain high abundances of primary minerals (King et al., 2016; Vitousek, 2004b). The high

permeability of the basalt and overlying soils leads to minimal surface runoff on the leeward side of Hawaii. Based on dissolved silica (Si) concentrations, a proxy for silicate weathering, up to 95% of the chemical weathering flux occurs via submarine groundwater discharge (Schopka and Derry, 2012). The majority (83%) of submarine groundwater discharge from the island of Hawaii is concentrated in the youngest bedrock in the Kilauea and Kona regions (Schopka and Derry, 2012).

In contrast, the windward side of Hawaii (Hilo-Hamakua Coast) is wetter (4,000-6,500 mm yr⁻¹) and older (64 – 300 kyr) than the Kona region, and is characterized by perennial rivers on the slopes of the Mauna Kea volcano (Sherrod et al., 2007; Strauch et al., 2015). As basalt ages, secondary non-crystalline minerals such as ferrihydrite, allophane, and imogolite form, decreasing the permeability of the landscape (Chorover et al., 2004), and the loss of primary mineral structure leads to a shift in hydrologic flowpaths from deep, groundwater flow to shallow flow (Schopka and Derry, 2012), and submarine groundwater discharge from the Hilo-Hamakua Coast accounts for 12% of the total discharge (Schopka and Derry, 2012). The oldest and most developed landscape on the island is the windward side of the Kohala peninsula (150 – 400 kyr), characterized by well-developed Andisols and the deeply dissected Pololu and Waipio river valleys (Chadwick et al., 2009; Schopka and Derry, 2012) (Figure 6.1a). Submarine groundwater discharge from the Kohala region accounts for 5% of the submarine groundwater discharge on the main island of Hawaii (Schopka and Derry, 2012).

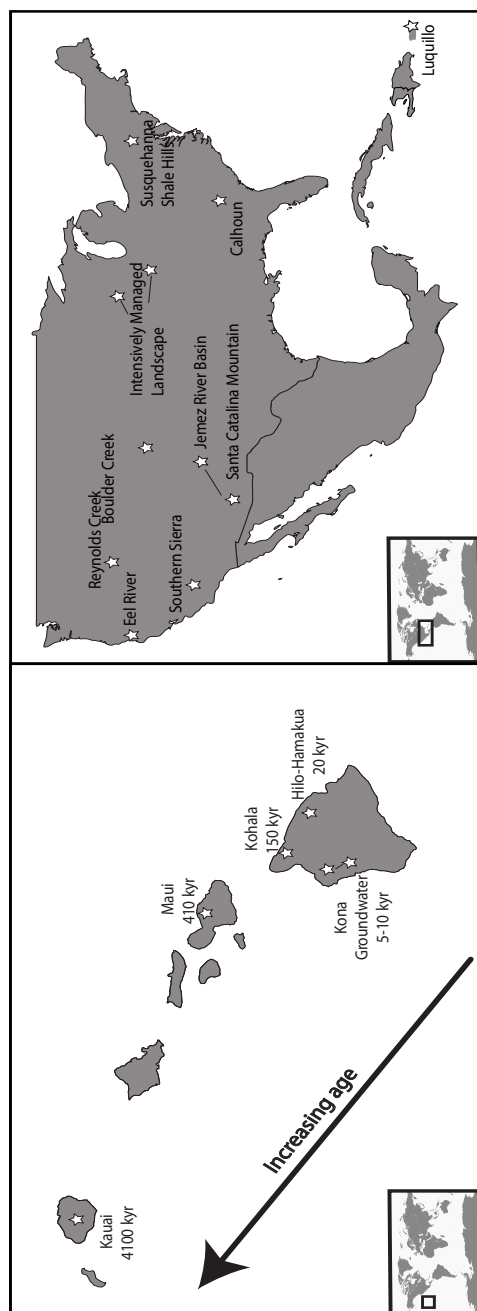


Figure 6.1: Approximate location of sample sites across Hawaii (A) and North America (B). The Hawaiian Islands get progressively older along a northwest transect.

The island of Maui also represents intermediate stages of chemical weathering in Hawaii. For this study, perennial rivers draining soils from the Maui Climate Gradient formed on a 410 kyr lava flow from the Haleakala volcano were sampled (Figure 6.1a). The gradient has MAP values that increase from 2,020 mm yr⁻¹ to 5,050 mm yr⁻¹ (Schuur and Matson, 2001; Thompson et al., 2011, 2007). Soils are classified as Inceptisols and Andisols with high amounts of short-range-ordered (SRO) Fe- (oxyhydr)oxides and mineral-organic matter complexes (Chorover et al., 2004; Thompson et al., 2006b). Strong relationships between soil Eh, iron (Fe) content, and carbon (C) content are well-documented for the Maui Climate Gradient, whereby Eh and Fe decrease and C increases with increasing MAP (Miller et al., 2001; Schuur and Matson, 2001; Thompson et al., 2011). At the dry end of the Maui Climate Gradient, rivers drain soils that are predominately oxic, while at the wet end, rivers drain soils weathered under progressively more anoxic conditions (Schuur and Matson, 2001; Thompson et al., 2011). Previous studies observed increasing Mo mobility with increasing precipitation both before and after an artificial reduction experiment, and a net retention of light Mo isotopes in reducing soils (King et al., 2014; Siebert et al., 2015). Thus, quantifying the dissolved Mo signature from this gradient may allow us to determine the role that redox state plays on riverine Mo.

Kauai is the oldest of the Hawaiian Islands (4,100 kyr) and represents the final stages of chemical weathering (Chadwick et al., 1999; Vitousek, 2004b) (Figure

6.1a). Soils on Kauai are highly-developed Oxisols, where SRO minerals have evolved to more crystalline minerals such as kaolinite, gibbsite, goethite, and hematite (Chorover et al., 2004). A prior study looking at river water chemistry in Waimea Canyon concluded that headwaters drained shallow flowpaths, while water from dissected landscapes drain both shallow flowpaths and groundwater (Schopka and Derry, 2012). The high plateau of Waimea Canyon is characterized by very high MAP ($> 11,000 \text{ mm yr}^{-1}$) with decreasing rainfall towards the coast (Schopka and Derry, 2012; Vitousek et al., 1997).

The Critical Zone Observatory (CZO) Network is comprised of nine catchments around the United States spanning a wide range of range of lithologies and climate conditions suitable for exploring patterns of Mo isotopic composition (Figure 6.1b). Research at the CZO sites investigates interactions between the lithosphere, hydrosphere, atmosphere and biosphere, including landscape evolution and chemical weathering (Brantley and Goldhaber, 2007). Unlike the Hawaiian Islands, in most places soil age cannot be approximated by bedrock age. However, many of the CZOs have published regolith residence times, which can be used to approximate the approximate duration of weathering (Table 6.1). The Eel River CZO watershed is in northern California and forms from complex terrains of argillite, sandstone, conglomerates, and metasedimentary and metavolcanic rocks (Giardino and Houser, 2015), very high denudation rates ($1,700 - 2,200 \text{ tons km}^2 \text{ yr}^{-1}$) and shallow soils (1.5 m) leads to an approximate regolith age of 0.8 kyr (Leithold et al., 2006; US Environmental Protection Agency, 2007). The Reynolds Creek CZO is

situated in southwestern Idaho north of the Owyhee Mountains and is underlain by Tertiary volcanic rocks overlying the Cretaceous granitic basement (Giardino and Houser, 2015), with approximate regolith ages of 3.8 kyr (Patton, 2016). The Clear Creek watershed in the Intensely Managed Landscapes (IML) CZO in northeastern Iowa is formed on loess and glacial till. Assuming modern erosion rates are anthropogenically-mediated and elevated by ~ 300% compared to natural erosion (Abaci and Papanicolaou, 2009), the IML has a regolith age of 5 kyr. The Santa Catalina Mountains – Jemez River Basin CZO (Marshall Gulch watershed) is in southern Arizona and northern New Mexico and is developed on Precambrian/Paleogene-age granite and schist formed from metamorphisms during the Paleozoic (Giardino and Houser, 2015), with a regolith age of 12 kyr (Lybrand et al., 2011; Rasmussen et al., 2008). The Susquehanna Shale Hills CZO (Rose Hill watershed) is situated in the central Appalachian Mountains and is underlain by Silurian Rose Hill Shale. Unlike black shales deposited under euxinic conditions with high Mo concentrations and heavy $\delta^{98}\text{Mo}$ values, the Silurian Rose Hill Formation is an organic- and sulfide- poor gray shale deposited in a more oxic environment (Jin et al., 2010; Liermann et al., 2011; Lyons et al., 2009). The approximate ridgetop soil age is 15 kyr (West et al., 2013). The Boulder Creek CZO (Gordon Gulch watershed) is located in the Colorado Front Range and underlain by Precambrian biotitic-gneiss, and the approximate soil age is 20 kyr (Dethier et al., 2012; Foster et al., 2015). The Luquillo CZO is in the Luquillo Mountains of northeast Puerto Rico. It is split into two main watersheds; the Mamayes watershed is underlain by volcaniclastic bedrock,

and the Rio Blanco watershed which drains into the Icacos River and its tributary, the Guaba River, is underlain by granodiorite (Giardino and Houser, 2015; Stallard and Murphy, 2012; White et al., 1998). Weathering produces soils with high clay content in the Mamayes watershed and soils with high sand content in the Rio Blanco watershed (McDowell et al., 2012). Approximate regolith age for the Mamayes is 55 kyr (Dosseto et al., 2012) and 125 kyr for the Icacos watershed (Pett-Ridge et al., 2009). The Southern Sierra CZO (Providence watershed) is developed from residuum and colluvium of granite, granodiorite, and quartz diorite, with weakly developed soils (Giardino and Houser, 2015); the approximate regolith age is 142 kyr (Dixon et al., 2009; Holbrook et al., 2014). The Calhoun CZO is in north-central South Carolina on the Southern Piedmont. Soils are 1,300 kyr-old, highly-weathered Ultisols formed from the residuum of metamorphic and igneous rocks, devoid of primary minerals (Bacon et al., 2012; Giardino and Houser, 2015).

6.3 Methods

Water samples were collected during field campaigns in July of 2013, 2015, and 2017. River samples were collected from the Maui Climate Gradient in July of 2013 from both a dry site (MAP = 2,800 mm yr⁻¹) and a wet site (MAP = 4,050 mm yr⁻¹). We collected four samples from the Kohala peninsula in July 2015. Pololu 1 was collected north of the Pololu Valley and drains gently sloping landscapes with little erosion, thus representing shallow flowpaths. Pololu 2 was collected within Pololu Valley and WP87 was collected directly adjacent to Pololu Valley. The last sample we collected was from the mouth of the Wailoa River in the Waipio Valley. The Waipio

Valley is a deeply dissected valley that formed after a giant landslide between 250 and 230 kyr (Lamb et al., 2007). Groundwater was also collected from a total of 10 wells in the Kona region of Hawaii. Molybdenum isotope data for 7 of the 10 groundwater samples have been previously reported in King et al., (2016). In July 2016, perennial rivers were sampled at gauge stations along the Hilo-Hamakua Coast and seven samples were also collected on Kauai along a river transect in the Waimea Valley previously studied by Shopka and Derry (2012). Water samples from the Critical Zone Observatories (CZOs) were collected from river gauge sites between July 2016 and May 2017. The particulate flux was not considered in this study and thus all samples were collected in acid-washed, 1 L Nalgene bottles, passed through 0.45- μ m filter paper, and acidified to pH 2 with 0.1 M ultrapure HNO_3 .

Samples were dried down on a hot plate, refluxed twice in concentrated ultrapure HNO_3 , and re-suspended in 5 mL of 0.5 M ultrapure HNO_3 . Trace metal (Mo, Rb, Nb, REE, Pb, Th, U) concentrations were measured on a Thermo X-Series II Inductively Couple Plasma Mass Spectrometer (ICP-MS) and major elements (Al, Mn, Fe, Ti) were measured on a Teledyne Leeman Prodigy ICP-OES. A mixed-element solution standard was used for instrument calibration. A USGS standard (BCR-2) was monitored and agreed with published concentrations within 2% (Li et al., 2014). Procedural blanks for Mo were less than 5% of the lowest Mo concentration collected in the concentrated samples.

Molybdenum isotope measurements were performed on a Nu Plasma Multicollector (MC)-ICP-MS at Oregon State University. A ^{97}Mo - ^{100}Mo double spike

targeted to yield a $^{97}\text{Mo}/^{98}\text{Mo}$ ratio of 3 was added to samples following trace metal elemental analyses. Samples were dissolved in a 1 M HF – 0.5 M HCl solution and 200 μL of H_2O_2 was added to each sample to ensure complete oxidation prior column chromatography. The procedures for the double-spike and column chromatography are outlined in King et al., (2016). Briefly, Bio-Rad AG1-X8 anion resin is used to separate Mo from possible elemental interferences including iron (Fe), manganese (Mn), and zirconium (Zr). Mo is eluted in 1 M HCl, dried down, and re-suspended in 0.5 M HNO_3 for isotopic analysis.

Isotope measurements are made relative to NIST SRM 3134 (Lot No.: 891307) (Goldberg et al., 2012; Greber et al., 2012) and are reported in delta notation ($\delta^{98}\text{Mo}$) for $^{98}\text{Mo}/^{95}\text{Mo}$ ratios:

$$\delta^{98}\text{Mo} = \left[\frac{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{sample}}}{\left(\frac{^{98}\text{Mo}}{^{95}\text{Mo}} \right)_{\text{NIST SRM 3134}}} - 1 \right] \cdot 1000$$

Repeated measurements of an in-house standard (Alfa Aesar Specpure® Product No.: 35758 (Lot No.: 23-16504a)) and USGS rock standards BCR-2 ($n = 72$), BHVO-2 ($n = 36$), and SDO-1 ($n = 45$), over two years yielded $\delta^{98}\text{Mo}$ values of -0.15‰, -0.01‰, -0.04‰, and +0.80‰. External reproducibility of the Alfa-Aesar in-house standard is $\pm 0.10\text{‰}$ (2σ , $n = 180$).

6.4 Results

In Hawaii, Mo dynamics change as a function of the duration of weathering that the environment has experience. Mo concentrations were highest in groundwater samples and decreased with increasing age, and on average Mo was 40x more concentrated (average = 41.4 nM) in groundwater relative to river samples (average = 0.93 nM), (Table 6.1 and Figures 6.2a and 6.3a). Small tributaries in Kauai, draining the oldest, most developed lithology had the lowest Mo concentrations (0.07 nM) (Table 6.1).

Overall, groundwater draining young bedrock was characterized by relatively uniform Mo isotope signatures ($\delta^{98}\text{Mo}$) slightly heavier than bedrock. Waters draining intermediate-aged sites were both lighter and heavier than bedrock, and waters collected from the oldest sites were the heaviest, and not as variable as the intermediate-aged sites (Figure 6.3b). The $\delta^{98}\text{Mo}$ of groundwater and most rivers were heavier than previously measured Hawaiian basalt values ($-0.13\text{‰} \pm 0.17\text{‰}$ 2σ , $n = 6$) (King et al., 2016; Liang et al., 2017; Siebert et al., 2015) (Table 6.1, Figures 6.2b and 6.3b). Rivers draining older, more developed lithology showed a greater variation in $\delta^{98}\text{Mo}$ with values ranging from: -0.53‰ to $+0.36\text{‰}$ on the main island of Hawaii, -0.47‰ to $+0.49\text{‰}$ on Maui, and $+0.11\text{‰}$ to $+0.87\text{‰}$ on Kauai (Figure 6.2b). The samples with the lightest $\delta^{98}\text{Mo}$ values were collected from areas where redox fluctuations were observed (Maui Climate Gradient site 5, mean annual precipitation $5,050 \text{ mm yr}^{-1}$) or hypothesized to be occurring (Hilo-Hamakua Coast, mean annual precipitation from $4,663$ to $6,426 \text{ mm yr}^{-1}$) (Table 6.1). On both Kohala

and Kauai, there was a decrease in $\delta^{98}\text{Mo}$ values between upstream and downstream samples. This shift from heavy $\delta^{98}\text{Mo}$ values to $\delta^{98}\text{Mo}$ values closer to bedrock was concurrent with a known shift from waters draining shallow flowpaths upstream to deeper groundwater flowpaths downstream (Figure 6.3b, 6.4a, and 6.4b).

Across the CZO network, Mo concentrations ranged from 0.15 nM to 81.1 nM (Figure 6.2a and 6.3a), and $\delta^{98}\text{Mo}$ values ranged from +0.21‰ to +1.92‰ (Figure 6.2b and 6.3b). The heaviest $\delta^{98}\text{Mo}$ value was measured in the Mamayes River from the Luquillo CZO and corresponded to a low Mo concentration (0.62 nM). The lightest $\delta^{98}\text{Mo}$ values was measured in the Marshall Gulch from the Santa Catalina Mountains-Jemez River Basin CZO and corresponded to the highest Mo concentration from the CZO sites (81.1 nM) (Table 6.1). Ancillary trace metal solute chemistry is also recorded in Appendix D.1 for both the Hawaiian Islands and the CZOs. Additionally, in areas where discharge data was available for the Hawaiian Islands (Schopka and Derry, 2012; Strauch et al., 2015) and the CZOs (<http://criticalzone.org/national/data/list-datasets/>, 2017), annual Mo fluxes were calculated. Generally, sites with the highest Mo concentrations also had the highest Mo discharge fluxes (Table 6.1).

Table 6.1: Mo geochemical data for groundwater and river samples

Location	Sample	Soil Order	Duration of weathering kyr	Discharge $\text{m}^3 \text{s}^{-1}$	Mo Discharge mol Mo yr^{-1}	MAP mm yr^{-1}	Mo nM	$\delta^{87}\text{Mo}$ ‰
Hawaii (main island) <i>Kona Region</i>	PW1	Inceptisols/Andisols	5 - 10	245	171682	385	22.46	0.20
	PW3	Inceptisols/Andisols	5 - 10	--	--	385	19.26	--
	PW4	Inceptisols/Andisols	5 - 10	245	166953	385	21.84	0.00
	PW7	Inceptisols/Andisols	5 - 10	245	315290	385	41.25	0.11
	IW5	Inceptisols/Andisols	5 - 10	--	--	376	51.15	--
	Puu Lani	Inceptisols/Andisols	5 - 10	245	288954	592	37.80	0.26
	Puu Waa Waa	Inceptisols/Andisols	5 - 10	--	--	672	29.89	--
	Keel	Inceptisols/Andisols	5 - 10	245	88279	1252	11.55	0.09
	Kalaoa	Inceptisols/Andisols	5 - 10	245	130714	955	17.10	0.19
	Honokuhua	Inceptisols/Andisols	5 - 10	245	1267683	1000	165.84	0.19
<i>Hilo-Hamaku Coast</i>	Makahiloa	Inceptisols/Andisols	64 - 300	0.02	0.07	4663	0.15	-0.01
	Pahale	Inceptisols/Andisols	64 - 300	--	--	4026	0.09	--
	Manoloa	Inceptisols/Andisols	64 - 300	0.01	0.02	5205	0.14	0.36
	Manowaiopae	Inceptisols/Andisols	64 - 300	--	--	4689	0.17	--
	Kapue	Inceptisols/Andisols	64 - 300	0.5	2	5696	0.14	0.63
	Honolii	Inceptisols/Andisols	64 - 300	1.06	3	5751	0.11	-0.53
	Kolekole	Inceptisols/Andisols	64 - 300	0.47	69	6426	4.72	-0.21
	Pololu 1	Andisols	400	64.8	3154	4000	1.56	0.25
	Pololu 2	Andisols	400	--	--	4000	0.61	--
	WP87	Andisols	400	64.8	2400	4000	1.19	0.07
Mauli, Hawaii	Waipio	Andisols	400	0.1	16	4000	7.56	-0.01
Mauli, Hawaii	MCG site 3	Inceptisols/Andisols	410	--	--	2800	0.13	0.49
	MCG site 5	Inceptisols/Andisols	410	--	--	5050	0.17	-0.47
Kauai, Hawaii								
	Kokee Upstream	Oxisols	4100	67	158	1600	0.08	0.87
	Kokee Downstream	Oxisols	4100	--	--	1600	0.07	--
	Kokee Tributary	Oxisols	4100	--	--	1600	0.59	--
	Waimea River, dam	Oxisols	4100	67	776	1142	0.37	0.11
	Waimea River, Poo Koea	Oxisols	4100	67	1136	1142	0.54	0.31
	Waimea River, powerhouse	Oxisols	4100	67	1519	906	0.73	0.29
	Waimea River, ford	Oxisols	4100	67	1055	546	0.50	0.65

Table 6.1 (continued)

Location	Sample	Soil Order	Duration of weathering kyr	Discharge $\text{m}^3 \text{ s}^{-1}$	Mo Discharge mol Mo yr^{-1}	MAP mm yr^{-1}	Mo nM	$\delta^{86}\text{Mo}$ ‰
Critical Zone Observatories (CZO)								
<i>Eel River</i>	S. fork Eel/Angelo Coast	Inceptisols	0.8	19	774	1500	1.31	0.90
<i>Reynolds</i>	Johnston Draw	Mollisols	3.8	1.2	74	616	1.93	0.77
<i>Intensely Managed Landscapes</i>	Reynolds Mountain	Mollisols	3.8	1.2	30	803	0.78	0.83
	Clear Creek	Alfisols/Mollisols	5.0	--	--	889	2.04	--
<i>Santa Catalina Mountains-Jemez River Basin</i>	Marshall Gulch	Inceptisols	12	1.9	4883	800	81.97	0.25
<i>Susquehanna Shale Hills</i>	Rose Hill	Inceptisols/Ultisols	15	0.001	0.01	1050	0.15	0.78
<i>Boulder</i>	Gordon Gulch	Entisols/Mollisols	20	0.01	2	519	9.14	1.11
<i>Luquillo</i>	Mamayes	Ultisols	55	1.6	31	4200	0.62	1.92
<i>Southern Sierra</i>	Icacos	Inceptisols	125	0.4	5	3080	0.39	0.21
	Guaba Ridge	Inceptisols	125	0.01	0.1	3080	0.30	1.70
	Providence Creek	Inceptisols	142	0.02	0.4	1200	0.70	0.91
<i>Calhoun</i>	Weir 3	Ultisols	1300	--	--	1300	0.15	--
	Weir 4	Ultisols	1300	0.001	0.005	1300	0.62	1.10
	Holcomb	Ultisols	1300	0.001	0.06	1300	2.03	0.67

^afor locations where regolith age data does not exist, approximate age was estimated using

published denudation rates, average soil depths, and assumed soil densities

^bMAP = mean annual precipitation

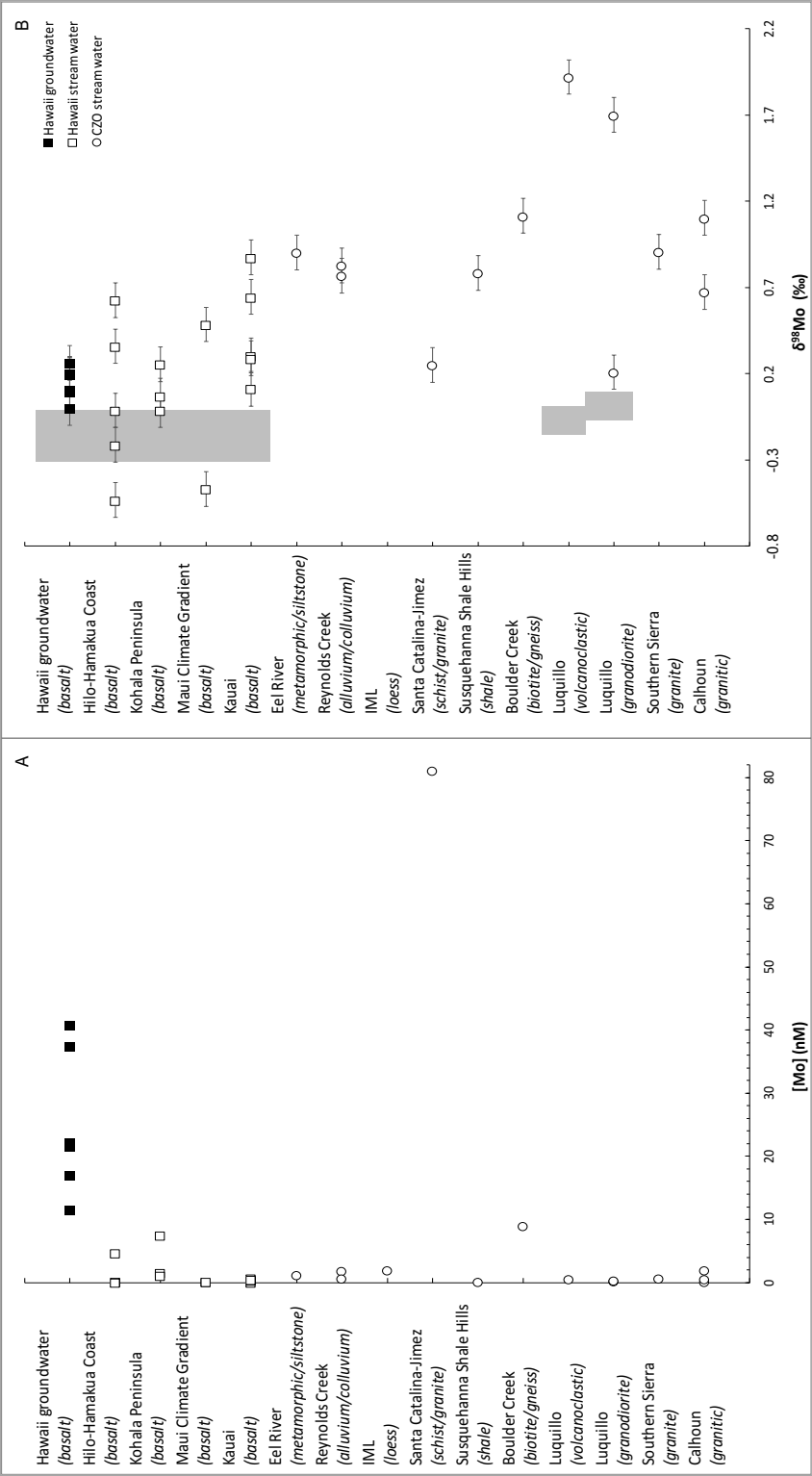


Figure 6.2: Mo concentration and $\delta^{98}\text{Mo}$ data for Hawaiian groundwater and rivers in Hawaii and the CZOs. A) Gray bars indicate average bedrock values for Hawaiian Islands and the Luquillo Critical Zone Observatory based on Chapter 5. Error on the $\delta^{98}\text{Mo}$ data refers to the external reproducibility of in-house standard ($\pm 0.10\text{‰}$).

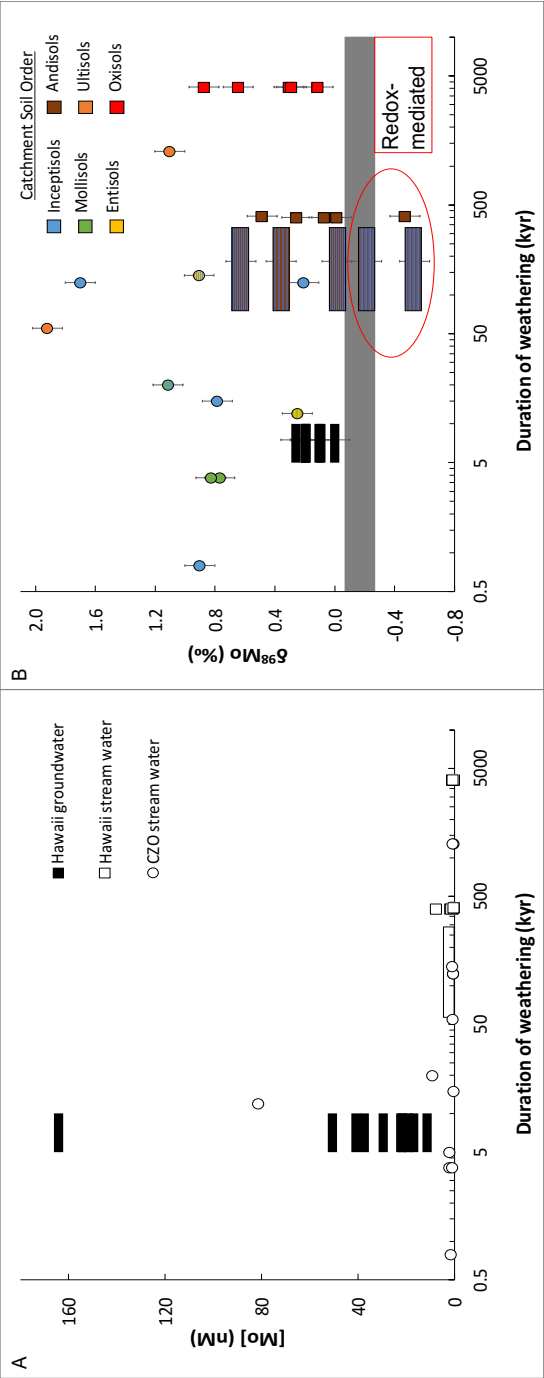


Figure 6.3: A) Mo concentration and B) $\delta^{98}\text{Mo}$ data plotted as a function of approximate regolith age. Hawaiian groundwater (black bars), river samples from Hawaii (squares), and the Critical Zone Observatories (circles). Symbol color represents soil order of the catchment. Gray bar indicates range of Hawaiian bedrock (-0.13‰ to -0.17‰). Error on the $\delta^{98}\text{Mo}$ data refers to the external reproducibility of in-house standard ($\pm 0.10\text{‰}$).

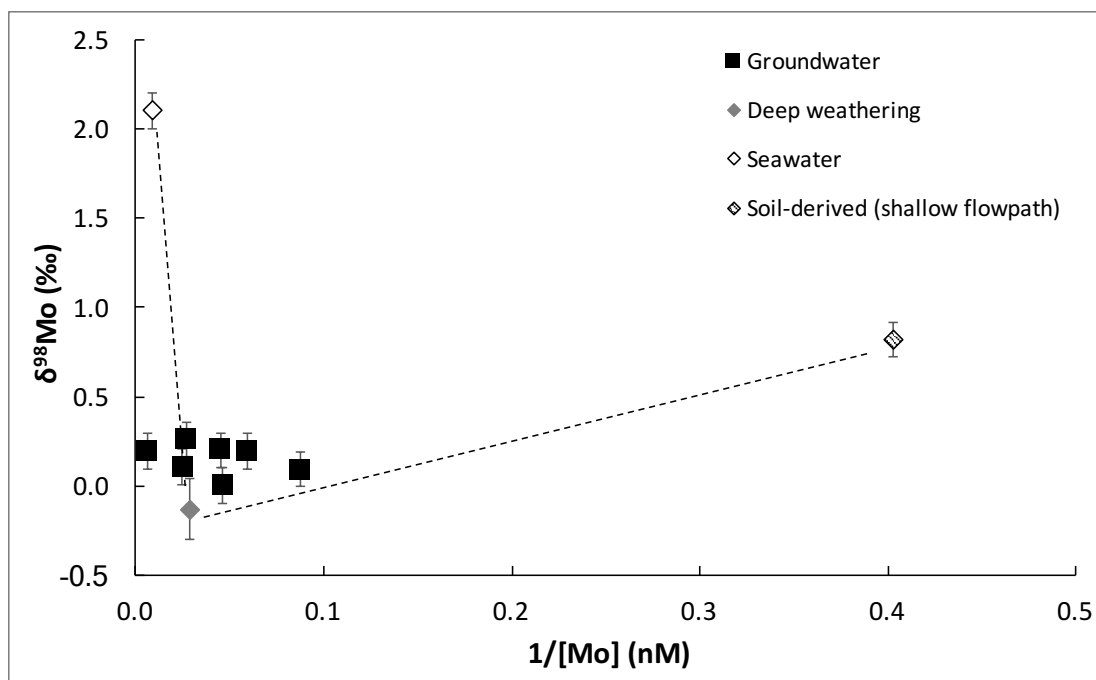


Figure 6.4: Mixing plot between seawater, Hawaiian basalt, and Mo leaching from soils.

Groundwater samples do not fall on a singly linear mixing plot (dashed lines) suggesting that both fractionation in soils and seawater input may affect $\delta^{98}\text{Mo}$ signatures. However, the majority of the $\delta^{98}\text{Mo}$ signal in groundwater comes from initial stages of weathering and Mo entering the dissolved phase relatively unfractionated relative to bedrock. An average leach $\delta^{98}\text{Mo}$ value was calculated using an isotopic mass balance assuming known values of the total groundwater flux, average seawater and Hawaiian basalt $\delta^{98}\text{Mo}$ values, and leaching fluxes based on King et al., (2016) ($\text{MAP} = 2,100 \text{ mm yr}^{-1}$) and groundwater flux data from Table 2 (Hawaii, "rest of island") of Schopka et al., (2012). This data allows us to calculate the leaching flux of Mo from soils along the Kona Coast to determine that 6% of the groundwater Mo flux is derived from shallow flowpaths, which can then be used to calculate a $\delta^{98}\text{Mo}$ leaching value of +0.82‰. Error on the $\delta^{98}\text{Mo}$ data for groundwater refers to the external reproducibility of in-house standard ($\pm 0.10\text{‰}$), seawater Mo concentrations and $\delta^{98}\text{Mo}$ is reported in Goldberg et al., (2013). Basalt $\delta^{98}\text{Mo}$ is an average of data reported in Siebert et al., (Siebert et al., 2015), King et al., (2016), and Liang et al., (2017) ($\pm 0.17\text{‰}$).

6.5 Discussion

6.5.1 *Mo behavior during initial stages of chemical weathering*

The main island of Hawaii represents a landscape undergoing initial (Kona) to intermediate (Hilo-Hamakua and Kohala) stages of chemical weathering, with a concurrent shift from deep, groundwater flowpaths to shallow flowpaths as soils age and the landscape becomes dissected and less permeable (Schopka and Derry, 2012; Strauch et al., 2015). Dissolved Mo concentrations on this island simultaneously undergo a large, two orders of magnitude, decrease between groundwater samples that drain 5 – 10 kyr Kona bedrock (where there is no surface runoff) and river samples draining shallow flowpaths from 64 – 300 kyr regolith from the Hilo-Hamakua Coast (Figure 6.2a and 6.3a). This decline in Mo concentrations coincides with a shift in $\delta^{98}\text{Mo}$ values; the $\delta^{98}\text{Mo}$ of groundwater is varies little (0.00‰ to +0.26‰) and is similar to bedrock ($-0.13 \text{ ‰} \pm 0.17 \text{ ‰ } 2\sigma, n = 6$) (King et al., 2016; Liang et al., 2017; Siebert et al., 2015), and the $\delta^{98}\text{Mo}$ of Hilo-Hamakua river waters is highly variable and both heavier (+0.63‰) and lighter (-0.53‰) than bedrock.

High Mo concentrations in groundwaters can be attributed to the initial stages of rapid primary mineral weathering from basalt. High chemical weathering fluxes in Hawaiian landscapes formed < 20 kyr ago have been shown to result from the rapid weathering of volcanic glass, olivine, and plagioclase and subsequent leaching (Chorover et al., 2004; Vitousek et al., 1997). In Hawaiian basalts, volcanic glass and titaniferous phases (titanite and ilmenite) are the major hosts of Mo (1 – 40 ppm) (Greaney et al., 2016). In neutral to alkaline pH, the oxidative weathering

leads to the release of Mo as the highly soluble molybdate (MoO_4^{2-}) oxyanion, where it remains a conservative metal during transport (Aiuppa et al., 2000; Leybourne and Cameron, 2008). Because Hawaiian groundwaters tend to be oxic (Kelly, 2012; Prouty et al., 2017), high Mo concentrations in groundwater are likely a result of the accumulation of weathering products in the subsurface environment.

Isotopically, groundwater Mo is slightly heavier (0.00‰ to +0.26‰) than the average $\delta^{98}\text{Mo}$ of Hawaiian basalt ($-0.13\text{‰} \pm 0.17\text{‰}$) (Table 6.1, Figures 6.2b and 6.3b). This suggests that there are mechanisms, albeit minor, that shift $\delta^{98}\text{Mo}$ even in the earliest stages of weathering. Possible mechanisms generating a heavy Mo signature include contamination by hydrothermal or seawater Mo, the incongruent dissolution of mineral phases, and adsorption processes in the terrestrial environment. It has been previously observed that hydrothermally altered Mo in marine environments is isotopically heavy (+0.5‰) (McManus et al., 2002). However, since Hawaiian groundwater has an average temperature of 20°C down to 500 m below sea level (Conrad et al., 1997; Johnson et al., 2008; Peterson et al., 2009), there is little evidence that Hawaiian waters are hydrothermally influenced, and none of the wells in this study have any reported hydrothermal influence (Bauer, 2003). Alternatively, seawater Mo is also isotopically heavy ($\delta^{98}\text{Mo} = +2.1\text{‰}$) and can contribute to the observed groundwater $\delta^{98}\text{Mo}$. In Hawaii, groundwater exists as a freshwater basal lens overlying seawater that has permeated into the bedrock, and there is potential for this input to affect our groundwater results. Schopka and Derry (2012) measured the influence of seawater on groundwater

samples collected in the Kona region of Hawaii and determined that seawater contamination accounted for < 10% of their groundwater samples. Assuming sodium (Na) is a proxy for seawater intrusion and has a concentration of 478 mM, < 1 % of groundwater is derived from seawater contamination (Na was measured for samples PW1 – PW7, IW5) (Table E.1). Nevertheless, since Na was not measured for every groundwater sample, we can explore the possible effect of seawater with a simple mixing model, whereby seawater has a Mo concentration of 111 nM and a $\delta^{98}\text{Mo}$ value of +2.1‰ and the primary mineral dissolution endmember has a Mo concentration of ~ 35 nM (average groundwater Mo concentration corrected for 10% seawater intrusion) and a $\delta^{98}\text{Mo}$ value of -0.13‰ (average Hawaiian basalt) (Figure 6.4). In this case, only two of the groundwater samples fall along the linear mixing line between basalt-derived and seawater Mo, implying other mechanisms are likely responsible for the observed $\delta^{98}\text{Mo}$ values.

The next possible explanation for the slightly heavier Mo signature in groundwater is the incongruent dissolution of mineral phases. A recent study measuring the $\delta^{98}\text{Mo}$ composition for a suite of lava samples that were formed from fractional crystallization from a singular source in Iceland show that the incompatible nature of Mo leads to no isotope fractionation during magmatic differentiation for lavas ranging from basalts to rhyolites (J. Yang et al., 2015), suggesting that preferential dissolution of certain mineral phases should not alter the $\delta^{98}\text{Mo}$ values relative to the bulk rock. However, the Mo isotopic composition of individual primary minerals in Hawaiian basalts is not known, and other studies from

both basalts and granites have shown that the incongruent dissolution of Mo phases may lead to $\delta^{98}\text{Mo}$ values that deviate from bedrock (Voegelin et al., 2014, 2012). For example, the fractional crystallization of light Mo into hornblende and biotite led to these mineral phases being 0.6‰ lighter than bulk rock, which requires other Mo phases to be isotopically heavy (Voegelin et al., 2014). Moreover, sulfide minerals—which are easily dissolved under oxidizing environments—are a major host phase for Mo and possess a wide variation in $\delta^{98}\text{Mo}$ values that range from -1.6‰ to +2.3‰ (Breillat et al., 2016). Although sulfides within Hawaiian basaltic glass contain low concentrations of Mo (< 6 ppm) (Greaney et al., 2016), if these phases are enriched in heavy isotopes there is potential for groundwater $\delta^{98}\text{Mo}$ to reflect the preferential dissolution of Mo from sulfide phases.

The final mechanism driving slightly heavy Mo isotope in groundwater is the retention of light Mo isotopes in soils, which has been previously observed in Hawaiian soils (King et al., 2016; Siebert et al., 2015). Groundwater samples were collected from environments with beginning stages of soil development, and the adsorption of light Mo isotopes onto preliminary secondary mineral phases may lead to the retention of heavy Mo in soils (Figure 6.5, Table E.2). Molybdenum has been shown to adsorb to both organic matter and (to a lesser extent) SRO Fe- and Mn-(oxyhydr)oxides in soils (King et al., 2016; Marks et al., 2015; Wichard et al., 2009). The isotopic composition of soils from a 10 kyr climate gradient in Kona are lighter than the bedrock from which the soil is derived, despite Mo inputs from isotopically heavy atmospheric sources, suggesting fractionation mechanisms during initial

stages of soil development (Figure 6.5) (King et al., 2016). The total Mo groundwater flux can be calculated by multiplying the (seawater-corrected) average Mo groundwater concentration (35 nM) by the total groundwater flux (Schopka and Derry, 2012) to yield a total Mo flux of 5.36×10^{14} ng Mo yr⁻¹. Assuming a soil-derived leaching flux of 6.35 ng Mo cm⁻² (King et al., 2016) and a weathering area of 5,090 km² [area of Hawaii where surface discharge is zero (Schopka and Derry, 2012)] we can estimate the annual flux of Mo leached via shallow flowpaths to be 3.23×10^{14} ng Mo yr⁻¹, which turns out to be 6% of the total Mo groundwater flux. Furthermore, if the $\delta^{98}\text{Mo}$ value of groundwater (+0.15‰) is a mixture of 10% seawater ($\delta^{98}\text{Mo} = +2.1\text{‰}$), 84% deep weathering ($\delta^{98}\text{Mo} = -0.13\text{‰}$, average Hawaiian basalt), and 6% soil-derived leaching, we can calculate a shallow flowpath $\delta^{98}\text{Mo}$ endmember of +0.82‰. Atmospheric inputs would also be accounted for in the shallow flowpath flux because they would initially cycle through soils prior to release into groundwater. This suggests that although vog and atmospheric inputs are important to the Mo isotopic composition of soils, they do not significantly alter groundwater Mo behavior. In this scenario, mixing between the deep weathering, shallow flowpaths, and seawater endmembers accounts for all but one groundwater sample (Honokuhua) (Figure 6.4).

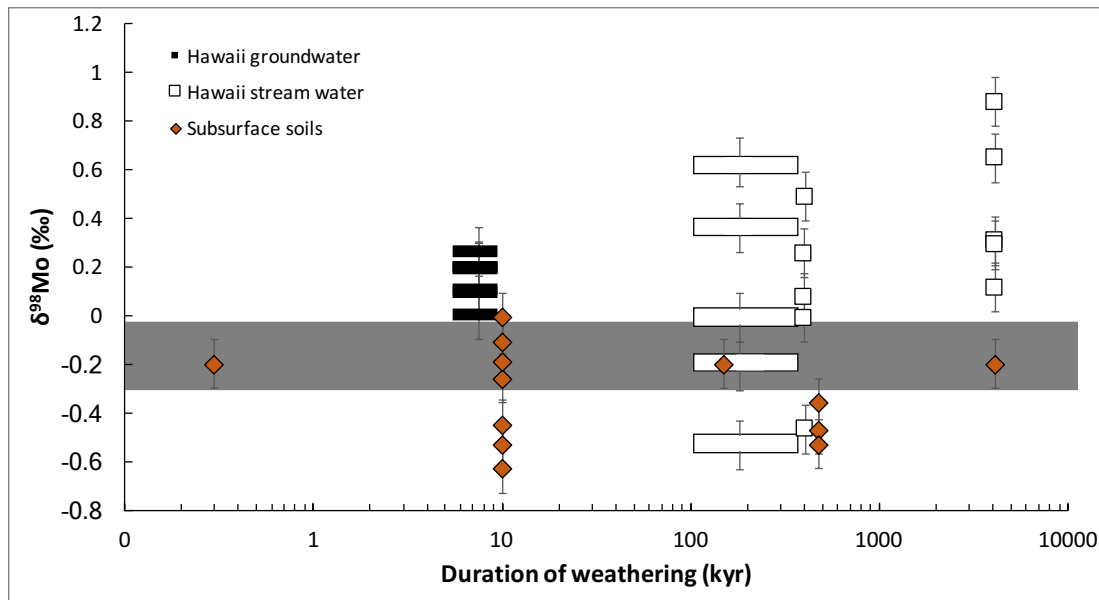


Figure 6.5: Hawaii water samples (groundwater = black, river water = white) compared to soil samples (brown diamonds) of similar ages. Waters tend to be enriched in heavy isotopes while soils tend to be enriched in light isotopes. Error on the $\delta^{98}\text{Mo}$ data for groundwater refers to the external reproducibility of in-house standard ($\pm 0.10\text{‰}$).

6.5.2 *Mo behavior during intermediate- to late- stages of chemical weathering*

As chemical weathering proceeds and landscapes evolve on the Hawaiian Islands, both groundwater and shallow flowpaths become important components of the total flux of weathering products. The relative effect of groundwater Mo and riverine Mo can be assessed by looking at water samples collected from the Hilo-Hamakua Coast, the Kohala peninsula, and Kauai. Rivers on the Hilo-Hamakua Coast are formed on 64 – 300 kyr lava flows and drain soils undergoing intermediate stages of chemical weathering under much wetter conditions (MAP = 4,663 – 6,426 mm yr⁻¹). Molybdenum concentrations are lower for these rivers than for the groundwater samples and the $\delta^{98}\text{Mo}$ is highly variable (Table 6.1, Figure 6.3). These observations can be explained by the ultimate source of water in the Hilo-Hamakua Coast region. Since the high permeability of bedrock underneath these soils prevents the formation of perched aquifers that would supply groundwater to rivers, water is supplied directly from shallow flowpaths draining these soils (Schopka and Derry, 2012; Strauch et al., 2015; Tribble, 2008). Low Mo concentrations in rivers and $\delta^{98}\text{Mo}$ values that range from -0.53‰ to +0.63‰ suggest that multiple mechanisms may be responsible for shifting $\delta^{98}\text{Mo}$ values relative to bedrock values, including the adsorption of Mo onto SRO Fe- and Mn- (oxyhydr)oxides and organic matter in soils, and direct atmospheric inputs from isotopically heavy sources (Chapters 3 and 4) (Figure 6.3).

In more geographically dissected parts of the Hawaiian Islands, the effect of groundwater inputs to river samples can be assessed. For example, headwaters of the Wailoa River drain shallow flowpaths, but once the Wailoa River plunges into Waipio Valley, Si concentrations dramatically increase, suggesting additional contribution from groundwater. Schopka and Derry (2012) estimated that between 15% and 50% of the water in Waipio Valley comes from groundwater. Our Mo data supports this conclusion as the concentration of Mo in Waipio Valley is elevated and the $\delta^{98}\text{Mo}$ value is lighter than the rest of the Kohala peninsula, likely signifying a Mo source that is less fractionated from bedrock (Figure 6.6a). Assuming the $\delta^{98}\text{Mo}$ of shallow flow in this region is represented by Pololu 1 (+0.25‰), which drains gently sloping soils, and the $\delta^{98}\text{Mo}$ of the deep weathering endmember reflects bedrock (-0.13‰), a mixing calculation between soil and groundwater Mo sources reveals that 32% of Mo in Waipio Valley is ultimately sourced from groundwater (Figure 6.6a).

The effect of groundwater versus shallow flowpaths is even more pronounced on samples collected along the Waimea River in Kauai, the most weathered of the Hawaiian Islands (Figures 6.3 and 6.6b). The headwaters are characterized by low Mo concentrations and the heaviest $\delta^{98}\text{Mo}$ signatures of all the samples measured in Hawaii (+0.87‰) (Table 6.1, Figure 6.2b). This signature likely arises from millions of years of soil development where light Mo is retained in soils. Once waters enter the Waimea Valley, there is an order of magnitude increase in Mo concentrations and a decrease in $\delta^{98}\text{Mo}$ from +0.87‰ to +0.11‰ (Figure 6.6b). Schopka and Derry (2012) estimate that groundwater is responsible for 30% of the

water volume; therefore, this rapid shift in Mo dynamics is likely a result of an increase in groundwater input. As the Waimea River proceeds downstream, Mo concentrations stay broadly constant and $\delta^{98}\text{Mo}$ shifts towards heavier values, eventually reaching a value of +0.65‰ prior to entering the ocean (Figure 6.6b). A possible explanation for the trend in $\delta^{98}\text{Mo}$ is that once waters enter the Waimea Valley and receive the initial pulse of groundwater input, small tributaries at Po'o Koeha and the Powerhouse sites add Mo from shallow flowpaths (Figure 6.6b).

This dataset reveals the importance of shallow and deep flowpaths to the overall river discharge, and may explain why other studies find no evidence of anthropogenic effects (Neubert et al., 2011; Wang et al., 2015). Anthropogenic Mo derived from the atmosphere (Lane et al., 2013) or fertilizers (Charter et al., 1995; McBride and Spiers, 2001) may lead to the addition of Mo with unique $\delta^{98}\text{Mo}$ signature to terrestrial environments (King et al., 2016). Moreover, the contribution of groundwater, which has higher Mo concentrations, would overprint anthropogenic effects to smooth out variable $\delta^{98}\text{Mo}$.

6.5.3 Effect of soil redox conditions on shallow flowpaths

A highlight of the Hawaii dataset is the possible effect of reducing conditions on the $\delta^{98}\text{Mo}$ signature of rivers along the Hilo-Hamakua Coast and the Maui Climate Gradient (Figures 6.3b and 6.6). Along the Hilo-Hamakua Coast, MAP increases from 4,663 mm yr⁻¹ to 6,426 mm yr⁻¹. With increasing precipitation, $\delta^{98}\text{Mo}$ values decrease such that high precipitation landscapes are enriched in light Mo isotopes (Table 6.1, Figures 6.3b). Although we do not have data to determine if the wettest

sites in the Hilo-Hamakua Coast experience consistent reducing conditions, it is likely that redox fluctuations are occurring since soils are actively accumulating products that affect soil aggregation and oxygen availability (SRO Fe- and Mn- (oxyhydr)oxides and organic matter) (Leffelaar, 1993; Schuur and Matson, 2001). The behavior of Mo in soils is attributed to the preferential adsorption of light Mo onto both SRO Fe- and Mn- (oxyhydr)oxides (Goldberg et al., 2009) and organic matter (Chapter 4) (e.g. Figure 6.5). Thus, under reducing conditions, the dissolution of Fe- and Mn- (oxyhydr)oxides and the dispersion of organic matter has the potential to release light Mo into porewaters and eventually rivers (Siebert et al., 2015).

Molybdenum data from the Maui Climate Gradient, which is a well-characterized redox gradient supports this observation. Soils at the driest site (MAP $\sim 2,800 \text{ mm yr}^{-1}$) are predominately oxic while soils at the wettest site (MAP $\sim 4,050 \text{ mm yr}^{-1}$) experience fluctuation reducing conditions (Schuur et al., 2001; Schuur and Matson, 2001). A river sample collected from the dry site is enriched in heavy Mo isotopes ($\delta^{98}\text{Mo} = +0.25\text{‰}$) while a river sample collected from the wet site is enriched in light Mo isotopes ($\delta^{98}\text{Mo} = -0.47\text{‰}$) (Table 6.1, Figure 6.2b and 6.3b). This indicates that in soils where reducing conditions persist, light Mo is leached into surface waters in contrast to the observation that under oxic conditions, light Mo is retained in soils and waters are isotopically heavy.

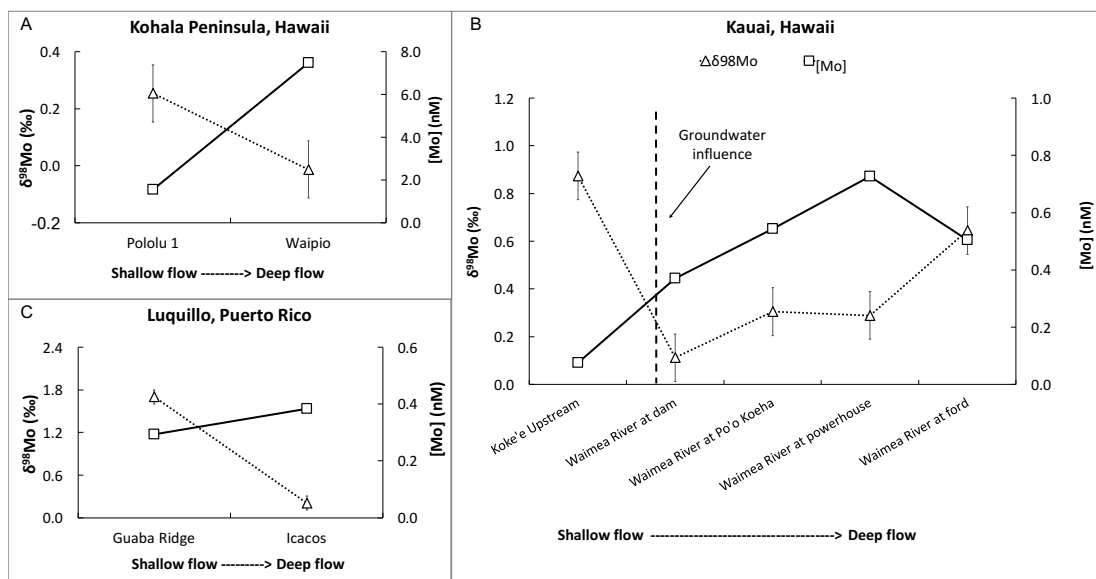


Figure 6.6: $\delta^{98}\text{Mo}$ and [Mo] values for the Kohala Peninsula, Hawaii (A), Kauai, Hawaii (B), and Luquillo, Puerto Rico (C) where there is a clear difference between Mo sourced from shallow flow and deep flow (groundwater). Groundwater Mo is more concentrated and will have a higher [Mo] value. It is also less fractionated towards heavy Mo relative to shallow flow.

6.5.4 Mo in Critical Zone Observatories (CZOs)

Molybdenum data from the CZOs illustrates the variability of Mo isotopes from a wide range of sedimentary, igneous, and metamorphic rock types (Table 6.1). Except for Marshall Gulch (Santa Catalina-Jimez CZO), Mo concentrations are lower than groundwater measured in Hawaii, and although bedrock $\delta^{98}\text{Mo}$ values for the CZOs are unconstrained, riverine $\delta^{98}\text{Mo}$ in this dataset tends to be heavier than the range of $\delta^{98}\text{Mo}$ values for the average continental crust (+0.1‰ to +0.4‰) (Willbold and Elliott, 2017) (Figure 6.3b). These observations suggest that the observed Mo trajectory from Hawaii is applicable to other lithologies (Figures 6.2 and 6.3).

The Luquillo CZO provides a lithological contrast to better understand Mo dynamics. The Mamayes is underlain by volcanoclastic bedrock that weathers to soils with low permeability and high clay content. The low permeability leads to shallow flowpaths through highly weathered soils (Larsen, 2012; Stallard and Murphy, 2012), where the retention of light Mo can explain the heavy $\delta^{98}\text{Mo}$ values of the Mamayes (+1.92‰) relative to bedrock (-0.07‰, Figure 6.2b). On the other hand, in the nearby Rio Icacos watershed, the granodiorite soil profile is characterized as having high permeability and deep flowpaths (Buss et al., 2008). As such, the $\delta^{98}\text{Mo}$ value of the Icacos is less fractionated (+0.21‰) relative to bedrock (+0.11‰ to +0.13‰, Figure 6.2b).

On the other hand, the effect of deep versus shallow flowpaths can be further explored within the granodiorite catchment of the Luquillo CZO. Despite draining the same catchment lithology, the $\delta^{98}\text{Mo}$ value of the Guaba River, a

tributary to the Icacos, is heavy (+1.70‰). To understand this paradox, the effect of scaling must be considered. Although Guaba is also formed on granodiorite, it drains products from shallow flowpaths at rates up to five times greater than the Icacos (Wymore et al., 2017). Guaba is also situated at the uppermost range of precipitation gradient at the Luquillo CZO (MAP = 4,200 mm yr⁻¹), where intense hotspots of weathering have been observed (Bhatt and McDowell, 2007), potentially leading to highly fractionated $\delta^{98}\text{Mo}$ values (Figure 6.6c). The mineralogy of the granodiorite soil profiles precludes the effects of redox-mediated dissolution events, such that the light $\delta^{98}\text{Mo}$ signatures observed for Hawaiian waters at this precipitation range are not achieved (see Chapter 5), and thus a heavy $\delta^{98}\text{Mo}$ flux, derived from shallow flowpaths, prevails (Figure 6.6c). Nevertheless, even though the riverine $\delta^{98}\text{Mo}$ of Guaba is heavy, the net flux of Mo transported out of the larger catchment (Icacos) is less fractionated relative to bedrock, suggesting that a modulation of $\delta^{98}\text{Mo}$ values is occurring, either through the mixing of tributaries or the input of deep weathering inputs via groundwater seepage. This is potentially a driving mechanisms for the observed $\delta^{98}\text{Mo}$ signatures entering larger catchments and eventually the ocean (Figure 6.6c).

Similar groundwater influences may also be seen in the Santa Catalina Mountains-Jemez River Basin CZO, where a high elevation river (Marshall Gulch) was sampled. Marshall Gulch is a zero-order basin where the dominance of macropores within the soils leads to a tight coupling between the surface and shallow groundwater flow (Heidbüchel et al., 2013; Trostle et al., 2016; Zhang et al., 2015).

High Mo concentrations may be a result of easily-weathered Mo-sulfide phases (molybdenite, wulfenite, powellite), all of which are found in the Santa Catalina Mountains (Wilt et al., 1985, 1984), and an unfractionated $\delta^{98}\text{Mo}$ value (+0.25‰) relative to average continental crust suggest aligns well with previously reported molybdenite values (Breillat et al., 2016), suggesting that Mo is derived from contact with unweathered bedrock. At the other end of the weathering spectrum is the Calhoun CZO, which drains highly-weathered soils and leaches water with heavy $\delta^{98}\text{Mo}$ signatures. Soils from the Calhoun CZO are devoid of primary minerals and have high contents of Fe- and Mn- (oxyhydr)oxides with low surface charge (Giardino and Houser, 2015). The Calhoun CZO is an example on the range of $\delta^{98}\text{Mo}$ values (+0.67‰ to +1.10‰) that can be expected from a highly-weathered soil endmember (Table 6.1, Figures 6.2b and 6.3b).

6.5.5 Implications for global Mo fluxes

We can combine the data from this study with literature discharge and $\delta^{98}\text{Mo}$ values to reassess the global Mo input to the ocean (Appendix D, Figures 6.7 and 8). Previously reported discharge fluxes span seven orders of magnitude, and the $\delta^{98}\text{Mo}$ signature is most variable in samples where the Mo flux is low (Figure 6.8). This is likely where the effects of fractionation during Mo adsorption in soils (Figure 6.5), atmospheric inputs, incongruent dissolution, and redox-mediated events contribute to the $\delta^{98}\text{Mo}$ values. The effect of mixing of tributaries with varying signatures smooths out the variability of the small catchments such that for rivers that account for high Mo fluxes to the ocean, the range of $\delta^{98}\text{Mo}$ values may

be constrained to narrow range closer to continental crust values (Figures 6.7 and 6.8). Groundwater samples provide a possible mechanism for the relationship between Mo flux and $\delta^{98}\text{Mo}$ variability, as high concentrations of weakly fractionated Mo enter rivers via groundwater seepage and modulate the riverine signal (e.g. Figure 6.6). Our results align well with hydrological studies that hypothesize that groundwater springs developed in riparian zones and floodplains are an important control on solute chemistry for large catchments (Shaman et al., 2004; Wolock et al., 1997). Alternatively, the pattern of decreasing variability with increasing catchment size may be driven by mixing of tributary streams with heterogeneous chemistry (Hrachowitz et al., 2010) (e.g. Figure 6.6b).

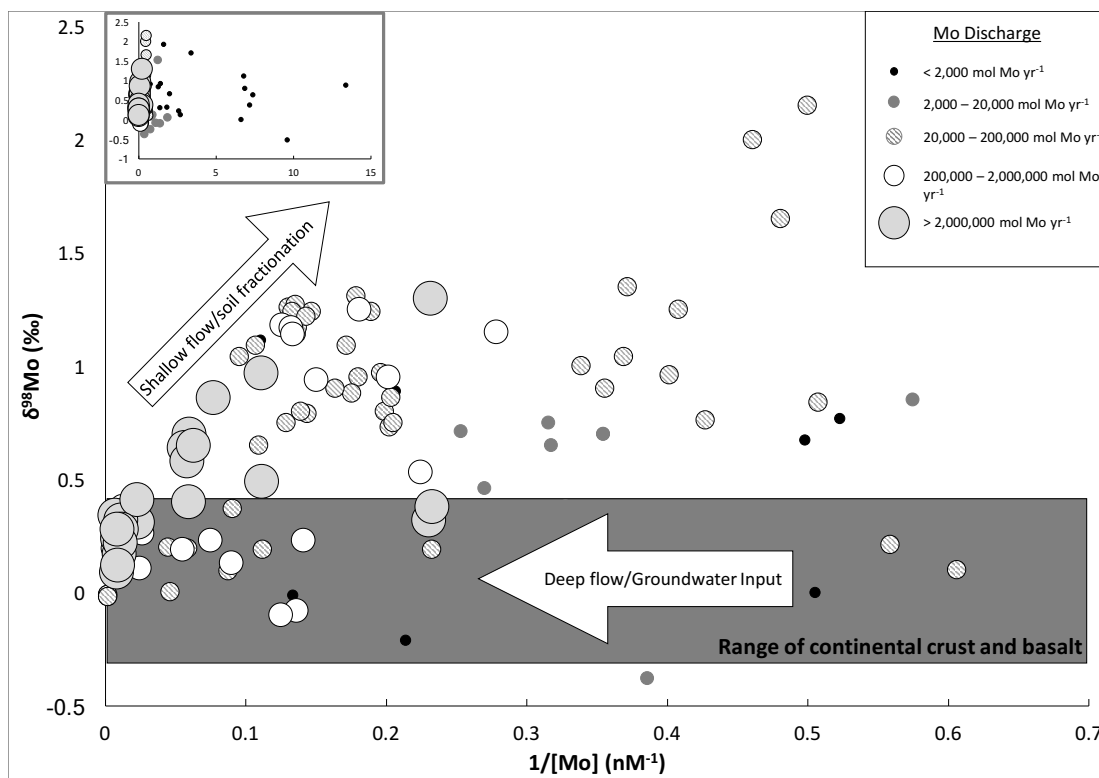


Figure 6.7: $\delta^{98}\text{Mo}$ values plotted as a function of the inverse of Mo concentrations from a suite of studies reporting Mo isotope data for rivers.

The size of the symbols reflects the Mo discharge of the catchment. Large rivers (catchments) have less variable Mo concentrations and $\delta^{98}\text{Mo}$ values relative to small catchments, and form a relatively linear trend where increased chemical weathering or shallow flow input leads to heavy Mo and lower concentrations as fractionation processes lead to the retention of light isotopes in soils. Samples with a high input of deep flow (groundwater) have higher Mo concentrations and less fractionated $\delta^{98}\text{Mo}$ values. As Mo discharge decreases, the non-linear variability in $\delta^{98}\text{Mo}$ values suggest that multiple fractionate processes are occurring including adsorption onto Fe- and Mn- (oxyhydr)oxides and organic matter, atmospheric inputs, and redox-mediated dissolution events. The dark gray horizontal bar shows the range in $\delta^{98}\text{Mo}$ values for continental crust (+0.1‰ to +0.4) and Hawaiian basalt ($-0.13\text{‰} \pm 0.17\text{‰}$). The inset reflects the full range of Mo concentration values.

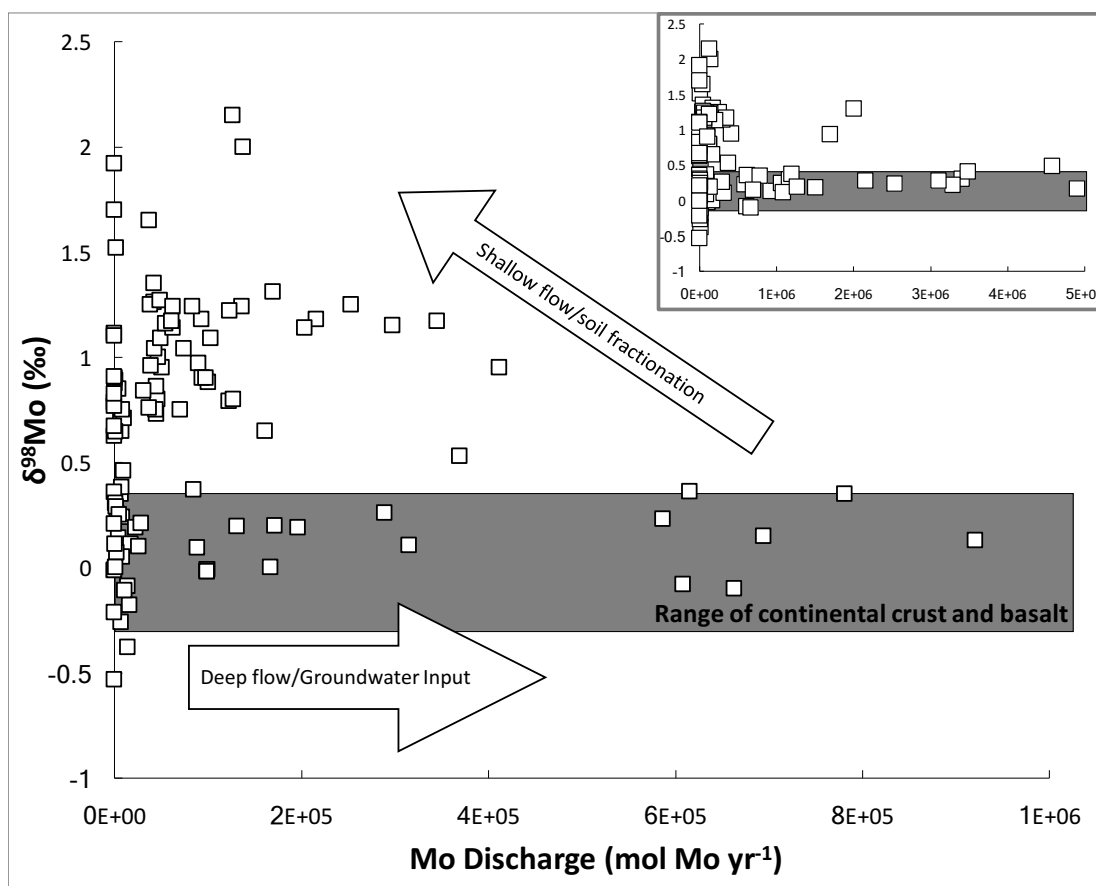


Figure 6.8: Direct plot of $\delta^{98}\text{Mo}$ values versus Mo discharge. As discharge increases, the range of $\delta^{98}\text{Mo}$ values is constrained towards bedrock values. As Mo discharge decreases, the non-linear variability in $\delta^{98}\text{Mo}$ values suggest that multiple fractionate processes are occurring including adsorption onto Fe- and Mn- (oxyhydr)oxides and organic matter, atmospheric inputs, and redox-mediated dissolution events. Redox events would lead to the input of light Mo as reductive dissolution of Fe- and Mn- (oxyhydr)oxides occurs. The dark gray horizontal bar shows the range in $\delta^{98}\text{Mo}$ values for continental crust (+0.1‰ to +0.4) and Hawaiian basalt ($-0.13\text{‰} \pm 0.17\text{‰}$). The inset reflects the full range of discharge values, which shift by nearly 6 orders of magnitude.

In addition to the effect of groundwater on stream base flow, the direct input of submarine groundwater discharge to oceans is comparable to the riverine discharge (Burnett et al., 2003; Jeong et al., 2012; Kim et al., 2005; Moore, 1996), and thus may be a significant source of trace metals (Charette and Buesseler, 2004; Jeong et al., 2012; Windom et al., 2006). If groundwater can contribute up to 40% of the total discharge flux to the oceans (Moore, 2010, 1996), and the total flux of Mo to the ocean is $3.1 \times 10^8 \text{ mol yr}^{-1}$ (Miller et al., 2011), we can calculate an isotopic mass balance to determine the $\delta^{98}\text{Mo}$ of the total input. Assuming that the riverine input has a $\delta^{98}\text{Mo}$ value of +0.5‰ (Archer and Vance, 2008) and the average groundwater signature is +0.15‰ (this study), the discharge-weighted $\delta^{98}\text{Mo}$ signature becomes +0.36‰, which falls within the range of average continental crust values (Archer and Vance, 2008). Albeit limited, in Hawaiian groundwater systems, only conservative mixing between seawater and submarine groundwater discharge has been observed (Prouty et al., 2017), but research efforts should be made to determine whether mechanisms exist that may drive non-conservative mixing patterns such as those seen in rivers (Pearce et al., 2010).

Groundwater inputs may constrain the possible range of $\delta^{98}\text{Mo}$ values through Earth's history to values near that of the average continental crust. Although our dataset is limited to groundwater samples from the main island of Hawaii, a basaltic lithology, previous studies have determined that basalt contributes disproportionately to global weathering fluxes relative to other bedrock types (Dessert et al., 2003). One potential application that highlights the importance

of the groundwater $\delta^{98}\text{Mo}$ signature throughout Earth's history is understanding the paleoredox implications of volcanism that generates large igneous provinces (LIP) (Deccan Traps, Siberian Plateau, etc.), which leads to oceanic anoxic events (Voegelin et al., 2012). Since LIP volcanism would lead to the rapid weathering of basalt, it is likely that the Mo flux to the oceans was higher than modern day but that the $\delta^{98}\text{Mo}$ of the flux was only weakly fractionated relative to bedrock. Thus, these periods of Earth history would be comparable to the Mo behavior we observe on the main island of Hawaii.

Complications still arise when Mo is used as a paleoredox tracer in regional basins or on short time-scales. For example, over glacial-interglacial timescales, the adsorption and subsequent fractionation of Mo in soils may be greater during deglaciations and interglacial periods where increased precipitation, temperature, and fresh minerals leads to increased chemical weathering (Vance et al., 2009), and thus the formation of secondary minerals and organic matter that adsorb Mo, generating low Mo fluxes fractionated from bedrock. This will be most pronounced in regional basins where the riverine input is not at steady-state with the rest of the global ocean (von Blanckenburg et al., 2015) and groundwater seepage is minimal. Studies looking at the sedimentary Mo over these timescales (Jilbert and Slomp, 2013; Nameroff et al., 2004; Scholz et al., 2014) will need to determine the proportion of deep versus shallow flowpaths draining terrestrial environments and the possible range of Mo fractionation in water samples to accurately use Mo as a paleoredox tracer.

6.6 Conclusion

This study illustrates that groundwater fluxes may be an important component of the global Mo budget, and likely constrains the signature of $\delta^{98}\text{Mo}$ oceanic inputs to values closer to that of the average continental crust. Overall, dissolved Mo behavior is driven by the ultimate source of the flux. Shallow flowpaths reflect the net signal of Mo as it cycles through the terrestrial environment, and are most apparent in small catchments where Mo discharge is low. Groundwater reflects less fractionated (relative to bedrock) $\delta^{98}\text{Mo}$ signatures and typically has higher Mo concentrations than rivers. The input of groundwater to base flow modulates small-scale $\delta^{98}\text{Mo}$ variability in rivers including fractionation mechanisms arising from Mo adsorption and desorption in soils, redox-mediated dissolution of soil components, and any anthropogenic or atmospheric Mo inputs. As such, groundwater has the potential to constrain the variation in ocean inputs throughout Earth's history.

6.7 Acknowledgements

We thank the many volunteers from each of the Critical Zone Observatories who helped with sample collection. NSF award EAR-1053470 to Pett-Ridge supported this work. We also acknowledge support from the NSF-supported Critical Zone Observatory Network.

Chapter 7: Conclusion

The goal at the outset of this dissertation was to determine the mechanisms driving Mo behavior and isotope fractionation in terrestrial environments to understand how Mo can be used as a tracer of biogeochemical processes. Overall, terrestrial Mo cycling leads to isotope fractionation and the retention of isotopically light Mo relative to bedrock. In environments with fluctuating redox conditions, short-term Mo behavior is a function of reductive dissolution of Fe- (oxyhydr)oxides and colloid mobilization. However, longer term retention in soils is dominated by adsorption to organic matter, and the preferential adsorption of light Mo leads to the retention of light Mo isotopes within soils. Furthermore, Mo isotope fractionation during adsorption onto organic matter is similar in magnitude and direction as fractionation during adsorption onto SRO Fe- (oxyhydr)oxides (Barling and Anbar, 2004; Goldberg et al., 2009; Wasylenki et al., 2011, 2008). This result has implications for the utility of Mo as a paleoredox proxy, as Mo adsorption onto organic matter in euxinic settings may shift the sedimentary record away from reflecting the seawater Mo isotope compositions.

Another conclusion from my dissertation is that atmospheric inputs represent a substantial flux of Mo to soil, and in many cases, exceed the flux of Mo from chemical weathering and the dissolution of primary minerals. As such, atmospheric inputs have the potential to overprint the fractionation signal within soils. The role of atmospheric inputs has been recognized for a number of major and trace metals (Bern et al., 2015a; Clergue et al., 2015; Monastra et al., 2004). Yet, the

role of atmospheric inputs for both Mo accumulation and the isotopic signature is still largely unconstrained. Atmospheric inputs via precipitation is isotopically heavy ($+1.1‰ \pm 0.14‰$), but does not consistently reflect the isotopic composition of seawater ($+2.1‰$), suggesting that other fractionation mechanisms or sources, i.e. scavenging of dust/volcanic aerosols/anthropogenic inputs, contribute to atmospheric Mo. Therefore, additional research should focus on quantifying possible atmospheric sources of Mo to the terrestrial system, especially in locations affected by anthropogenic emissions or dust-derived inputs (Chappaz et al., 2012; Lane et al., 2013).

Finally, I determined that the isotope signature of dissolved Mo entering the oceans is modulated by groundwater inputs exhibiting little to no isotope fractionation relative to bedrock. Therefore, even though terrestrial Mo cycling leads to complex Mo systematics, the input to the oceans may be constrained to a narrow range throughout Earth history. This result has important implications for periods of Earth's history where groundwater inputs may have been greater than they are today, such as during periods with high volcanism or glaciations where the amount of exposed bedrock was greater. In these instances, it may be reasonable to assume that the Mo isotopic composition entering the oceans reflects the average continental crust in order to calculate the extent of global euxinic conditions using the Mo sedimentary record.

My dissertation investigates the processes that fractionate Mo prior to input in the oceans. The importance of atmospheric inputs and the observation that Mo

adsorption onto organic matter pools is greater than adsorption onto Fe- and Mn-(oxyhydr)oxide pools suggests that the utility of Mo as a redox tracer in soils is suppressed by additional fractionation mechanisms. However, the weakly fractionated Mo groundwater flux to the ocean may modulate the Mo input to the oceans throughout Earth's history and help the scientific community to better predict the isotopic signature of Mo oceanic inputs, which is essential to employing Mo as a paleoredox proxy.

Chapter 8: Bibliography

- Abaci, O., Papanicolaou, A.N.T., 2009. Long-term effects of management practices on water-driven soil erosion in an intense agricultural sub-watershed: monitoring and modelling. *Hydrol. Process.* 23, 2818–2837. doi:10.1002/hyp
- Aiuppa, A., Allard, P., D'Alessandro, W., Michel, A., Parello, F., Treuil, M., Valenza, M., 2000. Mobility and fluxes of major, minor and trace metals during basalt weathering and groundwater transport at Mt. Etna volcano (Sicily). *Geochim. Cosmochim. Acta* 64, 1827–1841. doi:10.1016/S0016-7037(00)00345-8
- Algeo, T.J., Lyons, T.W., 2006. Mo-total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* 21, n/a-n/a. doi:10.1029/2004PA001112
- Alloway, B., 2013. *Heavy Metals in Soil: Trace Metals and Metalloids in Soil and Their Bioavailability*. Reading, UK Springer.
- Amrhein, C., Mosher, P.A., Strong, J.E., 1993. Colloid-Assisted Transport of Trace Metals in Roadside Soils Receiving Deicing Salts. *Soil Sci. Soc. Am. J.* 57, 1212. doi:10.2136/sssaj1993.03615995005700050009x
- Amundson, R., Richter, D.D., Humphreys, G.S., Jobbágy, E.G., Gaillardet, J., 2007. Coupling between Biota and Earth Materials in the Critical Zone. *Elements* 3.
- Anbar, A.D., 2004. Molybdenum Stable Isotopes: Observations, Interpretations and Directions. *Rev. Mineral. Geochemistry* 55, 429–454. doi:10.2138/gsrmg.55.1.429
- Anbar, A.D., Duan, Y., Lyons, T.W., Arnold, G.L., Kendall, B., Creaser, R.A., Kaufman, A.J., Gordon, G.W., Scott, C., Garvin, J., Buick, R., 2007. A Whiff of Oxygen Before the Great Oxidation Event? *Science* (80-.). 317.
- Anbar, A.D., Knab, K.A., Barling, J., 2001. Precise determination of mass-dependent variations in the isotopic composition of molybdenum using MC-ICPMS. *Anal. Chem.* 73, 1425–1431. doi:10.1021/ac000829w
- Anbar, A.D., Rouxel, O., 2007. Metal Stable Isotopes in Paleoceanography. *Annu. Rev. Earth Planet. Sci.* 35, 717–746. doi:10.1146/annurev.earth.34.031405.125029
- Anderson, S.P., von Blanckenburg, F., White, A.F., 2007. Physical and Chemical Controls on the Critical Zone. *Elements* 3.

- Archer, C., Vance, D., 2008. The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nat. Geosci.* 1, 597–600. doi:10.1038/ngeo282
- Ardakani, O.H., Chappaz, A., Sanei, H., Mayer, B., 2016. Effect of thermal maturity on remobilization of molybdenum in black shales. *Earth Planet. Sci. Lett.* 449, 311–320. doi:10.1016/j.epsl.2016.06.004
- Arnold, G.L., 2004. Molybdenum Isotope Evidence for Widespread Anoxia in Mid-Proterozoic Oceans. *Science* (80-). 304, 87–90. doi:10.1126/science.1091785
- Arnórsson, S., Óskarsson, N., 2007. Molybdenum and tungsten in volcanic rocks and in surface and <100 °C ground waters in Iceland. *Geochim. Cosmochim. Acta* 71, 284–304. doi:10.1016/j.gca.2006.09.030
- Bacon, A.R., Richter, D., Bierman, P.R., Rood, D.H., 2012. Coupling meteoric 10be with pedogenic losses of 9be to improve soil residence time estimates on an ancient North American interfluvium. *Geology* 40, 847–850. doi:10.1130/G33449.1
- Baes, C.F., Mesmer, R.E., 1976. *The Hydrolysis of Cations*. New York.
- Balistrieri, L.S., Chao, T., 1990. Adsorption of selenium by amorphous iron oxyhydroxide and manganese dioxide. *Geochim. Cosmochim. Acta* 54, 739–751. doi:10.1016/0016-7037(90)90369-V
- Barling, J., Anbar, A.D., 2004. Molybdenum isotope fractionation during adsorption by manganese oxides. *Earth Planet. Sci. Lett.* 217, 315–329. doi:10.1016/S0012-821X(03)00608-3
- Barling, J., Arnold, G.L., Anbar, A.D., 2001. Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth Planet. Sci. Lett.* 193, 447–457. doi:10.1016/S0012-821X(01)00514-3
- Barron, A.R., Wurzburger, N., Bellenger, J.P., Wright, S.J., Kraepiel, A.M.L., Hedin, L.O., 2008. Molybdenum limitation of symbiotic nitrogen fixation in tropical forest soils. *Nat. Geosci.* 2, 42–45. doi:10.1038/ngeo366
- Bauer, G.R., 2003. A study of the ground-water conditions in North and South Kona and South Kohala Districts, Island of Hawaii, 1991–2002 95 p.
- Bauer, M., Blodau, C., 2009. Arsenic distribution in the dissolved, colloidal and particulate size fraction of experimental solutions rich in dissolved organic matter and ferric iron. *Geochim. Cosmochim. Acta* 73, 529–542. doi:10.1016/j.gca.2008.10.030

- Bellenger, J.P., Arnaud-Neu, F., Asfari, Z., Myneni, S.C.B., Stiefel, E.I., Kraepiel, A.M.L., 2007. Complexation of oxoanions and cationic metals by the biscatecholate siderophore azotochelin. *J. Biol. Inorg. Chem.* 12, 367–376. doi:10.1007/s00775-006-0194-6
- Bellenger, J.P., Wichard, T., Kustka, A.B., Kraepiel, A.M.L., 2008. Uptake of molybdenum and vanadium by a nitrogen-fixing soil bacterium using siderophores. *Nat. Geosci.* 1, 243–246. doi:10.1038/ngeo161
- Bellenger, J.P., Wichard, T., Xu, Y., Kraepiel, A.M.L., 2011. Essential metals for nitrogen fixation in a free-living N₂-fixing bacterium: chelation, homeostasis and high use efficiency. *Environ. Microbiol.* 13, 1395–1411. doi:10.1111/j.1462-2920.2011.02440.x
- Bellenger, J.P., Xu, Y., Zhang, X., Morel, F.M.M., Kraepiel, A.M.L., 2014. Possible contribution of alternative nitrogenases to nitrogen fixation by symbiotic N₂-fixing bacteria in soils. *Soil Biol. Biochem.* 69, 413–420. doi:10.1016/j.soilbio.2013.11.015
- Berg, B., Laskowski, R., 2006. *Litter Decomposition : A Guide to Carbon and Nutrient Turnover*. Elsevier, San Diego, CA.
- Bern, C.R., Chadwick, O.A., Kendall, C., Pribil, M.J., 2015a. Steep spatial gradients of volcanic and marine sulfur in Hawaiian rainfall and ecosystems. *Sci. Total Environ.* 514, 250–260. doi:10.1016/j.scitotenv.2015.02.001
- Bern, C.R., Thompson, A., Chadwick, O.A., 2015b. Quantification of colloidal and aqueous element transfer in soils: The dual-phase mass balance model. *Geochim. Cosmochim. Acta* 151, 1–18. doi:10.1016/j.gca.2014.12.008
- Bhatt, M.P., McDowell, W.H., 2007. Controls on major solutes within the drainage network of a rapidly weathering tropical watershed. *Water Resour. Res.* 43, 1–9. doi:10.1029/2007WR005915
- Bibak, A., Borggaard, O.K., 1994. Molybdenum adsorption by aluminum and iron oxides and humic acid. *Soil Sci.* 158, 323–328.
- Bigalke, M., 2010. Copper and zinc stable isotope ratios as traces of biogeochemical processes, sources and transport of Cu and Zn in soils. Dissertation. doi:10.1016/j.gca.2010.08.044
- Bigalke, M., Weyer, S., Wilcke, W., 2010. Copper isotope fractionation during complexation with insolubilized humic acid. *Environ. Sci. Technol.* 44, 5496–5502. doi:10.1021/es1017653
- Binkley, D., Sollins, P., 1990. Factors Determining Differences in Soil pH in Adjacent

- Conifer and Alder-Conifer Stands. *Soil Sci. Soc. Am. J.* 54, 1427–1433.
doi:10.2136/sssaj1990.03615995005400050036x
- Bittner, F., Mendel, R.R., 2006. Cell biology of molybdenum. *Plant Cell Monogr.* 17, 119–143. doi:10.1007/978-3-642-10613-2_6
- Brantley, S.L., Goldhaber, M.B., 2007. The Critical Zone ;, *Elements*.
- Brantley, S.L., Goldhaber, M.B., Ragnarsdottir, K.V., 2007. Crossing Disciplines and Scales to Understand the Critical Zone. *Elements* 3.
- Brantley, S.L., White, A.F., 2009. Approaches to Modeling Weathered Regolith. *Rev. Mineral. Geochemistry* 70.
- Breillat, N., Guerrot, C., Marcoux, E., Négrel, P., 2016. A new global database of $\delta^{98}\text{Mo}$ in molybdenites: A literature review and new data. *J. Geochemical Explor.* 161, 1–15. doi:10.1016/j.gexplo.2015.07.019
- Brimhall, G.H., Chadwick, O.A., Lewis, C.J., Compston, W., Williams, I.S., Danti, K.J., Dietrich, W.E., Power, M.E., Hendricks, D., Bratt, J., 1992. Deformational mass transport and invasive processes in soil evolution. *Science* 255, 695–702.
doi:10.1126/science.255.5045.695
- Brimhall, G.H., Dietrich, W.E., 1987. Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemical systems: Results on weathering and pedogenesis.
- Brinza, L., Benning, L.G., Statham, P.J., 2008. Adsorption studies of Mo and V onto ferrihydrite. *Mineral. Mag.* 72.
- Brucker, R.L.P., McManus, J., Severmann, S., Berelson, W.M., 2009. Molybdenum behavior during early diagenesis: Insights from Mo isotopes. *Geochemistry, Geophys. Geosystems* 10. doi:10.1029/2008GC002180
- Brun, C.B., Åström, M.E., Peltola, P., Johansson, M.B., 2008. Trends in major and trace elements in decomposing needle litters during a long-term experiment in Swedish forests. *Plant Soil* 306, 199–210. doi:10.1007/s11104-008-9572-x
- Bunn, R.A., Magelky, R.D., Ryan, J.N., Elimelech, M., 2002. Mobilization of natural colloids from an iron oxide-coated sand aquifer: Effect of pH and ionic strength. *Environ. Sci. Technol.* 36, 314–322. doi:10.1021/es0109141
- Burkhardt, C., Hin, R.C., Kleine, T., Bourdon, B., 2014. Evidence for Mo isotope fractionation in the solar nebula and during planetary differentiation. *Earth Planet. Sci. Lett.* 391, 201–211. doi:10.1016/j.epsl.2014.01.037

- Burnett, W.C., Bokuniewicz, H., Huettel, M., Moore, W., Taniguchi, M., 2003. Groundwater and pore water inputs to the coastal zone. *Biogeochemistry* 66, 3–33. doi:10.1023/B:BIOG.0000006066.21240.53
- Buss, H.L., Brantley, S.L., Scatena, F.N., Bazilievskaya, E.A., Blum, A., Schulz, M., Jiménez, R., White, A.F., Rother, G., Cole, D., 2013. Probing the deep critical zone beneath the luquillo experimental forest, Puerto Rico. *Earth Surf. Process. Landforms* 38, 1170–1186. doi:10.1002/esp.3409
- Buss, H.L., Bruns, M.A., Schultz, M.J., Moore, J., Mathur, C.F., Brantley, S.L., 2005. The coupling of biological iron cycling and mineral weathering during saprolite formation, Luquillo Mountains, Puerto Rico. *Geobiology* 3, 247–260. doi:10.1111/j.1472-4669.2006.00058.x
- Buss, H.L., Chapela Lara, M., Moore, O.W., Kurtz, A.C., Schulz, M.S., White, A.F., 2017. Lithological influences on contemporary and long-term regolith weathering at the Luquillo Critical Zone Observatory. *Geochim. Cosmochim. Acta* 196, 224–251. doi:10.1016/j.gca.2016.09.038
- Buss, H.L., Sak, P.B., Webb, S.M., Brantley, S.L., 2008. Weathering of the Rio Blanco quartz diorite, Luquillo Mountains, Puerto Rico: Coupling oxidation, dissolution, and fracturing. *Geochim. Cosmochim. Acta* 72, 4488–4507. doi:10.1016/j.gca.2008.06.020
- Campbell, J., Bradfield, G.E., Prescott, C.E., Fredeen, A.L., 2010. The influence of overstorey *Populus* on epiphytic lichens in subboreal spruce forests of British Columbia. *Can. J. For. Res.* 40, 143–154. doi:10.1139/X09-175
- Chacon, N., Silver, W.L., Dubinsky, E.A., Cusack, D.F., 2006. Iron reduction and soil phosphorus solubilization in humid tropical forests soils: The roles of labile carbon pools and an electron shuttle compound. *Biogeochemistry* 78, 67–84. doi:10.1007/s10533-005-2343-3
- Chadwick, O.A., Brimhall, G.H., Hendricks, D.M., 1990. From a black to a gray box — a mass balance interpretation of pedogenesis. *Geomorphology* 3, 369–390. doi:10.1016/0169-555X(90)90012-F
- Chadwick, O.A., Derry, L. a., Bern, C.R., Vitousek, P.M., 2009. Changing sources of strontium to soils and ecosystems across the Hawaiian Islands. *Chem. Geol.* 267, 64–76. doi:10.1016/j.chemgeo.2009.01.009
- Chadwick, O.A., Derry, L. a, Vitousek, P.M., Huebert, B.J., Hedin, L.O., 1999. Changing sources of nutrients during four million years of ecosystem development. *Nature* 397, 491–497. doi:10.1038/17276
- Chadwick, O.A., Gavenda, R.T., Kelly, E.F., Ziegler, K., Olson, C.G., Crawford Elliott,

- W., Hendricks, D.M., Elliott, W.C., Hendricks, D.M., 2003. The impact of climate on the biogeochemical functioning of volcanic soils. *Chem. Geol.* 202, 195–223. doi:10.1016/j.chemgeo.2002.09.001
- Chappaz, A., Lyons, T.W., Gordon, G.W., Anbar, A.D., 2012. Isotopic Fingerprints of Anthropogenic Molybdenum in Lake Sediments. *Env. Sci Technol* 46, 10934–10940. doi:10.1021/es3019379
- Chappaz, A., Lyons, T.W., Gregory, D.D., Reinhard, C.T., Gill, B.C., Li, C., Large, R.R., 2014. Does pyrite act as an important host for molybdenum in modern and ancient euxinic sediments? *Geochim. Cosmochim. Acta* 126, 112–122. doi:10.1016/j.gca.2013.10.028
- Charette, M.A., Buesseler, K.O., 2004. Submarine groundwater discharge of nutrients and copper to an urban subestuary of Chesapeake Bay (Elizabeth River). *Limnol. Oceanogr.* 49, 376–385. doi:10.4319/lo.2004.49.2.0376
- Charter, R.A., Tabatabai, M.A., Schafer, J.W., 1995. Arsenic, molybdenum, selenium, and tungsten contents of fertilizers and phosphate rocks ¹. *Commun. Soil Sci. Plant Anal.* 26, 3051–3062. doi:10.1080/00103629509369508
- Chen, H., Berndtsson, R., Ma, M., Zhu, K., 2009. Characterization of insolubilized humic acid and its sorption behaviors. *Environ. Geol.* 57, 1847–1853. doi:10.1007/s00254-008-1472-0
- Chinea, J.D., Beymer, R.J., Rivera, C., Sastre de Jesús, I., Scatena, F.N., 1993. An Annotated list of the flora of the Bisley area, Luquillo Experimental Forest, Puerto Rico, 1987 to 1992. *Gen. Tech. Rep. SO* 94 12.
- Chorover, J., Amistadi, M.K., Chadwick, O.A., 2004. Surface charge evolution of mineral-organic complexes during pedogenesis in Hawaiian basalt. *Geochim. Cosmochim. Acta* 68, 4859–4876. doi:10.1016/j.gca.2004.06.005
- Chorover, J., Kretzschmar, R., Garcia-Pichel, F., Sparks, D.L., 2007. Soil Biogeochemical Processes within the Critical Zone. *Elements* 3.
- Chorover, J., Sposito, G., 1995. Colloid chemistry of kaolinitic tropical soils. *Soil Sci. Soc. Am. J.* 59, 1558–1564. doi:10.2136/sssaj1995.03615995005900060007x
- Clergue, C., Dellinger, M., Buss, H.L., Gaillardet, J., Benedetti, M.F., Dessert, C., 2015. Influence of atmospheric deposits and secondary minerals on Li isotopes budget in a highly weathered catchment, Guadeloupe (Lesser Antilles). *Chem. Geol.* 414, 28–41. doi:10.1016/j.chemgeo.2015.08.015
- Conrad, M.E., Thomas, D.M., Flexser, S., Vennemann, T.W., 1997. Fluid Flow and Water-Rock Interaction In the East Rift Zone Of Kilauea Volcano, Hawaii. *J.*

- Geophys. Res. Earth 102, 15021–15037.
- Cornish, A.S., Page, W.J., 2000. Role of molybdate and other transition metals in the accumulation of protochelin by *Azotobacter vinelandii*. *Appl. Environ. Microbiol.* 66, 1580–1586. doi:10.1128/AEM.66.4.1580-1586.2000
- Crowe, B.M., Finnegan, D.L., Zoller, W.H., Boynton, W. V., 1987. Trace element geochemistry of volcanic gases and particles from 1983–1984 eruptive episodes of Kilauea Volcano. *J. Geophys. Res.* 92, 13708. doi:10.1029/JB092iB13p13708
- Czaja, A.D., Johnson, C.M., Roden, E.E., Beard, B.L., Voegelin, A.R., Naegler, T.F., Beukes, N.J., Wille, M., 2012. Evidence for free oxygen in the Neoproterozoic ocean based on coupled iron-molybdenum isotope fractionation. *Geochim. Cosmochim. Acta* 86, 118–137. doi:10.1016/j.gca.2012.03.007
- Dahl, T.W., Anbar, A.D., Gordon, G.W., Rosing, M.T., Frei, R., Canfield, D.E., 2010. The behavior of molybdenum and its isotopes across the chemocline and in the sediments of sulfidic Lake Cadagno, Switzerland. *Geochim. Cosmochim. Acta* 74, 144–163. doi:10.1016/j.gca.2009.09.018
- Dahl, T.W., Anbar, A.D., Gordon, G.W., Rosing, M.T., Frei, R.E., Canfield, D.E., 2008. Molybdenum isotope variations in a redox-stratified lake; Removal mechanism and preservation in euxinic sediments. *Geochim. Cosmochim. Acta* 72, A194–A194.
- Dahl, T.W., Chappaz, A., Hoek, J., McKenzie, C.J., Svane, S., Canfield, D.E., 2016. Evidence of molybdenum association with particulate organic matter under sulfidic conditions. *Geobiology* 1–13. doi:10.1111/gbi.12220
- Dahl, T.W., Ruhl, M., Hammarlund, E.U., Canfield, D.E., Rosing, M.T., Bjerrum, C.J., 2013. Tracing euxinia by molybdenum concentrations in sediments using handheld X-ray fluorescence spectroscopy (HHXRF). *Chem. Geol.* 360, 241–251. doi:10.1016/j.chemgeo.2013.10.022
- Dai, M., Martin, J.-M., Cauwet, G., 1995. The significant role of colloids in the transport and transformation of organic carbon and associated trace metals (Cd, Cu and Ni) in the Rhône delta (France). *Mar. Chem.* 51, 159–175. doi:10.1016/0304-4203(95)00051-R
- Dessert, C., Dupré, B., Gaillardet, J., François, L.M., Allègre, C.J., 2003. Basalt weathering laws and the impact of basalt weathering on the global carbon cycle. *Chem. Geol.* 202, 257–273. doi:10.1016/j.chemgeo.2002.10.001
- Dethier, D.P., Birkeland, P.W., McCarthy, J.A., 2012. Using the accumulation of CBD-extractable iron and clay content to estimate soil age on stable surfaces and nearby slopes, Front Range, Colorado. *Geomorphology* 173–174, 17–29.

doi:10.1016/j.geomorph.2012.05.022

- Dixon, J.L., Heimsath, A.M., Amundson, R., 2009. The critical role of climate and saprolite weathering in landscape evolution. *Earth Surf. Process. Landforms* 34, 1507–1521. doi:10.1002/esp.1836
- Dosseto, A., Buss, H.L., Suresh, P.O., 2012. Rapid regolith formation over volcanic bedrock and implications for landscape evolution. *Earth Planet. Sci. Lett.* 337–338, 47–55. doi:10.1016/j.epsl.2012.05.008
- Duce, R. a, Tindale, N.W., 1991. Chemistry and biology of iron and other trace metals in the ocean. *Limnol. Oceanogr.* 36, 1715–1726. doi:10.4319/lo.1991.36.8.1715
- Erickson, B.E., Helz, G.R., 2000. Molybdenum(VI) speciation in sulfidic waters: Stability and lability of thiomolybdates. *Geochim. Cosmochim. Acta* 64, 1149–1158. doi:10.1016/S0016-7037(99)00423-8
- Foster, M.A., Anderson, R.S., Wyshnytzky, C.E., Ouimet, W.B., Dethier, D.P., 2015. Hillslope lowering rates and mobile-regolith residence times from in situ and meteoric ¹⁰Be analysis, Boulder Creek Critical Zone Observatory, Colorado. *Bull. Geol. Soc. Am.* 127, 862–878. doi:10.1130/B31115.1
- Gardner, C.B., Lyons, W.B., Litt, G., Ogden, F.L., 2014. Rock-derived Micronutrient Transport in the Tropics: Molybdenum Cycling in Deeply-weathered Panama Soils. *Procedia Earth Planet. Sci.* 10, 266–270. doi:10.1016/j.proeps.2014.08.057
- Giambelluca, T.W., Chen, Q., Frazier, A.G., Price, J.P., Chen, Y.-L., Chu, P.-S., Eischeid, J.K., Delaporte, D.M., 2013. Rainfall Atlas of Hawaii [WWW Document]. *Bull. Am. Meteorol. Soc.* URL <http://rainfall.geography.hawaii.edu/> (accessed 9.3.15).
- Giambelluca, T.W., Nullet, M.A., Schroeder, T.A., 1986. Rainfall Atlas of Hawai'i, Report R76, Hawai'i Division of Water and Land Development, Department of Land and Natural Resources. Honolulu.
- Giardino, J.R., Houser, C., 2015. Principles and dynamics of the Critical Zone.
- Ginn, B.R., Habteselassie, M.Y., Meile, C., Thompson, A., 2014. Effects of sample storage on microbial Fe-reduction in tropical rainforest soils. *Soil Biol. Biochem.* 68, 44–51. doi:10.1016/j.soilbio.2013.09.012
- Ginn, B.R., Meile, C., Wilmoth, J., Tang, Y., Thompson, A., 2017. Rapid iron reduction rates are stimulated by high-amplitude redox fluctuations in a tropical forest soil. *Environ. Sci. Technol.* acs.est.6b05709. doi:10.1021/acs.est.6b05709
- Goldberg, S., Forster, H.S., Godfrey, C.L., 1996. Molybdenum Adsorption on Oxides,

- Clay Minerals, and Soils. *Soil Sci. Soc. Am. J.* 60, 425.
doi:10.2136/sssaj1996.03615995006000020013x
- Goldberg, T., Archer, C., Vance, D., Poulton, S.W., 2009. Mo isotope fractionation during adsorption to Fe (oxyhydr)oxides. *Geochim. Cosmochim. Acta* 73, 6502–6516. doi:10.1016/j.gca.2009.08.004
- Goldberg, T., Archer, C., Vance, D., Thamdrup, B., McAnena, A., Poulton, S.W., 2012. Controls on Mo isotope fractionations in a Mn-rich anoxic marine sediment, Gullmar Fjord, Sweden. *Chem. Geol.* 296–297, 73–82.
doi:10.1016/j.chemgeo.2011.12.020
- Goldberg, T., Gordon, G., Izon, G., Archer, C., Pearce, C.R., McManus, J., Anbar, A.D., Rehkämper, M., 2013. Resolution of inter-laboratory discrepancies in Mo isotope data: an intercalibration. *J. Anal. At. Spectrom.* 28, 724.
doi:10.1039/c3ja30375f
- Goodfellow, B.W., Chadwick, O.A., Hilley, G.E., 2014. Depth and character of rock weathering across a basaltic-hosted climosequence on Hawai'i. *Earth Surf. Process. Landforms* 39, 381–398. doi:10.1002/esp.3505
- Greaney, A.T., Rudnick, R.L., Gaschnig, R.M., 2016. Crustal Sources of Molybdenum. *Goldschmidt Conf.* June 2016, Yokohama, Japan 982.
- Greber, N.D., Pettke, T., Nägler, T.F., 2014. Magmatic–hydrothermal molybdenum isotope fractionation and its relevance to the igneous crustal signature. *LITHOS* 190–191, 104–110. doi:10.1016/j.lithos.2013.11.006
- Greber, N.D., Siebert, C., Nägler, T.F., Pettke, T., 2012. $\delta^{98}/^{95}\text{Mo}$ values and Molybdenum Concentration Data for NIST SRM 610, 612 and 3134: Towards a Common Protocol for Reporting Mo Data. *Geostand. Geoanalytical Res.* 36, 291–300. doi:10.1111/j.1751-908X.2012.00160.x
- Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? *J. Colloid Interface Sci.* 314, 490–501. doi:10.1016/j.jcis.2007.04.062
- Gupta, U.C., 1997. *Molybdenum in Agriculture*. Cambridge University Press.
- Hall, S.J., Liptzin, D., Buss, H.L., DeAngelis, K., Silver, W.L., 2016. Drivers and patterns of iron redox cycling from surface to bedrock in a deep tropical forest soil: a new conceptual model. *Biogeochemistry* 130, 177–190. doi:10.1007/s10533-016-0251-3
- Hall, S.J., McDowell, W.H., Silver, W.L., 2013. When Wet Gets Wetter: Decoupling of Moisture, Redox Biogeochemistry, and Greenhouse Gas Fluxes in a Humid

- Tropical Forest Soil. *Ecosystems* 16, 576–589. doi:10.1007/s10021-012-9631-2
- Hall, S.J., Silver, W.L., 2015. Reducing conditions, reactive metals, and their interactions can explain spatial patterns of surface soil carbon in a humid tropical forest. *Biogeochemistry* 125, 149–165. doi:10.1007/s10533-015-0120-5
- Hall, S.J., Silver, W.L., 2013. Iron oxidation stimulates organic matter decomposition in humid tropical forest soils. *Glob. Chang. Biol.* 19, 2804–2813. doi:10.1111/gcb.12229
- Hannah, J.L., Stein, H.J., Wieser, M.E., de Laeter, J.R., Varner, M.D., 2007. Molybdenum isotope variations in molybdenite: Vapor transport and Rayleigh fractionation of Mo. *Geology* 35, 703–706. doi:10.1130/G23538A.1
- Heartsill-Scalley, T., Scatena, F.N., Estrada, C., McDowell, W.H., Lugo, A.E., 2007. Disturbance and long-term patterns of rainfall and throughfall nutrient fluxes in a subtropical wet forest in Puerto Rico. *J. Hydrol.* 333, 472–485. doi:10.1016/j.jhydrol.2006.09.019
- Heath, J.A., Huebert, B.J., 1999. Cloudwater deposition as a source of fixed nitrogen in a Hawaiian montane forest. *Biogeochemistry* 44, 119–134. doi:10.1023/A:1006091429143
- Heidbüchel, I., Troch, P.A., Lyon, S.W., 2013. Separating physical and meteorological controls of variable transit times in zero-order catchments. *Water Resour. Res.* 49, 7644–7657. doi:10.1002/2012WR013149
- Heil, D., Sposito, G., 1993. Organic Matter Role in Illitic Soil Colloids Flocculation: I. Counter Ions and pH. *Soil Sci. Soc. Am. J.* 57, 1241. doi:10.2136/sssaj1993.03615995005700050014x
- Helz, G.R., Bura-Nakić, E., Mikac, N., Ciglencčki, I., 2011. New model for molybdenum behavior in euxinic waters. *Chem. Geol.* 284, 323–332. doi:10.1016/j.chemgeo.2011.03.012
- Helz, G.R., Miller, C. V., Charnock, J.M., Mosselmans, J.F.W., Patrick, R. a D., Garner, C.D., Vaughan, D.J., 1996. Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochim. Cosmochim. Acta* 60, 3631–3642. doi:10.1016/0016-7037(96)00195-0
- Helz, G.R., Vorlicek, T.P., Kahn, M.D., 2004. Molybdenum scavenging by iron monosulfide. *Environ. Sci. Technol.* 38, 4263–4268. doi:10.1021/es034969+
- Henderson, R., Kabengi, N., Mantripragada, N., Cabrera, M., Hassan, S., Thompson, a., 2012. Anoxia-induced release of colloid- and nanoparticle-bound phosphorus in grassland soils. *Environ. Sci. Technol.* 46, 11727–11734.

doi:10.1021/es302395r

- Hernandez, L., Probst, A., Probst, J.L., Ulrich, E., 2003. Heavy metal distribution in some French forest soils: Evidence for atmospheric contamination. *Sci. Total Environ.* 312, 195–219. doi:10.1016/S0048-9697(03)00223-7
- Hiemstra, T., Van Riemsdijk, A.W.H., 1996. A Surface Structural Approach to Ion Adsorption: The Charge Distribution (CD) Model. *J. Colloid Interface Sci.* 179, 488–508.
- Hin, R.C., Burkhardt, C., Schmidt, M.W., Bourdon, B., Kleine, T., 2013. Experimental evidence for Mo isotope fractionation between metal and silicate liquids. *Earth Planet. Sci. Lett.* 379, 38–48. doi:10.1016/j.epsl.2013.08.003
- Holbrook, W.S., Riebe, C.S., Elwaseif, M., Hayes, J.L., Basler-reeder, K., Harry, D.L., Malazian, A., Dosseto, A., Hartsough, P.C., Hopmans, J.W., 2014. Geophysical constraints on deep weathering and water storage potential in the Southern Sierra Critical Zone Observatory 380, 366–380. doi:10.1002/esp.3502
- Hotchkiss, S., Vitousek, P.M., Chadwick, O.A., Price, J., 2000. Climate cycles, geomorphological change, and the interpretation of soil and ecosystem development. *Ecosystems* 3, 522–533. doi:10.1007/s100210000046
- Hrachowitz, M., Soulsby, C., Tetzlaff, D., Speed, M., 2010. Catchment transit times and landscape controls—does scale matter? *Hydrol. Process.* 24, 117–125.
- <http://criticalzone.org/national/data/list-datasets/>, 2017. National Critical Zone Observatory [WWW Document]. URL <http://criticalzone.org/national/infrastructure/observatories-1national/> (accessed 8.8.17).
- Hynicka, J.D., Pett-Ridge, J.C., Perakis, S.S., 2016. Nitrogen enrichment regulates calcium sources in forests. *Glob. Chang. Biol.* 22, 4067–4079. doi:10.1111/gcb.13335
- Jean, M.-E., Phalyvong, K., Forest-Drolet, J., Bellenger, J.-P., 2013. Molybdenum and phosphorus limitation of asymbiotic nitrogen fixation in forests of Eastern Canada: Influence of vegetative cover and seasonal variability. *Soil Biol. Biochem.* 67, 140–146. doi:10.1016/j.soilbio.2013.08.018
- Jeong, J., Kim, G., Han, S., 2012. Influence of trace element fluxes from submarine groundwater discharge (SGD) on their inventories in coastal waters off volcanic island, Jeju, Korea. *Appl. Geochemistry* 27, 37–43. doi:10.1016/j.apgeochem.2011.08.014
- Jilbert, T., Slomp, C.P., 2013. Rapid high-amplitude variability in baltic sea hypoxia

- during the holocene. *Geology* 41, 1183–1186. doi:10.1130/G34804.1
- Jin, L., Ravella, R., Ketchum, B., Bierman, P.R., Heaney, P., White, T., Brantley, S.L., 2010. Mineral weathering and elemental transport during hillslope evolution at the Susquehanna/Shale Hills Critical Zone Observatory. *Geochim. Cosmochim. Acta* 74, 3669–3691. doi:10.1016/j.gca.2010.03.036
- Johnson, A.G., Glenn, C.R., Burnett, W.C., Peterson, R.N., Lucey, P.G., 2008. Aerial infrared imaging reveals large nutrient-rich groundwater inputs to the ocean. *Geophys. Res. Lett.* 35, 1–6. doi:10.1029/2008GL034574
- Johnson, A.J., Hao, X., 2012. Northeastern Puerto Rico and the Luquillo Mountain - Soil Survey (2011-2012).
- Jolly, W.T., Lidiak, E.G., Dickin, A.P., Wu, T.-W., 1998. Geochemical diversity of Mesozoic island arc tectonic blocks in eastern Puerto Rico. *Geol. Soc. Am. Spec. Pap.* 322, 67–98. doi:10.1130/0-8137-2322-1.67
- Kabata-Pendias, A., 2010. *Trace Elements in Soils and Plants*, Fourth Edition. CRC Press.
- Karimian, N., Cox, F.R., 1978. Adsorption and extractability of molybdenum in relation to some chemical properties of soil. *Soil Sci. Soc. Am. J.* 42, 757–761. doi:10.2136/sssaj1978.03615995004200050021x
- Kashiwabara, T., Takahashi, Y., Tanimizu, M., 2009. A XAFS study on the mechanism of isotopic fractionation of molybdenum during its adsorption on ferromanganese oxides. *Geochem. J.* 43, 31–36. doi:10.2343/geochemj.1.0060
- Kelly, J., 2012. Identification and quantification of submarine groundwater discharge on the Hawaiian Islands. University of Hawaii at Manoa.
- Kelly, T.D., Matos, G.R., 2014. Historical statistics for mineral and material commodities in the United States (2016 version): U.S. Geological Survey Data Series 140 [WWW Document]. URL <https://minerals.usgs.gov/minerals/pubs/historical-statistics/> (accessed 7.20.17).
- Kendall, B., Creaser, R.A., Gordon, G.W., Anbar, A.D., 2009. Re-Os and Mo isotope systematics of black shales from the Middle Proterozoic Velkerri and Wollongorang Formations, McArthur Basin, northern Australia. *Geochim. Cosmochim. Acta* 73, 2534–2558. doi:10.1016/j.gca.2009.02.013
- Kendall, B., Dahl, T.W., Anbar, A.D., 2017. the Stable Isotope Geochemistry of Molybdenum. *Rev. Mineral. Geochemistry* 82, 683–732. doi:10.2138/rmg.2017.82.16

- Kendall, B., Dahl, T.W., Anbar, A.D., 2016. Good Golly, Why Moly? The Stable Isotope Geochemistry of Molybdenum, in: *Reviews in Mineralogy and Geochemistry*. pp. 683–732.
- Kendall, B., Gordon, G.W., Poulton, S.W., Anbar, A.D., 2011. Molybdenum isotope constraints on the extent of late Paleoproterozoic ocean euxinia. *Earth Planet. Sci. Lett.* 307, 450–460. doi:10.1016/j.epsl.2011.05.019
- Kendall, B., Komiya, T., Lyons, T.W., Bates, S.M., Gordon, G.W., Romaniello, S.J., Jiang, G., Creaser, R.A., Xiao, S., McFadden, K., Sawaki, Y., Tahata, M., Shu, D., Han, J., Li, Y., Chu, X., Anbar, A.D., 2015. Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late ediacaran period. *Geochim. Cosmochim. Acta* 156, 173–193. doi:10.1016/j.gca.2015.02.025
- Kendall, B., Reinhard, C.T., Lyons, T.W., Kaufman, A.J., Poulton, S.W., Anbar, A.D., 2010. Pervasive oxygenation along late Archaean ocean margins. *Nat. Geosci.* 3, 647–652. doi:10.1038/ngeo942
- Kerl, C.F., Lohmayer, R., Bura-Nakić, E., Vance, D., Planer-Friedrich, B., 2017. Experimental Confirmation of Isotope Fractionation in Thiomolybdates Using Ion Chromatographic Separation and Detection by Multicollector ICPMS. *Anal. Chem.* 89, 3123–3129. doi:10.1021/acs.analchem.6b04898
- Khalili, F., Al-Banna, G., 2015. Adsorption of uranium(VI) and thorium(IV) by insolubilized humic acid from Ajloun soil - Jordan. *J. Environ. Radioact.* 146, 16–26. doi:10.1016/j.jenvrad.2015.03.035
- Kim, G., Ryu, J.W., Yang, H.S., Yun, S.T., 2005. Submarine groundwater discharge (SGD) into the Yellow Sea revealed by ²²⁸Ra and ²²⁶Ra isotopes: Implications for global silicate fluxes. *Earth Planet. Sci. Lett.* 237, 156–166. doi:10.1016/j.epsl.2005.06.011
- King, E.K., Thompson, A., Chadwick, O.A., Pett-Ridge, J.C., 2016. Molybdenum sources and isotopic composition during early stages of pedogenesis along a basaltic climate transect. *Chem. Geol.* doi:10.1016/j.chemgeo.2016.01.024
- King, E.K., Thompson, A., Hodges, C., Pett-Ridge, J.C., 2014. Towards Understanding Temporal and Spatial Patterns of Molybdenum in the Critical Zone. *Procedia Earth Planet. Sci.* 10, 56–62. doi:10.1016/j.proeps.2014.08.011
- Knobler, C.B., Wilson, A.J., Hider, R.N., Jensen, I.W., Penfold, B.R., Robinson, W.T., Wilkins, C.J., 1983. Molybdenum(VI) complexes with malic acid: their inter-relationships, and the crystal structure of dicaesium bis[(S)-malato(2-)]-cis-dioxomolybdate(VI)–water (1/1). *J. Chem. Soc., Dalt. Trans.* 0, 1299–1303.

doi:10.1039/DT9830001299

- Kowalski, N., Dellwig, O., Beck, M., Gröwe, U., Neubert, N., Nögl, T.F., Badewien, T.H., Brumsack, H.J., van Beusekom, J.E.E., Böttcher, M.E., 2013. Pelagic molybdenum concentration anomalies and the impact of sediment resuspension on the molybdenum budget in two tidal systems of the North Sea. *Geochim. Cosmochim. Acta* 119, 198–211. doi:10.1016/j.gca.2013.05.046
- Kraepiel, A.M.L., Dere, A.L., Herndon, E.M., Brantley, S.L., 2015. Natural and anthropogenic processes contributing to metal enrichment in surface soils of central Pennsylvania 265–283. doi:10.1007/s10533-015-0068-5
- Kretzschmar, R., Borkovec, M., Grollmund, D., Elimelech, M., 1999. Mobile Subsurface Colloids and Their Role in Contaminant Transport. *Adv. Agron.* 66, 121–193. doi:10.1016/S0065-2113(08)60427-7
- Kretzschmar, R., Sticher, H., 1997. Transport of Humic-Coated Iron Oxide Colloids in a Sandy Soil: Influence of Ca^{2+} and Trace Metals. *Environ. Pollut.* 31, 3497–3504. doi:10.1021/ES970244S
- Kurtz, A.C., Derry, L.A., Chadwick, O.A., 2001. Accretion of Asian dust to Hawaiian soils: Isotopic, elemental, and mineral mass balances. *Geochim. Cosmochim. Acta* 65, 1971–1983. doi:10.1016/S0016-7037(01)00575-0
- Kurtz, A.C., Derry, L.A., Chadwick, O.A., Alfano, M.J., 2000. Refractory element mobility in volcanic soils. *Geology* 28, 683–686. doi:10.1130/0091-7613(2000)28<683:REMIVS>2.0.CO
- Lalonde, A.E., Rancourt, D.G., Ping, J.Y., 1998. Accuracy of ferric/ferrous determinations in micas: A comparison of Mössbauer spectroscopy and the Pratt and Wilson wet-chemical methods. *Hyperfine Interact.* 117, 175–204. doi:10.1023/A:1012607813487
- Lamb, M.P., Howard, A.D., Dietrich, W.E., Perron, J.T., 2007. Formation of amphitheater-headed valleys by waterfall erosion after large-scale slumping on Hawai'i. *Bull. Geol. Soc. Am.* 119, 805–822. doi:10.1130/B25986.1
- Lane, S., Proemse, B.C., Tennant, A., Wieser, M.E., 2013. Concentration measurements and isotopic composition of airborne molybdenum collected in an urban environment. *Anal. Bioanal. Chem.* 1–7. doi:10.1007/s00216-012-6660-9
- Lang, F., Kaupenjohann, M., 2000. Molybdenum at German Norway spruce sites: contents and mobility. *Can. J. For. ...* 1040, 1034–1040. doi:10.1139/cjfr-30-7-1034

- Larsen, M.C., 2012. Landslides and Sediment Budgets in Four Watersheds in Eastern Puerto Rico Water Quality and Landscape Processes of Four Watersheds in Eastern Puerto Rico, in: Murphy, S.F., Stallard, R.F. (Eds.), *Water Quality and Landscape Processes of Four Watersheds in Eastern Puerto Rico*: U.S. Geological Survey Professional Paper. pp. 153–178.
- Lead, J.R., Wilkinson, K.J., 2007. Environmental colloids and particles: current knowledge and future developments. *IUPAC Ser. Anal. Phys. Chem. Environ. Syst.* 10, 1–15.
- Leffelaar, P.A., 1993. Water movement, oxygen supply and biological processes on the aggregate scale. *Geoderma* 57, 143–165. doi:10.1016/0016-7061(93)90152-B
- Leithold, E.L., Blair, N.E., Perkey, D.W., 2006. Geomorphologic controls on the age of particulate organic carbon from small mountainous and upland rivers. *Global Biogeochem. Cycles* 20, 1–11. doi:10.1029/2005GB002677
- Leybourne, M.I., Cameron, E.M., 2008. Source, transport, and fate of rhenium, selenium, molybdenum, arsenic, and copper in groundwater associated with porphyry-Cu deposits, Atacama Desert, Chile. *Chem. Geol.* 247, 208–228. doi:10.1016/j.chemgeo.2007.10.017
- Li, J., Liang, X.-R., Zhong, L.-F., Wang, X.-C., Ren, Z.-Y., Sun, S.-L., Zhang, Z.-F., Xu, J.-F., 2014. Measurement of the Isotopic Composition of Molybdenum in Geological Samples by MC-ICP-MS using a Novel Chromatographic Extraction Technique. *Geostand. Geoanalytical Res.* 38, 345–354. doi:10.1111/j.1751-908X.2013.00279.x
- Liang, Y.H., Halliday, A.N., Siebert, C., Fitton, J.G., Burton, K.W., Wang, K.L., Harvey, J., 2017. Molybdenum isotope fractionation in the mantle. *Geochim. Cosmochim. Acta* 199, 91–111. doi:10.1016/j.gca.2016.11.023
- Liermann, L.J., Gwynn, R.L., Anbar, A., Brantley, S.L., 2005. Production of a molybdophore during metal-targeted dissolution of silicates by soil bacteria. *Chem. Geol.* 220, 285–302. doi:10.1016/j.chemgeo.2005.04.013
- Liermann, L.J., Mathur, R., Wasylenki, L.E., Nuester, J., Anbar, A.D., Brantley, S.L., 2011. Extent and isotopic composition of Fe and Mo release from two Pennsylvania shales in the presence of organic ligands and bacteria. *Chem. Geol.* 281, 167–180. doi:10.1016/j.chemgeo.2010.12.005
- Liptzin, D., Silver, W.L., Detto, M., 2011. Temporal Dynamics in Soil Oxygen and Greenhouse Gases in Two Humid Tropical Forests. *Ecosystems* 14, 171–182. doi:10.1007/s10021-010-9402-x

- Lybrand, R., Rasmussen, C., Jardine, A., Troch, P., Chorover, J., 2011. Applied Geochemistry The effects of climate and landscape position on chemical denudation and mineral transformation in the Santa Catalina mountain critical zone observatory. *Appl. Geochemistry* 26, S80–S84. doi:10.1016/j.apgeochem.2011.03.036
- Lyons, T.W., Anbar, A.D., Severmann, S., Scott, C., Gill, B.C., 2009. Tracking Euxinia in the Ancient Ocean: A Multiproxy Perspective and Proterozoic Case Study. *Annu. Rev. Earth Planet. Sci.* 37, 507–534. doi:10.1146/annurev.earth.36.031207.124233
- Malinovsky, D., Baxter, D.C., Rodushkin, I., 2007. Ion-specific isotopic fractionation of molybdenum during diffusion in aqueous solutions. *Environ. Sci. Technol.* 41, 1596–1600. doi:10.1021/es062000q
- Marks, J.A., Perakis, S.S., King, E.K., Pett-Ridge, J.C., 2015. Soil organic matter regulates molybdenum storage and mobility in forests. *Biogeochemistry* 125, 167–183. doi:10.1007/s10533-015-0121-4
- Mather, T. a., Witt, M.L.I., Pyle, D.M., Quayle, B.M., Aiuppa, a., Bagnato, E., Martin, R.S., Sims, K.W.W., Edmonds, M., Sutton, a. J., Ilyinskaya, E., 2012. Halogens and trace metal emissions from the ongoing 2008 summit eruption of K??lauea volcano, Hawa??i. *Geochim. Cosmochim. Acta* 83, 292–323. doi:10.1016/j.gca.2011.11.029
- Maynard, R.H., Premakumar, R., Bishop, P.E., 1994. Mo-independent nitrogenase 3 is advantageous for diazotrophic growth of *Azotobacter vinelandii* on solid medium containing molybdenum. *J. Bacteriol.* 176, 5583–5586.
- McBride, M.B., Spiers, G., 2001. Trace Element Content of Selected Fertilizers and Dairy Manures As Determined By Icp–Ms. *Commun. Soil Sci. Plant Anal.* 32, 139–156. doi:10.1081/CSS-100102999
- McClintock, M.A., Brocard, G., Willenbring, J., Tamayo, C., Porder, S., Pett-Ridge, J.C., 2015. Spatial variability of African dust in soils in a montane tropical landscape in Puerto Rico. *Chem. Geol.* 412, 69–81. doi:10.1016/j.chemgeo.2015.06.032
- McDowell, W.H., Scatena, F.N., Waide, R.B., Brokaw, N., Camilo, G.R., Covich, A.P., Crowl, T.A., Gonzalez, G., Greathouse, E.A., Klawinski, P., Lodge, D.J., Lugo, A.E., Pringle, C.M., Richardson, B.A., Richardson, M.J., Schaefer, D.A., Silver, W.L., Thomp, J.K., 2012. Geographic and Ecological Setting of the Luquillo Mountains, in: *A Caribbean Forest Tapestry: The Multidimensional Nature of Disturbance and Response*. Oxford University Press, pp. 72–163.
- McManus, J., Berelson, W.M., Severmann, S., Poulson, R.L., Hammond, D.E.,

- Klinkhammer, G.P., Holm, C., 2006. Molybdenum and uranium geochemistry in continental margin sediments: Paleoproxy potential. *Geochim. Cosmochim. Acta* 70, 4643–4662. doi:10.1016/j.gca.2006.06.1564
- McManus, J., Nägler, T.F., Siebert, C., Wheat, C.G., Hammond, D.E., 2002. Oceanic molybdenum isotope fractionation: Diagenesis and hydrothermal ridge-flank alteration. *Geochemistry, Geophys. Geosystems* 3, 1–9. doi:10.1029/2002GC000356
- Miller, A.J., Schuur, E.A.G., Chadwick, O.A., 2001. Redox control of phosphorus pools in Hawaiian montane forest soils. *Geoderma* 102, 0.
- Miller, C.A., Peucker-Ehrenbrink, B., Walker, B.D., Marcantonio, F., 2011. Re-assessing the surface cycling of molybdenum and rhenium. *Geochim. Cosmochim. Acta* 75, 7146–7179. doi:10.1016/j.gca.2011.09.005
- Monastra, V., Derry, L.A., Chadwick, O.A., 2004. Multiple sources of lead in soils from a Hawaiian chronosequence. *Chem. Geol.* 209, 215–231. doi:10.1016/j.chemgeo.2004.04.027
- Moore, W.S., 2010. The effect of submarine groundwater discharge on the ocean. *Ann. Rev. Mar. Sci.* 2, 59–88. doi:10.1146/annurev-marine-120308-081019
- Moore, W.S., 1996. Large groundwater inputs to coastal water revealed by ²²³Ra enrichments. *Nature*.
- Murad, E., Cashion, J., 2004. Mössbauer spectroscopy of environmental materials and their industrial utilization. Kluwer Academic Publishers Group, Norwell, MA.
- Murad, E., Wagner, U., 1994. Mössbauer study of pure illite and its firing products. *Hyperfine Interact.* 91, 685–688. doi:10.1007/BF02064591
- Nameroff, T.J., Calvert, S.E., Murray, J.W., 2004. Glacial-interglacial variability in the eastern tropical North Pacific oxygen minimum zone recorded by redox-sensitive trace metals. *Paleoceanography* 19, 1–19. doi:10.1029/2003PA000912
- NCSS, 2015. National Cooperative Soil Characterization Database [WWW Document]. URL <http://ncsslabsdatamart.sc.egov.usda.gov/> (accessed 9.3.15).
- Neubert, N., Heri, A.R., Voegelin, A.R., Nägler, T.F., Schlunegger, F., Villa, I.M., 2011. The molybdenum isotopic composition in river water: Constraints from small catchments. *Earth Planet. Sci. Lett.* 304, 180–190. doi:10.1016/j.epsl.2011.02.001
- Neubert, N., Nägler, T.F., Böttcher, M.E., 2008. Sulfidity controls molybdenum

- isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* 36, 775–778. doi:10.1130/G24959A.1
- Nicholson, F.A., Smith, S.R., Alloway, B.J., Carlton-Smith, C., Chambers, B.J., 2003. An inventory of heavy metals inputs to agricultural soils in England and Wales. *Sci. Total Environ.* 311, 205–219. doi:10.1016/S0048-9697(03)00139-6
- Nriagu, J.O., Pacyna, J.M., 1988. Quantitative assessment of worldwide contamination of air, water, and soils by trace metals. *Nature* 333, 134–139. doi:10.1038/332141a0
- Ostwald, W., 1900. On the assumed isomerism of red and yellow mercury oxide and the surface-tension of solid bodies. *J. Phys. Chem.* 495–503.
- Oyerinde, O.F., Weeks, C.L., Anbar, A.D., Spiro, T.G., 2008. Solution structure of molybdic acid from Raman spectroscopy and DFT analysis. *Inorganica Chim. Acta* 361, 1000–1007. doi:10.1016/j.ica.2007.06.025
- Pacyna, J.M., Pacyna, E.G., 2001. An assessment of global and regional emissions of trace metals to the atmosphere from anthropogenic sources worldwide. *Environ. Rev.* 9, 269–298. doi:10.1139/er-9-4-269
- Patton, N.R., 2016. Topographic Controls on Total Mobile Regolith and Total Soil Organic Carbon in Complex Terrain. Idaho State University.
- Pearce, C.R., Burton, K.W., Pogge von Strandmann, P.A.E., James, R.H., Gíslason, S.R., 2010. Molybdenum isotope behaviour accompanying weathering and riverine transport in a basaltic terrain. *Earth Planet. Sci. Lett.* 295, 104–114. doi:10.1016/j.epsl.2010.03.032
- Pearce, C.R., Cohen, A.S., Coe, A.L., Burton, K.W., 2008. Molybdenum isotope evidence for global ocean anoxia coupled with perturbations to the carbon cycle during the early Jurassic. *Geology* 36, 231–234. doi:10.1130/G24446A.1
- Pearce, C.R., Cohen, A.S., Parkinson, I.J., 2009. Quantitative separation of molybdenum and rhenium from geological materials for isotopic determination by MC-ICP-MS. *Geostand. Geoanalytical Res.* 33, 219–229.
- Pedersen, H.D., Postma, D., Jakobsen, R., Larsen, O., 2005. Fast transformation of iron oxyhydroxides by the catalytic action of aqueous Fe(II). *Geochim. Cosmochim. Acta* 69, 3967–3977. doi:10.1016/j.gca.2005.03.016
- Perakis, S.S., Pett-Ridge, J.C., Catricala, C.E., 2017. Nutrient feedbacks to soil heterotrophic nitrogen fixation in forests. *Biogeochemistry*.
- Perakis, S.S., Sinkhorn, E.R., 2011. Biogeochemistry of a temperate forest nitrogen

- gradient. *Ecology* 92, 1481–1491. doi:10.1890/10-1642.1
- Peretyazhko, T., Sposito, G., 2005. Iron(III) reduction and phosphorous solubilization in humid tropical forest soils. *Geochim. Cosmochim. Acta* 69, 3643–3652. doi:10.1016/j.gca.2005.03.045
- Peterson, R.N., Burnett, W.C., Glenn, C.R., Johnson, A.G., 2009. Quantification of point-source groundwater discharges to the ocean from the shoreline of the Big Island, Hawaii. *Limnol. Oceanogr.* 54, 890–904. doi:10.4319/lo.2009.54.3.0890
- Pett-Ridge, J.C., Derry, L.A., Kurtz, A.C., 2009. Sr isotopes as a tracer of weathering processes and dust inputs in a tropical granitoid watershed, Luquillo Mountains, Puerto Rico. *Geochim. Cosmochim. Acta* 73, 25–43. doi:10.1016/j.gca.2008.09.032
- Pett-Ridge, J.C., Monastera, V.M., Derry, L. a., Chadwick, O.A., 2007. Importance of atmospheric inputs and Fe-oxides in controlling soil uranium budgets and behavior along a Hawaiian chronosequence. *Chem. Geol.* 244, 691–707. doi:10.1016/j.chemgeo.2007.07.016
- Poitrasson, F., Viers, J., Martin, F., Braun, J.J., 2008. Limited iron isotope variations in recent lateritic soils from Nsimi, Cameroon: Implications for the global Fe geochemical cycle. *Chem. Geol.* 253, 54–63. doi:10.1016/j.chemgeo.2008.04.011
- Porder, S., Chadwick, O.A., 2009. Climate and soil-age constraints on nutrient uplift and retention by plants. *Ecology* 90, 623–636. doi:10.1890/07-1739.1
- Porder, S., Hilley, G.E., Chadwick, O.A., 2007. Chemical weathering, mass loss, and dust inputs across a climate by time matrix in the Hawaiian Islands. *Earth Planet. Sci. Lett.* 258, 414–427. doi:10.1016/j.epsl.2007.03.047
- Poulson, R.L., Siebert, C., McManus, J., Berelson, W.M., 2006. Authigenic molybdenum isotope signatures in marine sediments. *Geology* 34, 617–620. doi:10.1130/G22485.1
- Pourhassan, N., Bruno, S., Davidson, M., Shipley, B., Roy, S., Bellenger, J., 2016. Phosphorus and micronutrient dynamics during gymnosperm and angiosperm litters decomposition in temperate cold forest from Eastern Canada. *Geoderma* 273, 25–31. doi:10.1016/j.geoderma.2016.03.018
- Prouty, N.G., Swarzenski, P.W., Fackrell, J.K., Johannesson, K., Palmore, C.D., 2017. Groundwater-derived nutrient and trace element transport to a nearshore Kona coral ecosystem: Experimental mixing model results. *J. Hydrol. Reg. Stud.* 11, 166–177. doi:10.1016/j.ejrh.2015.12.058

- Rahaman, W., Goswami, V., Singh, S.K., Rai, V.K., 2014. Molybdenum isotopes in two Indian estuaries: Mixing characteristics and input to oceans. *Geochim. Cosmochim. Acta* 141, 407–422. doi:10.1016/j.gca.2014.06.027
- Rancourt, D.G., 2001. Magnetism of Earth, Planetary, and Environmental Nanomaterials. *Rev. Mineral. Geochemistry* 44.
- Rancourt, D.G., 1998. Mössbauer spectroscopy in clay science. *Hyperfine Interact.* 117, 3–38.
- Rancourt, D.G., Ping, J.Y., 1991. Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mossbauer spectroscopy. *Nucl. Inst. Methods Phys. Res. B* 58, 85–97. doi:10.1016/0168-583X(91)95681-3
- Rancourt, D.G., Thibault, P.-J., Mavrocordatos, D., Lamarche, G., 2005. Hydrous ferric oxide precipitation in the presence of nonmetabolizing bacteria: Constraints on the mechanism of a biotic effect. *Geochim. Cosmochim. Acta* 69, 553–577. doi:10.1016/j.gca.2004.07.018
- Rasmussen, B., Fletcher, I.R., Brocks, J.J., Kilburn, M.R., 2008. Reassessing the first appearance of eukaryotes and cyanobacteria. *Nature* 455, 1101–1104. doi:10.1038/nature07381
- Reddy, K.J., Gloss, S.P., 1993. Geochemical speciation as related to the mobility of F, Mo and Se in soil leachates. *Appl. Geochemistry* 8, 159–163. doi:10.1016/S0883-2927(09)80029-2
- Rousk, K., Sorensen, P.L., Michelsen, A., 2016. Nitrogen Transfer from Four Nitrogen-Fixer Associations to Plants and Soils. *Ecosystems* 19, 1491–1504. doi:10.1007/s10021-016-0018-7
- Sansone, F.J., Benitez-Nelson, C.R., Resing, J.A., DeCarlo, E.H., Vink, S.M., Heath, J. a., Huebert, B.J., 2002. Geochemistry of atmospheric aerosols generated from lava-seawater interactions. *Geophys. Res. Lett.* 29, 2–5. doi:10.1029/2001GL013882
- Scatena, F.N., 1990. Watershed scale rainfall interception on two forested watersheds in the Luquillo Mountains of Puerto Rico. *J. Hydrol.* 113, 89–102. doi:10.1016/0022-1694(90)90168-W
- Schellekens, J.H., 1998. Geochemical evolution and tectonic history of Puerto Rico. *Geol. Soc. Am. Spec. Pap.* 322.
- Scholz, F., McManus, J., Mix, A.C., Hensen, C., Schneider, R.R., 2014. The impact of ocean deoxygenation on iron release from continental margin sediments. *Nat. Geosci.* 7, 433–437. doi:10.1038/ngeo2162

- Schopka, H.H., Derry, L. a., 2012. Chemical weathering fluxes from volcanic islands and the importance of groundwater: The Hawaiian example. *Earth Planet. Sci. Lett.* 339–340, 67–78. doi:10.1016/j.epsl.2012.05.028
- Schulz, M.S., White, A.F., 1999. Chemical weathering in a tropical watershed, Luquillo Mountains, Puerto Rico III: Quartz dissolution rates. *Geochim. Cosmochim. Acta* 63, 337–350. doi:10.1016/S0016-7037(99)00056-3
- Schuur, E.A.G., 2001. The effect of water on decomposition dynamics in mesic to wet Hawaiian montane forests. *Ecosystems* 4, 259–273. doi:10.1007/s10021-001-0008-1
- Schuur, E.A.G., Chadwick, O.A., Matson, P.A., 2001. Carbon Cycling and Soil Carbon Storage in Mesic to Wet Hawaiian Montane Forests 82, 3182–3196.
- Schuur, E. a., Matson, P. a., 2001. Net primary productivity and nutrient cycling across a mesic to wet precipitation gradient in Hawaiian montane forest. *Oecologia* 128, 431–442. doi:10.1007/s004420100671
- Scribner, A.M., Kurtz, A.C., Chadwick, O.A., 2006. Germanium sequestration by soil: Targeting the roles of secondary clays and Fe-oxyhydroxides. *Earth Planet. Sci. Lett.* 243, 760–770. doi:10.1016/j.epsl.2006.01.051
- Seki, H., Suzuki, A., 1995. Adsorption of Heavy-Metal Ions Onto Insolubilized Humic-Acid. *J. Colloid Interface Sci.* doi:10.1006/jcis.1995.1207
- Shaman, J., Stieglitz, M., Burns, D., 2004. Are big basins just the sum of small catchments? *Hydrol. Process.* 18, 3195–3206. doi:10.1002/hyp.5739
- Shan, X., Lian, J., Wen, B., 2002. Effect of organic acids on adsorption and desorption of rare earth elements. *Chemosphere* 47, 701–710. doi:10.1016/S0045-6535(02)00032-2
- Sherrod, D.R., Sinton, J.M., Watkins, S.E., Brunt, K.M., 2007. Geologic Map of the State of Hawai'i. USGS Open-File Rep. 2007–1089.
- Siebert, C., Nägler, T.F., Kramers, J.D., Na, T.F., Kramers, J.D., 2001. Determination of molybdenum isotope fractionation by double-spike multicollector inductively coupled plasma mass spectrometry. *Geochemistry, Geophys. Geosystems* 2, n/a-n/a. doi:10.1029/2000GC000124
- Siebert, C., Nägler, T.F., von Blanckenburg, F., Kramers, J.D., 2003. Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth Planet. Sci. Lett.* 211, 159–171. doi:10.1016/S0012-821X(03)00189-4
- Siebert, C., Pett-Ridge, J.C.C., Opfergelt, S., Guicharnaud, R.A.A., Halliday, A.N.N.,

- Burton, K.W.W., 2015. Molybdenum isotope fractionation in soils: Influence of redox conditions, organic matter, and atmospheric inputs. *Geochim. Cosmochim. Acta* 162, 1–24. doi:10.1016/j.gca.2015.04.007
- Silver, W.L., Liptzin, D., Almaraz, M., 2013. Soil redox dynamics and biogeochemistry along a tropical elevation gradient. *Ecol. Bull.* 1–16.
- Silver, W.L., Lugo, A.E., Keller, M., 1999. Soil oxygen availability and biogeochemistry along rainfall and topographic gradients in upland wet tropical forest soils. *Biogeochemistry* 44, 301–328. doi:10.1023/A:1006034126698
- Silvester, W., 1989. Molybdenum limitation of asymbiotic nitrogen fixation in forests of Pacific Northwest America. *Soil Biol. Biochem.* 21, 283–289. doi:10.1016/0038-0717(89)90106-5
- Skierszkan, E.K., Amini, M., Weis, D., 2015. A practical guide for the design and implementation of the double-spike technique for precise determination of molybdenum isotope compositions of environmental samples. *Anal. Bioanal. Chem.* 407, 2–4. doi:10.1007/s00216-014-8448-6
- Smith, A.L., Schellekens, J.H., Diaz, A.L.M., 1998. Batholiths as markers of tectonic change in the northeastern Caribbean. *Tectonics geochemistry Northeast. Caribb.* 322, 99–122. doi:10.1130/0-8137-2322-1.99
- Soil Survey Staff, U., 2002. Soil survey of caribbean national forest and Luquillo experimental forest, commonwealth of Puerto Rico., United States Department of Agriculture, Natural resources Conservation Service. Washington, D.C.
- Sposito, G., 2004. *The Surface Chemistry of Natural Particles*. Oxford University Press, New York.
- Stallard, R.F., Murphy, S.F., 2012. Water Quality and Mass Transport in Four Watersheds in Eastern Puerto Rico. *Water Qual. Landsc. Process. four watersheds East. Puerto Rico. Prof. Pap.* 1789 117–147.
- Stewart, B.W., Capo, R.C., Chadwick, O.A., 2001. Effects of rainfall on weathering rate, base cation provenance, and Sr isotope composition of Hawaiian soils. *Geochim. Cosmochim. Acta* 65, 1087–1099. doi:10.1016/S0016-7037(00)00614-1
- Strauch, A.M., MacKenzie, R.A., Giardina, C.P., Bruland, G.L., 2015. Climate driven changes to rainfall and streamflow patterns in a model tropical island hydrological system. *J. Hydrol.* 523, 160–169. doi:10.1016/j.jhydrol.2015.01.045
- Teutsch, N., Erel, Y., Halicz, L., Chadwick, O.A., 1999. The influence of rainfall on metal concentration and behavior in the soil. *Geochim. Cosmochim. Acta* 63,

3499–3511. doi:10.1016/S0016-7037(99)00152-0

- Thompson, A., Chadwick, O.A., Boman, S., Chorover, J., 2006a. Colloid mobilization during soil iron redox oscillations. *Environ. Sci. Technol.* 40, 5743–5749. doi:10.1021/es061203b
- Thompson, A., Chadwick, O.A., Rancourt, D.G., Chorover, J., 2006b. Iron-oxide crystallinity increases during soil redox oscillations. *Geochim. Cosmochim. Acta* 70, 1710–1727. doi:10.1016/j.gca.2005.12.005
- Thompson, A., Rancourt, D.G., Chadwick, O.A., Chorover, J., 2011. Iron solid-phase differentiation along a redox gradient in basaltic soils. *Geochim. Cosmochim. Acta* 75, 119–133. doi:10.1016/j.gca.2010.10.005
- Thompson, A., Ruiz, J., Chadwick, O.A., Titus, M., Chorover, J., 2007. Rayleigh fractionation of iron isotopes during pedogenesis along a climate sequence of Hawaiian basalt. *Chem. Geol.* 238, 72–83. doi:10.1016/j.chemgeo.2006.11.005
- Tishchenko, V., Meile, C., Scherer, M.M., Pasakarnis, T.S., Thompson, A., 2015. Fe²⁺ catalyzed iron atom exchange and re-crystallization in a tropical soil. *Geochim. Cosmochim. Acta* 148, 191–202. doi:10.1016/j.gca.2014.09.018
- Tkac, P., Paulenova, A., 2008. Speciation of Molybdenum (VI) In Aqueous and Organic Phases of Selected Extraction Systems. *Sep. Sci. Technol.* 43, 2641–2657. doi:10.1080/01496390802122261
- Tossell, J.A., 2005. Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution. *Geochim. Cosmochim. Acta* 69, 2981–2993. doi:10.1016/j.gca.2005.01.016
- Tribble, G., 2008. Ground Water on Tropical Pacific Islands — Understanding a Vital Resource 1–35.
- Trostle, K.D., Ray Runyon, J., Pohlmann, M.A., Redfield, S.E., Pelletier, J., McIntosh, J., Chorover, J., 2016. Colloids and organic matter complexation control trace metal concentration-discharge relationships in Marshall Gulch stream waters. *Water Resour. Res.* 52, 7931–7944. doi:10.1002/2016WR019072
- Tsukuda, S., Sugiyama, M., Harita, Y., Nishimura, K., 2005. Atmospheric bulk deposition of soluble phosphorus in Ashiu Experimental Forest, Central Japan: Source apportionment and sample contamination problem. *Atmos. Environ.* 39, 823–836. doi:10.1016/j.atmosenv.2004.10.028
- Ure, A.M., Quevauviller, P.H., Muntau, H., Griepink, B., 1993. Speciation of heavy metals in soils and sediments- an account of the improvement and harmonization of extraction Techniques undertaken under the auspices of the

- BCR of the commission of the European Communities. *Int. J. Environ. Anal. Chem.*
- Urey, H.C., 1947. The thermodynamic properties of isotopic substances. *J. Chem. Soc.* 0, 562. doi:10.1039/jr9470000562
- US Environmental Protection Agency, 2007. Appendix C - Sediment Source Assessment for the Lower Eel River Watershed.
- van Soest, P.J., Wine, R.H., 1967. Use of detergents in the analysis of fibrous feeds. IV. Determination of plant cell-wall constituents. *J. Assoc. Off. Anal. Chem.* 50, 50–55.
- Vance, D., Teagle, D.A.H., Foster, G.L., 2009. Variable Quaternary chemical weathering fluxes and imbalances in marine geochemical budgets. *Nature* 458, 493–496. doi:10.1038/nature07828
- Viers, J., Dupre, B., Braun, J.J., Deberdt, S., Angeletti, B., Ngoupayou, J.N., Michard, A., 2000. Major and trace element abundances, and strontium isotopes in the Nyong basin rivers (Cameron): constraints on chemical weathering processes and elements transport mechanisms in humid tropical environments. *Chem. Geol.* 169, 211–241. doi:10.1016/S0009-2541(00)00298-9
- Viers, J., Wasserburg, G.J., 2004. Behavior of Sm and Nd in a lateritic soil profile. *Geochim. Cosmochim. Acta* 68, 2043–2054. doi:10.1016/j.gca.2003.10.034
- Vitousek, P.M., 2004a. Nutrient cycling and limitation : Hawai'i as a model system. Princeton University Press.
- Vitousek, P.M., 2004b. Nutrient Cycling and Limitation: Hawai'i as a Model System. Princeton University Press.
- Vitousek, P.M., Chadwick, O.A., 2013. Pedogenic Thresholds and Soil Process Domains in Basalt-Derived Soils. *Ecosystems* 16, 1379–1395. doi:10.1007/s10021-013-9690-z
- Vitousek, P.M., Chadwick, O.A., Crews, T.E., Fownes, J.H., Hendricks, D.M., Herbert, D., 1997. Soil and Ecosystem Development Across the Hawaiian Islands. *GSA Today* 7, 1–8.
- Vitousek, P.M., Kennedy, M.J., Derry, L.A., Chadwick, O.A., 1999. Weathering versus atmospheric sources of strontium in ecosystems on young volcanic soils. *Oecologia* 121, 255–259. doi:10.1007/s004420050927
- Voegelin, A.R., Nägler, T.F., Pettke, T., Neubert, N., Steinmann, M., Pourret, O., Villa, I.M., 2012. The impact of igneous bedrock weathering on the Mo isotopic

- composition of stream waters: Natural samples and laboratory experiments. *Geochim. Cosmochim. Acta* 86, 150–165. doi:10.1016/j.gca.2012.02.029
- Voegelin, A.R., Pettke, T., Greber, N.D., Von Niederhäusern, B., Nägler, T.F., 2014. Magma differentiation fractionates Mo isotope ratios: Evidence from the Kos Plateau Tuff (Aegean Arc). *Lithos* 190–191, 440–448. doi:10.1016/j.lithos.2013.12.016
- von Blanckenburg, F., Bouchez, J., Ibarra, D.E., Maher, K., 2015. Stable runoff and weathering fluxes into the oceans over Quaternary climate cycles. *Nat. Geosci.* 8, 538–542. doi:10.1038/ngeo2452
- Vorliceck, T.P., Kahn, M.D., Kasuya, Y., Helz, G.R., 2004. Capture of molybdenum in pyrite-forming sediments: Role of ligand-induced reduction by polysulfides. *Geochim. Cosmochim. Acta* 68, 547–556. doi:10.1016/S0016-7037(00)00444-7
- Wagner, M., Chappaz, A., Lyons, T.W., 2017. Molybdenum speciation and burial pathway in weakly sulfidic environments: Insights from XAFS. *Geochim. Cosmochim. Acta* 206, 18–29. doi:10.1016/j.gca.2017.02.018
- Wang, Z., 2011. Northeastern Puerto Rico and the Luquillo Mountain - Soil Mineralogy - Mineral content of soils 0-20 cm XRD (2010-2011). Luquillo Critical Zone Observatory, Miguel Leon.
- Wang, Z., Ma, J., Li, J., Wei, G., Chen, X., Deng, W., Xie, L., Lu, W., Zou, L., 2015. Chemical weathering controls on variations in the molybdenum isotopic composition of river water: Evidence from large rivers in China. *Chem. Geol.* 410, 201–212. doi:10.1016/j.chemgeo.2015.06.022
- Wasylenki, L.E., Anbar, A.D., Liermann, L.J., Mathur, R., Gordon, G.W., Brantley, S.L., 2007. Isotope fractionation during microbial metal uptake measured by MC-ICP-MS. *J. Anal. At. Spectrom.* 22, 905–910. doi:10.1039/B705476A
- Wasylenki, L.E., Rolfe, B.A., Weeks, C.L., Spiro, T.G., Anbar, A.D., 2008. Experimental investigation of the effects of temperature and ionic strength on Mo isotope fractionation during adsorption to manganese oxides. *Geochim. Cosmochim. Acta* 72, 5997–6005. doi:10.1016/j.gca.2008.08.027
- Wasylenki, L.E., Weeks, C.L., Bargar, J.R., Spiro, T.G., Hein, J.R., Anbar, A.D., 2011. The molecular mechanism of Mo isotope fractionation during adsorption to birnessite. *Geochim. Cosmochim. Acta* 75, 5019–5031. doi:10.1016/j.gca.2011.06.020
- Weber, T., Allard, T., Tipping, E., Benedetti, M.F., 2006. Modeling Iron Binding to Organic 40, 7488–7493.

- West, N., Kirby, E., Bierman, P., Slingerland, R., Ma, L., Rood, D., Brantley, S., 2013. Regolith production and transport at the Susquehanna Shale Hills Critical Zone Observatory, part 2: Insights from meteoric ^{10}Be . *J. Geophys. Res. Earth Surf.* 118, 1877–1896. doi:10.1002/jgrf.20121
- White, A.F., Blum, A.E., Schulz, M.S., Vivit, D. V., Stonestrom, D. a., Larsen, M., Murphy, S.F., Eberl, D., 1998. Chemical Weathering in a Tropical Watershed, Luquillo Mountains, Puerto Rico: I. Long-Term Versus Short-Term Weathering Fluxes. *Geochim. Cosmochim. Acta* 62, 209–226. doi:10.1016/S0016-7037(97)00335-9
- Wichard, T., Mishra, B., Myneni, S.C.B., Bellenger, J.-P., Kraepiel, A.M.L., 2009. Storage and bioavailability of molybdenum in soils increased by organic matter complexation. *Nat. Geosci.* 2, 625–629. doi:10.1038/ngeo589
- Wiederhold, J.G., 2015. Metal stable isotope signatures as tracers in environmental geochemistry. *Environ. Sci. Technol.* 49, 2606–2624. doi:10.1021/es504683e
- Wiederhold, J.G., Kraemer, S.M., Teutsch, N., Borer, P.M., Halliday, A.N., Kretzschmar, R., 2006. Iron isotope fractionation during proton-promoted, ligand-controlled, and reductive dissolution of goethite. *Environ. Sci. Technol.* 40, 3787–3793. doi:10.1021/es052228y
- Wiederhold, J.G., Teutsch, N., Kraemer, S.M., Halliday, A.N., Kretzschmar, R., 2007a. Iron isotope fractionation in oxic soils by mineral weathering and podzolization. *Geochim. Cosmochim. Acta* 71, 5821–5833. doi:10.1016/j.gca.2007.07.023
- Wiederhold, J.G., Teutsch, N., Kraemer, S.M., Halliday, A.N., Kretzschmar, R., 2007b. Iron Isotope Fractionation during Pedogenesis in Redoximorphic Soils. *Soil Sci. Soc. Am. J.* 71, 1840. doi:10.2136/sssaj2006.0379
- Willbold, M., Elliott, T., 2017. Molybdenum isotope variations in magmatic rocks. *Chem. Geol.* 449, 253–268. doi:10.1016/j.chemgeo.2016.12.011
- Wille, M., Kramers, J.D., Nägler, T.F., Beukes, N.J., Schröder, S., Meisel, T., Lacassie, J.P., Voegelin, a. R., 2007. Evidence for a gradual rise of oxygen between 2.6 and 2.5 Ga from Mo isotopes and Re-PGE signatures in shales. *Geochim. Cosmochim. Acta* 71, 2417–2435. doi:10.1016/j.gca.2007.02.019
- Wilmoth, J.L., 2016. Effects of redox-cycling on iron-mineral transformations and metatranscriptome of iron(III)-reducing bacteria in a humid tropical forest soil. UGA.
- Wilt, J.C., Keith, S.B., Peterson, J.A., Huber, D.F., Theodore, T.G., 1984. Preliminary report of molybdenum occurrences in Arizona.

- Wilt, J.C., Keith, S.B., Theodore, T.G., 1985. A listing and map showing molybdenum occurrences in Arizona.
- Windom, H.L., Moore, W.S., Niecheski, L.F.H., Jahnke, R.A., 2006. Submarine groundwater discharge: A large, previously unrecognized source of dissolved iron to the South Atlantic Ocean. *Mar. Chem.* 102, 252–266. doi:10.1016/j.marchem.2006.06.016
- Wolfe, E.W., Morris, J., 1996. Geologic Map of the Island of Hawaii.
- Wolock, D.M., Fan, J., Lawrence, G.B., 1997. Effects of basin size on low-flow stream chemistry and subsurface contact time in the Neversink River watershed, New York. *Hydrol. Process.* 11, 1273–1286. doi:10.1002/(SICI)1099-1085(199707)11:9<1273::AID-HYP557>3.3.CO;2-J
- Wurzburger, N., Bellenger, J.P., Kraepiel, A.M.L., Hedin, L.O., 2012. Molybdenum and phosphorus interact to constrain asymbiotic nitrogen fixation in tropical forests. *PLoS One* 7, 2–8. doi:10.1371/journal.pone.0033710
- Wymore, A.S., Brereton, R.L., Ibarra, D.E., Maher, K., Mcdowell, W.H., 2017. Critical zone structure controls concentration-discharge relationships and solute generation in forested tropical montane watersheds. *Water Resour. Res.* doi:10.1074/jbc.M109.090936
- Yang, J., Siebert, C., Barling, J., Savage, P., Liang, Y.-H.H., Halliday, A.N., 2015. Absence of molybdenum isotope fractionation during magmatic differentiation at Hekla volcano, Iceland. *Geochim. Cosmochim. Acta* 162, 126–136. doi:10.1016/j.gca.2015.04.011
- Yang, W.H., Liptzin, D., Yavitt, J.B., 2015. High potential for iron reduction in upland soils. *Ecology* 96, 2015–2020. doi:10.1890/14-2097.1
- Zerkle, A.L., Scheiderich, K., Maresca, J.A., Liermann, L.J., Brantley, S.L., 2011. Molybdenum isotope fractionation by cyanobacterial assimilation during nitrate utilization and N₂ fixation. *Geobiology* 9, 94–106. doi:10.1111/j.1472-4669.2010.00262.x
- Zhang, W., Tang, X.Y., Weisbrod, N., Zhao, P., Reid, B.J., 2015. A coupled field study of subsurface fracture flow and colloid transport. *J. Hydrol.* 524, 476–488. doi:10.1016/j.jhydrol.2015.03.001

APPENDICES

Appendix A. Supplementary material for “Molybdenum sources and isotopic composition during early stages of pedogenesis along a basaltic climate gradient”

A.1. Tephra calculations

The KCG has received alkalic tephra from the Hualalai Volcano over the past 5 kyr (Porder et al., 2007). This input contributes to the parent material for the soil profiles. In our case, the close proximity of the soil sites to one another (< 7.5 km separates the most disparate sites) means that each site has received similar amounts of tephra over time so that any across site comparisons are valid. Assuming the chemical composition of the tephra input is identical to the chemical composition of the Hualalai flow it was produced from, absolute values for mass loss can be calculated by estimating the amount of tephra parent material input into the system (Porder et al., 2007).

Preferential weathering of tephra over clinkers has the potential to alter τ Mo calculations if the chemistry of the tephra is different from the chemistry of the parent material. We collected rock samples from a 3 – 5 kyr Hualalai lava flow that would have corresponded to the primary tephra input to these sites. Mo and Nb concentrations in the 3 – 5 kyr Hualalai rock sample were $0.52 \mu\text{g g}^{-1}$ and $6.81 \mu\text{g g}^{-1}$, respectively, similar to that of the KCG underlying lava flows. Assuming 40% void space (Porder et al., 2007) (which can be filled by tephra) for Hawaiian basalt, τ Mo values were recalculated using new parent material concentrations for Mo and Nb that reflect both tephra and a’a clinkers. Thus, the concentration variables in Equation (1) now reflect the proportional elemental concentrations for tephra (40%

$\pm 10\%$) and a'a clinkers ($60\% \pm 10\%$). This serves as a maximum estimate of τ Mo if all void space was filled by tephra. For the KCG, the tephra-influenced τ Mo calculations deviated from our original τ Mo calculations by less than 5% and the patterns across the KCG remained the same. As such, we chose to report our original τ Mo values and avoid any error propagation associated with estimating void space for each site (Tables A.1 and A.2).

A.2. Seawater contamination of groundwater

Three of the heaviest groundwater samples (4161-01, 4161-02, and 4061-01) were collected on the Kona Coast during a flooding tide and have an isotopic composition affected by seawater intrusion ($\delta^{98}\text{Mo}_{\text{seawater}} = +2.1\text{‰}$), where the isotopic composition of the samples becomes heavier with increasing sodium (Na) content (Table A.3). These three samples will not be included in our discussion of groundwater fluxes from the soil to the ocean.

Table A.1: Tephra influence on Mo mobility

Sample name	τ Mo %	τ Mo (30% void space) %	τ Mo (40% void space) %	τ Mo (50% void space) %
<i>KCG 3</i>				
A1	71	64	61	54
A2/2C2	17	12	11	7
B1/2C3	4	1	0	-2
B2/2C4	2	1	0	-1
B4/2C6	-1	-2	-2	-3
<i>KCG 4</i>				
A1	31	25	23	20
A2	1	-4	-6	-7
Bw1/2C1	-5	-6	-7	-7
Bw2/2C2	0	-1	-1	-1
<i>KCG 6</i>				
A1	92	82	79	75
A2	67	59	56	53
Bw1/2C2	5	4	4	3
Bw2/2C3	0	0	-1	-1
<i>KCG 7</i>				
A1	78	75	74	74
A2	56	53	53	52
Bw1	57	54	54	53
Bw2/2C1	16	16	16	15
<i>KCG 9</i>				
A1	81	91	94	97
A2	85	95	99	102
BW1	29	36	38	40
Bw2/2C1	4	5	5	5
Bw2/2C2	2	3	3	3
<i>KCG 10</i>				
A1	121	118	117	116
A2	87	84	83	83
Bw1/2C1	29	27	27	27
Bw2/2C2	87	85	85	84
<i>KCG 11</i>				
A1	182	178	177	176
A2	170	166	165	164
Bw1/2C1	65	63	62	62

Table A.2: Profile integrated tephra influence

Sample name	Depth range (cm)	τ Mo %	τ Mo (30% void space) %	τ Mo (40% void space) %	τ Mo (50% void space) %
KCG 3	0--99	11	8	7	7
KCG 4	0--70	1	-1	-1	-2
KCG 6	0--90	19	16	15	14
KCG 7	0--70	41	40	39	39
KCG 9	0--99	21	24	26	27
KCG 10	0--75	79	77	76	76
KCG 11	0--50	75	73	73	72

Table A.3: Groundwater influenced by seawater intrusion

Sample name	Mo ng g ⁻¹	Na μg g ⁻¹	δ ⁹⁸ Mo	
			‰	2 s.d.
<i>Groundwater</i>				
4161-01	0.46	869.1	1.06	0.06
4161-02	1.29	338.8	1.01	0.04
4061-01	2.51	2336.8	1.17	0.04

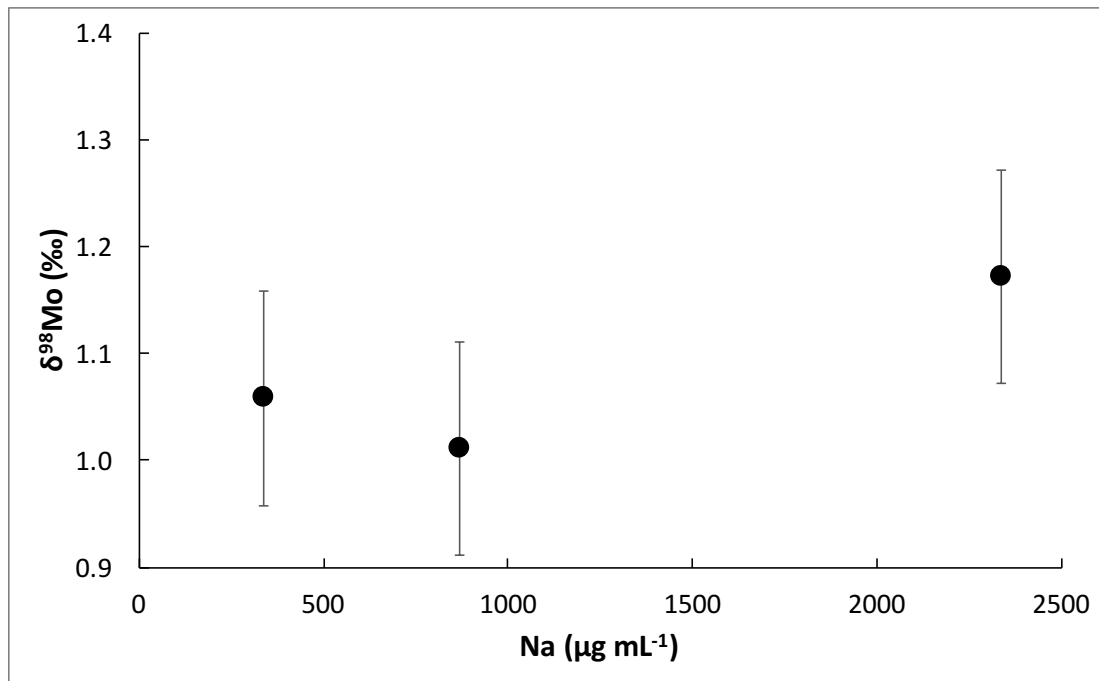


Figure A.1: $\delta^{98}\text{Mo}$ versus Na concentrations of groundwater samples affected by seawater intrusion.

Appendix B. Supplementary material for “Molybdenum isotope fractionation during adsorption onto organic matter”

Table B.1: Dissolved organic carbon concentrations

Sample	DOC
	mg C L ⁻¹
pH 2 A	0.5
pH 2 B	0.0
pH 3 A	0.6
pH 3 B	0.7
pH 4 A	0.7
pH 4 B	0.6
pH 5 A	0.7
pH 5 B	0.5
pH 6 A	0.8
pH 6 B	0.9
pH 7 A	0.1
pH 7 B	0.1
Mo stock solution	0.7

Table B.2: O horizon chemical parameters (Perakis et al., 2017)

Site Name	O horizon pH	Total C mg C g ⁻¹	Total Fe mg Fe g ⁻¹	Soluble C %	Hemicellulose C %	Cellulose C %	Lignin C %	Ash and Silica C %
8	5.7	527.3	0.9	40.1	9.6	18.1	32.0	0.1
14	5.6	514.9	3.6	41.2	7.7	17.0	31.0	3.1
19	5.4	516.3	2.0	42.0	9.9	17.5	29.9	0.7
BC1	5.3	526.4	0.4	41.0	8.5	18.4	31.8	0.3
Jensen	6.1	529.0	2.1	44.7	8.9	16.9	28.5	1.1
NFT	5.7	500.8	1.8	46.9	6.8	15.5	27.9	3.0
Stein	5.8	515.2	0.7	45.0	9.3	18.6	26.5	0.7
GV1	5.2	517.6	1.9	38.0	8.8	18.8	32.5	1.9
54	5.5	496.4	4.7	39.5	10.4	18.2	30.2	1.6
56	5.9	517.9	0.9	37.9	8.3	16.7	36.4	0.7
143	5.5	528.2	0.6	38.1	9.4	17.9	33.8	0.8
Trask	5.1	520.3	1.5	38.6	7.7	19.4	31.8	2.4

Table B.3: Regression statistics for O horizon chemical parameters (95% C.I.)

Sample	[Mo]		$\delta^{98} \text{Mo}$	
	r^2	p-value	r^2	p-value
pH	-0.06	0.44	-0.43	0.02
% total Fe	0.02	0.70	0.09	0.34
% total C	0.00	0.91	-0.06	0.43
% Soluble C	-0.13	0.25	-0.39	0.03
% Hemicellulose	0.05	0.48	0.10	0.33
% Cellulose	0.00	0.41	0.28	0.08
%Lignin	-0.43	0.03	0.11	0.33
%Silica	0.00	0.83	0.02	0.63

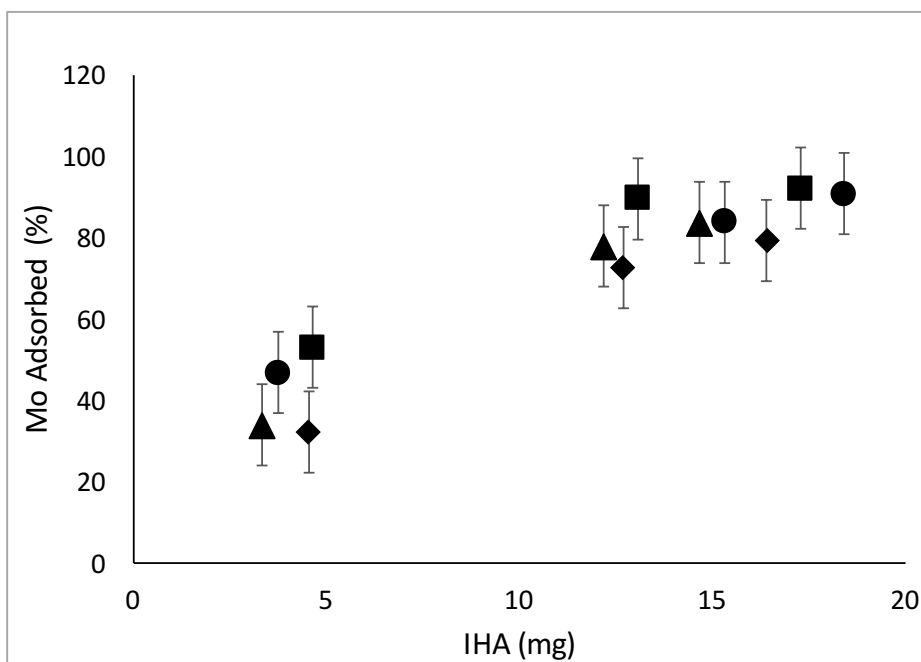


Figure B.1: Percentage of Mo adsorbed as a function of the exact mass of IHA. Using four different Mo concentrations ($2 \mu\text{g Mo mL}^{-1}$ (squares), $5 \mu\text{g Mo mL}^{-1}$ (circles), $10 \mu\text{g Mo mL}^{-1}$ (triangles), and $20 \mu\text{g Mo mL}^{-1}$ (diamonds)). Error bars represent the error propagation assuming a 5% error on Mo concentrations and an average 11% error associated with Mo loss during filtration of Mo solution from IHA. Experiment performed at ambient light and temperature for 7 days.

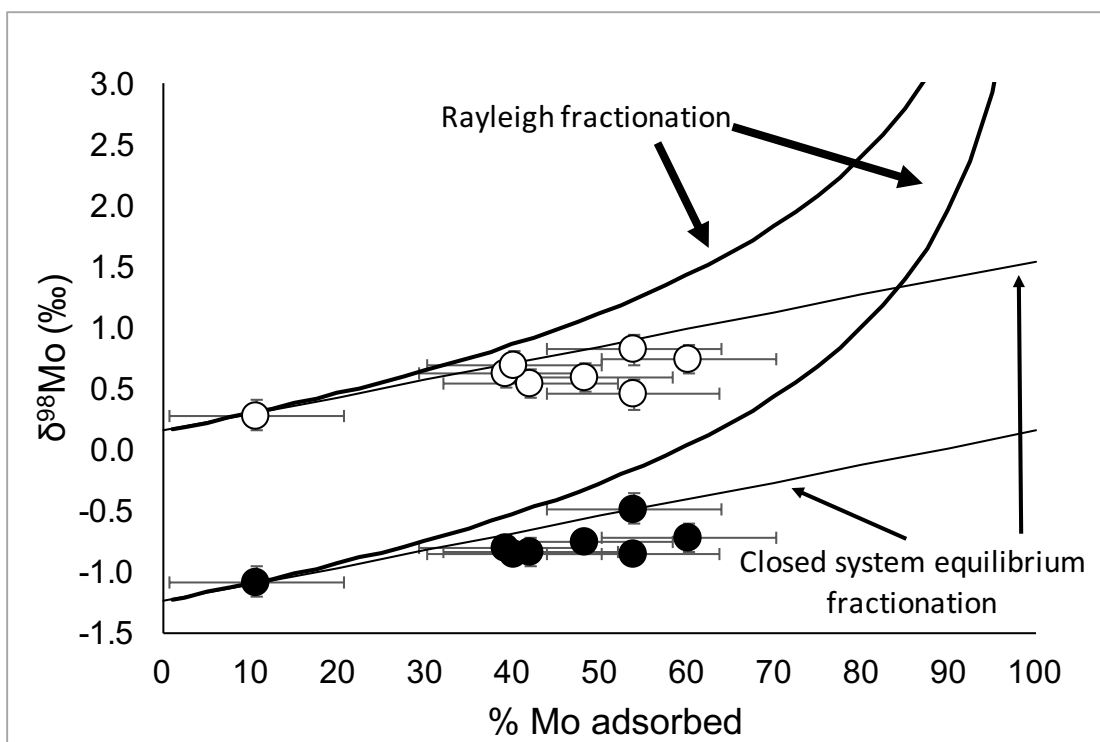


Figure B.2: Percentage of Mo adsorbed by IHA versus Mo isotopic composition ($\delta^{98}\text{Mo}$) from the time series experiment.

Closed circles represent Mo adsorbed onto IHA and open circles represent Mo remaining in solution. Adsorption error bars represent the error propagation assuming a 5% error on Mo concentrations and an average 11% error associated with Mo loss during filtration of Mo solution from IHA. Error bars for $\delta^{98}\text{Mo}$ represent $\pm 2\sigma$ of the external reproducibility. Closed-system equilibrium fractionation is represented by the equations: 1) $\delta^{98}\text{Mo}_{\text{solution}} = \delta^{98}\text{Mo}_{\text{initial}} + f(\ln(\alpha_{\text{solution-IHA}}) * 1000)$ and 2) $\delta^{98}\text{Mo}_{\text{IHA}} = \delta^{98}\text{Mo}_{\text{initial}} + (1-f)(\ln(\alpha_{\text{solution-IHA}}) * 1000)$. Rayleigh fractionation is represented by the equations: 1) $\delta^{98}\text{Mo}_{\text{solution}} = \{(1-f)^{\alpha_{\text{IHA-solution}} - 1} * (\delta^{98}\text{Mo}_{\text{initial}} + 1000)\} - 1000$ and 2) $\delta^{98}\text{Mo}_{\text{IHA}} = \{\alpha_{\text{IHA-solution}} * (1-f)^{\alpha_{\text{IHA-solution}} - 1} * (\delta^{98}\text{Mo}_{\text{initial}} + 1000)\} - 1000$. In both equations, f is the fraction of Mo adsorbed to the IHA and initial Mo stock solution $\delta^{98}\text{Mo} = +0.24\text{‰}$.

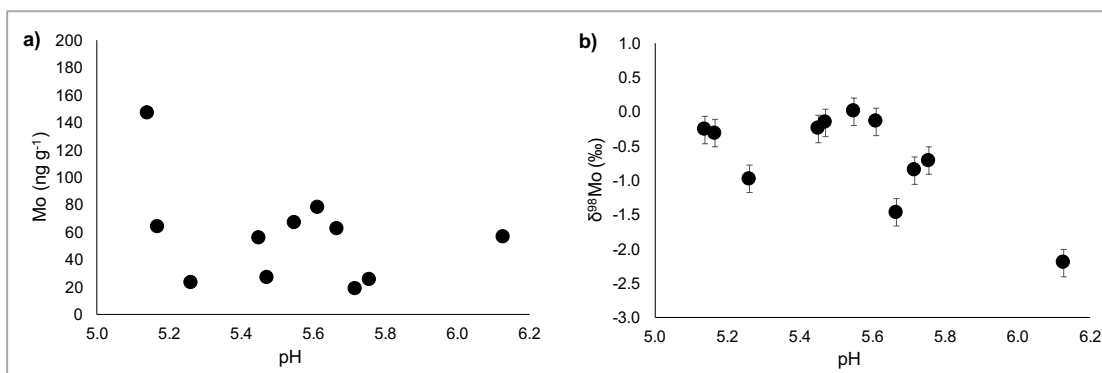


Figure B.3: O horizon Mo concentrations (a) and O horizon Mo isotopic composition ($\delta^{98}\text{Mo}$) (b) versus O horizon pH along the Oregon Coast Range.

As pH increases, Mo content may decrease ($r^2 = 0.05$, $p = 0.44$) in O horizon and $\delta^{98}\text{Mo}$ becomes light ($r^2 = 0.43$, $p = 0.03$). Error bars for Mo $\delta^{98}\text{Mo}$ represent $\pm 2\sigma$ of the external reproducibility.

Appendix C. Supplementary material for “Interactions between lithology and redox cycling in controlling trace metal mobilization and Mo isotope dynamics in soil”

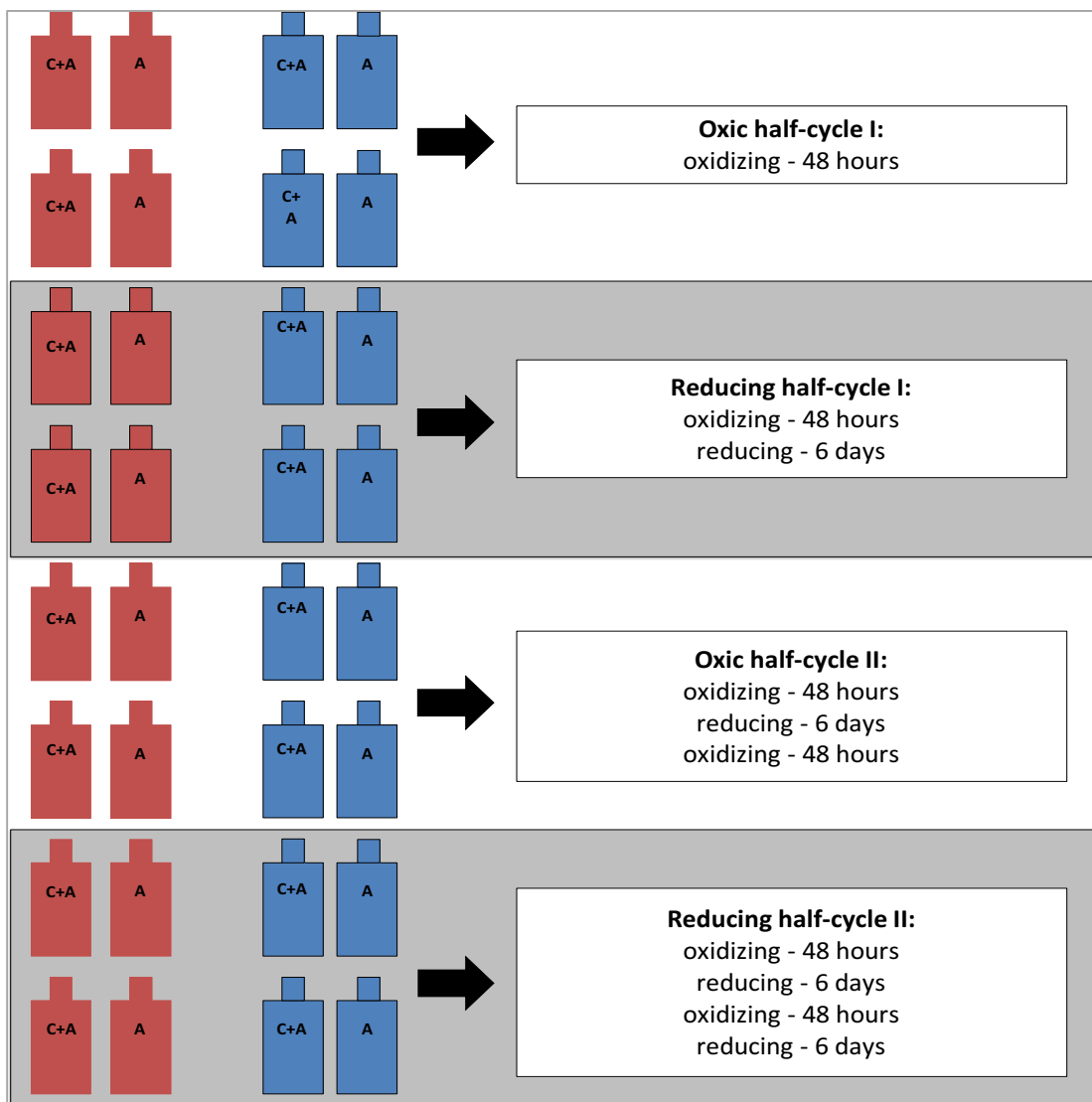


Figure C.1: Schematic of artificial redox experiment.

Duplicate samples were combined following elemental analysis to allow for measurement of Mo isotopic composition. Oxidizing half-cycles were 48 hours long and reducing half-cycles were 6 days. Bottles labeled "C+A" were size-fractionated for the < 415 nm fraction (solution; colloidal and dissolved). Bottles labeled "A" were size-fractionated for the < 10 nm fraction (aqueous; dissolved) for Bisley (red bottles) and Guaba Ridge (blue bottles).

Table C.1: Trace metal bulk soil and bedrock chemistry ($\mu\text{g g}^{-1}$)

	Bisley		Guaba Ridge	
	Bulk Soil	Bedrock ^a	Bulk Soil	Bedrock ^b
<i>Mn</i>	2134	1162	2858	481
<i>Rb</i>	20.0	--	19.0	32.0
<i>Zr</i>	137	82	225	92
<i>Nb</i>	1.1	< 10	1.2	2.9
<i>La</i>	7.1	11.0	3.5	8.2
<i>Ce</i>	11.0	19.0	7.7	16.0
<i>Pr</i>	1.1	3.5	0.6	2.0
<i>Nd</i>	5.4	16.0	2.2	7.9
<i>Sm</i>	1.3	4.3	0.5	1.8
<i>Eu</i>	0.4	1.4	0.1	0.6
<i>Gd</i>	1.3	4.4	0.4	1.8
<i>Tb</i>	0.2	0.6	0.1	0.3
<i>Dy</i>	1.1	3.8	0.3	1.9
<i>Ho</i>	0.2	0.8	0.1	0.4
<i>Er</i>	0.8	2.0	0.2	1.2
<i>Tm</i>	0.1	0.3	0.0	0.2
<i>Yb</i>	0.8	1.9	0.2	1.5
<i>Lu</i>	0.1	0.3	0.1	0.3
<i>Ta</i>	1.8	--	2.5	--
<i>Pb</i>	13.0	--	35.0	3.5
<i>Th</i>	0.8	1.0	0.4	1.1
<i>U</i>	1.0	0.7	0.8	0.6

^aBuss et al., (2017), Dosseto et al., (2012)^bMcClintock (2015)

C.1. ^{57}Fe Mössbauer spectroscopy of the Bisley and Guaba Ridge soils and the Ferrihydrite and Goethite standards

C.1.1. *Introduction*

We employ ^{57}Fe Mössbauer spectroscopy (MBS) to evaluate the Fe site populations in the Bisley and Guaba Ridge bulk soils.

C.1.2. *Methods*

Transmission ^{57}Fe Mössbauer spectroscopy was performed with a variable temperature He-cooled system with a 1024 channel detector. A ^{57}Co source (~50 mCi or less) embedded in a Rh matrix was used at room temperature. Freeze-dried powder samples were mounted between two pieces of 0.127 mm thickness Kapton tape and transferred to the spectrometer cryostat. Velocity (i.e., gamma-ray energy) was calibrated using α -Fe foil at 295 K and all center shifts (CSs) and peak positions are reported with respect to this standard. The transducer was operated in constant acceleration mode and folding was performed to achieve a flat background.

Mössbauer spectral fitting of all spectra was performed using the Voigt-based fitting (VBF) method of Rancourt and Ping (1991) for quadrupole splitting distributions (QSDs) and combined hyperfine field distributions (HFDs), as implemented in the RecoilTM software, ISA Inc. All VBF Mössbauer parameter definitions and a description of the relevant notation are given by Rancourt and Ping¹. All errors in Mössbauer fitting parameters are two-standard deviation (2σ) errors, as calculated by RecoilTM. In reporting quantitative phase abundances or site populations it is assumed that the Mössbauer recoilless fractions of all detected

phases or Fe-bearing components are equal, such that subspectral areas (expressed as fractions of total spectral area) are equal to the amounts of Fe (expressed as fractions of total Fe) in the corresponding phases or components. This assumption is expected to be valid at cryogenic temperatures, and also to be a good approximation at RT with dry samples (Lalonde et al., 1998; Rancourt, 1998).

In Mössbauer spectroscopy, each spectral component corresponds to one Fe-bearing solid phase or to a group of unresolved Fe-bearing solid phases. These components take the form of a doublet, sextet, octet (none resolved here) or a collapsed sextet—indicating a solid-phase near its magnetic ordering temperature (T_N). Solid-phases well above (doublet) or below (sextet) their T_N will not exhibit any vertical (i.e. count axis) distance between the peak troughs and the baseline. When Fe solid-phases are near their T_N , they exhibit an intermediate shape between a doublet and full sextet, which fills the area between the upper baseline and the inverse troughs of the peaks. We approximate this by using a separate collapsed sextet component (i.e., a sextet with exceedingly large line widths and $B_{hf} = 0$ T).

Assuming equal Mössbauer recoilless fractions (that the *measurable* gamma rays emitted by each phase are proportional to the phase abundance), the total spectral area of a given component is proportional to the amount of Fe in the corresponding solid phase(s). Furthermore, it can then be assumed that each phase occupies the same spectral area at all temperatures, although not the same spectral shape. For instance, nano-scale Fe^{III} -(oxyhydr)oxide minerals form a doublet at 295K and magnetically order to form a sextet only when cooled sufficiently to prevent

thermal disordering of the macroscopic magnetic ordering within the material (Rancourt, 2001).

We left all fitting parameters normally used to fine-tune the fit at their most general, conservative values: These include: constraining all Lorentzian half widths at twice the Heisenberg values; disallowing parameter coupling between the center shift (CS), quadrupole splitting (QS or ε , for sextets) and average hyperfine field (Bhf); and constraining the area ratios between the doublet lines to 1:1 and area ratios between sextet lines 2 and 3 to 2:1 and lines 1 and 3 to 3:1 (see Table C.2). The expectation is the Lorentzian half-width values, which we set at the value optimized for an α -Fe foil standard on our spectrometer (i.e. 0.1425 mm s^{-1}), which is slightly larger than the ideal theoretical value. An explanation of the four key MB spectral parameters used in our analysis (center shift, quadrupole splitting, hyperfine field strength and the line width) is summarized in the electronic annex of Thompson et al. (2011).

C.1.3. Mössbauer spectral components in the Bisley and Guaba Ridge bulk soils

Across the three collection temperatures (295K, 77K, and 4.8K) we resolved five distinct spectral components. Spectral components include: (1) an Fe^{III} quadrupole doublet (labelled Q- Fe^{III}) corresponding to Fe^{III} in clays, silicates, surface-complexed to solids, and in all Fe^{III} -(oxyhydr)oxides that are superparamagnetic (SP) at the collection temperature; (2) a wide Fe^{II} quadrupole doublet (labelled Q- Fe^{II} -clay) that we attribute to paramagnetic ferrous in silicate phases; (3) a broadened Fe^{III} sextet (labelled HFD-OxHy) that corresponds to magnetically-ordered Fe^{III}

oxyhydroxides, including ferrihydrite (Fh) and nano-goethite (nGt) phases; (4) a broadened Fe^{III} sextet (labelled Lp-like) that has a near zero quadrupole splitting and narrow sextet width corresponding to phases best approximated by lepidocrocite (Lp); and (5) a partially collapsed Fe^{III} 'sextet' (labelled HFD-(b)Oxhy) due to a Fe^{III} - (oxyhydr)oxide having its SP blocking temperature near the collection temperature. In the 4.8 K spectra, if we assume all the Fe^{III} -oxyhydroxides have magnetically ordered we can refine our component descriptions of the Fe^{III} quadrupole doublet (Q- Fe^{III}) to correspond to Fe^{III} complexed to solids such as organic matter or in non-Fe-rich silicates; the Fe^{III} sextets (HFD-OxHy and Lp-like) would represent phases with clear distinctive similarity to Fh/nGt and Lp, whereas the most disordered end-members of all Fe-oxide phases would be contained in the HFD-(b)OxHy component that is represented by the partially collapsed Fe^{III} 'sextet' attributed to Fe^{III} - (oxyhydr)oxides having their SP blocking temperatures near 4.8K.

We calculated the abundance of each Fe-bearing phase from the spectral area of each respective component in the 4.8K spectra. Fe^{III} -clay and Fe^{II} -clay abundances are calculated from spectra area of the Q- Fe^{III} and Q- Fe^{II} -clay component spectra areas of the 4.8K spectra, respectively. The total Fe^{III} -oxyhydroxide abundance can be calculated by summing the HFD-Oxhy, Lp-like, and HFD-(b)OxHy components at 4.8K (Figure C.2 and Table C.2).

C.1.4. Mössbauer phase analysis of Bisely and Guaba Ridge bulk soils

Collection of Mössbauer spectra at 295K, 77K, and 4.8K allows us to characterize the crystallinity-continuum of the Fe^{III} -oxyhydroxide solid phases in

these soils. All resolved Fe^{III} -(oxyhydr)oxides at 295K are superparamagnetic or near their blocking temperature. As temperature is reduced, portions of the Fe^{III} -oxyhydroxide populations are resolved as they magnetically order into a sextet (Figure C.3), with the more crystalline portions of the population ordering at higher temperatures.

At Bisley, the spectral area assigned to the full Fe^{III} Fe^{III} -oxyhydroxide (HFD-Oxhy) sextets increases from 33.2%, 46.4%, 69.4%, at 295K, 77K, and 4.8K, respectively. At 77K, we are able to split out a nano-goethite (nGt) component with a QS splitting values of -0.13 mm s^{-1} . At 4.8K, the spectral area of the nGt component increases in area relative to the 77K spectra. At Guaba Ridge, the spectral area assigned to the full Fe^{III} -oxyhydroxide (HFD-Oxhy) sextets increases from 7.8% to 52.1% to 52.8%, at 295K, 77K, and 4.8K, respectively. At 77K, we are able to split out a nano-goethite (nGt) component with a QS splitting value of -0.13 mm s^{-1} . At 4.8K, the spectral area of the nGt component stays the same relative to the 77K spectra, but we are able to split out a spectral component resembling lepidocrocite (Lp-like) with a spectral area of 32.5% and a QS splitting value of 0.006 mm s^{-1} .

At both Bisley and Guaba, Fe^{III} -oxyhydroxides that are blocked or near their blocking temperature at 4.8K comprise $\sim 10\%$ of the spectral area (Table C.2). These phases may represent even more disordered Fh or n-Gt phases or phases that are so disordered assigning them to a bulk pure mineral phases is un-justified.

Fe atoms in silicates and monomeric organic complexes are too distant from each other to order magnetically, and thus both site populations produce a doublet

at 4.8K with similar CS values near 0.47 mm s^{-1} and QS values near 0.9 mm s^{-1} . These are consistent with octahedrally coordinated, trivalent Fe. Fe^{III} substituted layered silicates typically yields QS values in this range—perhaps slightly lower (~ 0.8), however, the likely presence of Fe^{2+} in these clays (see below) would likely increase structural distortion and lead to higher Fe^{3+} quadropole splitting values (Murad and Cashion, 2004). Fe^{III} in octahedral positions of Fe-poor 2:1 minerals also yield larger Fe^{III} quadropole splitting values consistent with our observations (Murad and Wagner, 1994).

At Bisley (but not at Guaba) we observe a paramagnetic ferrous contributions in this sample consistent with sheet silicates or sorbed Fe^{2+} . No octets consistent with the presence of magnetite are observed, although highly substituted magnetite is difficult to distinguish from other Fe-oxides. The position of the high-velocity (H_L) line of Q- Fe^{II} -clay at $2.6 - 2.75 \text{ mm s}^{-1}$ is consistent with those commonly reported for aluminosilicate clays, which has a H_L value of 2.66 mm s^{-1} (Murad and Cashion, 2004). In addition, adsorbed Fe^{2+} may also contribute to this peak, as Rancourt et al. (2005) have shown Fe^{2+} sorbed to bacterial cells can yield H_L lines even above 2.8 mm yr^{-1} . There are no paramagnetic ferrous populations detected at Guaba Ridge.

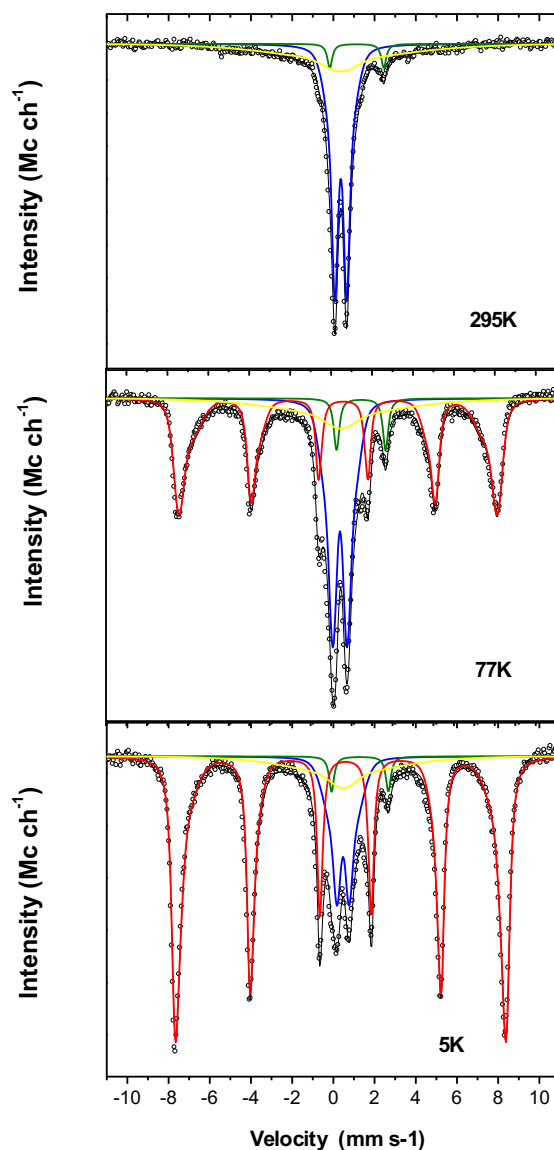


Figure C.2: ^{57}Fe Mössbauer spectra of the unreacted Bisley soil at 295K, 77K, and 4.8K.

In each spectrum, the black solid line is the total calculated fit, through the discrete data points. The resolved spectral components and assignments are: (1) Q- Fe^{III} , the deep central doublet (blue line) corresponding to Fe^{III} in aluminosilicate minerals or organically-bound Fe; (2) Q- Fe^{II} -2 the wider ferrous doublet corresponding to Fe^{II} in clays (green line); (3) HFD-OxHy, the dominant sextet (red line) corresponding to Fe^{III} -oxyhydroxides that are magnetically ordered and characterized as nano-goethite (nGt)-like; and (4) HFD-(b)OxHy the collapsed 'sextet' (yellow line) corresponding to Fe^{III} -oxyhydroxides near their blocking temperature.

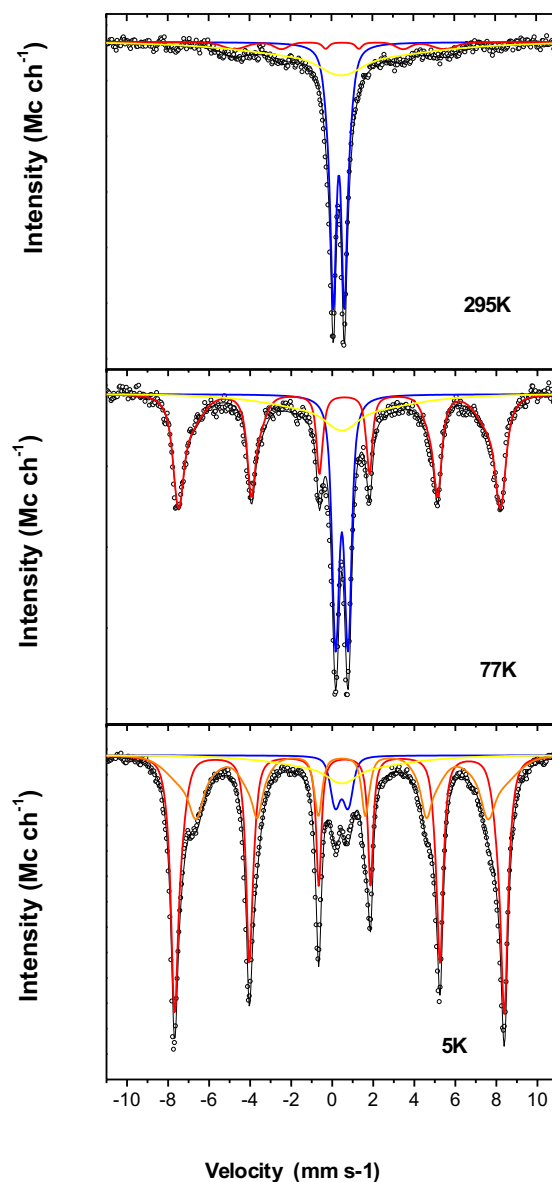


Figure C.3: ^{57}Fe Mössbauer spectra of the unreacted Guaba Ridge soil at 295K, 77K, and 4.8K.

In each spectrum, the black solid line is the total calculated fit, through the discrete data points. The resolved spectral components and assignments are: (1) Q- Fe^{III} , the deep central doublet (**blue line**) corresponding to Fe^{III} in aluminosilicate minerals or organically-bound Fe; (2) HFD-OxHy, the dominant sextet (**red line**) corresponding to Fe^{III} -oxyhydroxides that are magnetically ordered and characterized as nano-goethite (nGt)-like; (3) Lp-like, the minor sextet (**orange line**) corresponding to lepidocrocite (Lp-like) to Fe^{III} -oxyhydroxides that are magnetically ordered; and (4) HFD-(b)OxHy the collapsed 'sextet' (**yellow line**) corresponding to Fe^{III} -oxyhydroxides near their blocking temperature.

Table C.2: Mössbauer spectroscopy parameters

Sample		Fe-phase		Spectral Area	$\langle CS \rangle$ or δ	P	σ	Red-X ²
				%	mm s ⁻¹	%	mm s ⁻¹ or T	
Bisley (incubation) 295K (2Q, 1H) (BG =4.7 MC/ch)	QSD site 1	e(III)-silicates	Q-Fe ³⁺	62.3(12)	n/a	74.725*	0.141(23)	1.00
	QSD site 2	Fe(II) clays	Q-Fe ³⁺ -clay	4.50	1.136(18)	25.3(91)	0.54(12)	0.72
	HFD site 1	disordered	HFD-(b)Oxhy	33.2(12)	0.35(12)	100*	0(140)	
Bisley (incubation) 77K(Q,2H)	QSD site 1	e(III)-silicates	Q-Fe ³⁺	34.2(11)	n/a	73.3455*	0.251(25)	1.50
	QSD site 2	Fe(II) clays	Q-Fe ³⁺ -clay	4.61	1.465(15)	27(10)	0.48(16)	0.91
	HFD site 1	Gt-like	HFD-Oxhy	46.4(13)	0.4675(47)	100*	0.089(61)	
Bisley (incubation) (BG =5.3 MC/ch)	HFD site 2	disordered	HFD-(b)Oxhy	14.8(14)	0.47*	40(13)	1.13(15)	46.81
	QSD site 1	e(III)-silicates	Q-Fe ³⁺	17.5(13)	n/a	100*	25.4(62)	
	QSD site 2	Fe(II) clays	Q-Fe ³⁺ -clay	2.40	1.292(21)	49.184*	0.20(11)	1.10
5K(2Q,2H)	HFD site 1	Gt-like	HFD-Oxhy	69.4(15)	0.4756(19)	51(33)	0.74(30)	0.91
						100*	0.03(26)	
						38.8633*	0.49(21)	
(BG =5.8 MC/ch)	HFD site 2	disordered	HFD-(b)Oxhy	10.8(12)	0.48*	39(29)	1.10(31)	48.73
	QSD site 1	e(III)-silicates	Q-Fe ³⁺	51.5(20)	n/a	22.5(92)	2.83(63)	
						100*	21.1(60)	
Guaba (incubation) 295K (1Q, 2H)	HFD site 1	Gt-like	HFD-Oxhy	7.8(18)	0.457(89)	75.3517*	0.097(46)	0.60
	HFD site 2	disordered	HFD-(b)Oxhy	40.7(20)	0.474(97)	25(23)	0.32(17)	0.62
						100*	3.12(93)	31.82
Guaba (incubation) 77K(1Q, 2H) (BG =3.7 MC/ch)	QSD site 1	e(III)-silicates	Q-Fe ³⁺	29.14(98)	n/a	100*	0.194(11)	1.00
	HFD site 1	Gt-like	HFD-Oxhy	52.1(15)	0.4762(59)	50.3696*	1.02(13)	
	HFD site 2	disordered	HFD-(b)Oxhy	18.8(17)	0.47*	49.6(54)	3.85(36)	47.45
Guaba (incubation) 5K(1Q, 3H) (BG =12.7 MC/ch)	QSD site 1	e(III)-silicates	Q-Fe ³⁺	5.27	0.463(15)	100*	0.340(35)	1.10
	HFD site 1	Gt-like	HFD-Oxhy	52.8(12)	0.4798(16)	48.2104*	0.399(71)	49.51
	HFD site 2	Lp-like	Lp-like	32.5(12)	0.4751(85)	51.8(48)	1.74(14)	
	HFD site 3	disordered	HFD-(b)Oxhy	9.50(67)	0.48*	45.93(33)	5.69(37)	45.47
						24.8(61)	1.34(26)	
						100*	21.9999*	
						0*		

Table C.2. Notes:

All fits performed using the Voigt-based fitting method of Rancourt and Ping (1991) with the Recoil™ software.

All fitting and calculated parameters are as defined in by Rancourt and Ping (1991).

All delta-1 couplings between CS and z (or DELTA) were taken to be zero.

All line-1 to line-2 area ratios in all (distributed) elemental doublets were taken to be 1.

All line-2/line-3 and line-1/line-3 area ratios in all (distributed and symmetric) elemental sextets were taken to be 2 and 3, respectively.

All epsilon-1 couplings between epsilon and z (in a HFD) are taken to be 0.

All Lorentzian half widths at half maximum (HWHM) are set at 0.1425 mm/s as measured on Fe foil standards on the instrument.

All center shifts <CS> are given with respect to the CS of metallic Fe at 295K.

BG = background level, in mega-counts per channel (MC/ch). phase = assigned spectral component, as described in the text.

<CS> = the center shift of a Gaussian component in the quadrupole splitting distribution (QSD) of the hyperfine field distribution (HFD) of a given spectral component.

z = the center (or position) of a Gaussian component in the hyperfine field distribution (HFD) of a given 'sextet' spectral component.

σ = the Gaussian standard deviation width of a given Gaussian component of a given QSD or HFD.

p (in %) is the weight factor for a given Gaussian component in a given QSD or HFD.

<H> is the average magnitude of the hyperfine field (expressed as an excited state Zeeman splitting, in mm/s) in a given HFD of a given sextet spectral component.

Δ is the average magnitude of the quadrupole splitting in a given QSD of a given doublet spectral component.

< ϵ > is the average magnitude of the slave distribution of quadrupole shifts (epsilons) associated to a given HFD of a given sextet spectral component.

Red-X2 is the reduced chi-squared value for the fit: chi-squared divided by the number of degrees of freedom. It has an ideal value of 1 for a correct model.

Table C.3: Artificial redox experiment chemistry: Trace metals ($\mu\text{g g}^{-1}$)

	Oxic Half-Cycle I				Reducing Half-Cycle I			
	Bisley		Guaba Ridge		Bisley		Guaba Ridge	
	Solution ^a	Aqueous ^b	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous
Mn	6.50E-01	2.10E-01	5.60E-02	5.90E-02	2.53E+00	1.50E+00	2.40E-01	2.40E-01
Rb	4.10E-03	3.50E-03	2.80E-03	1.60E-03	8.91E-03	3.80E-03	5.40E-03	1.80E-03
Y	2.00E-03	1.04E-03	6.14E-04	2.64E-04	1.42E-02	3.39E-03	7.76E-04	8.08E-04
Zr	2.20E-03	1.30E-03	2.50E-03	6.40E-04	1.10E-02	2.50E-03	1.50E-03	1.60E-03
Nb	5.80E-05	1.10E-04	2.20E-04	3.70E-05	1.10E-04	3.30E-05	1.70E-04	1.30E-04
La	8.10E-04	1.80E-04	1.80E-04	1.80E-04	3.30E-03	7.80E-04	2.60E-04	2.80E-04
Ce	5.50E-03	2.50E-03	2.40E-03	4.40E-04	4.30E-02	8.30E-03	3.00E-03	3.20E-03
Pr	4.70E-04	2.00E-04	1.70E-04	3.80E-05	3.30E-03	6.60E-04	2.10E-04	2.10E-04
Nd	2.20E-03	9.30E-04	7.20E-04	1.70E-04	1.60E-02	3.20E-03	9.20E-04	9.60E-04
Sm	5.80E-04	2.40E-04	1.80E-04	4.50E-05	3.90E-03	7.60E-04	2.20E-04	2.30E-04
Eu	1.70E-04	6.90E-05	5.10E-05	1.30E-05	1.10E-03	2.50E-04	6.70E-05	8.00E-05
Gd	5.40E-04	2.20E-04	1.70E-04	4.60E-05	3.80E-03	7.80E-04	2.10E-04	2.20E-04
Tb	9.20E-05	3.70E-05	2.80E-05	3.60E-06	5.90E-04	1.20E-04	3.20E-05	3.30E-05
Dy	5.00E-04	2.50E-04	1.60E-04	4.80E-05	3.50E-03	7.10E-04	1.90E-04	2.00E-04
Ho	1.00E-04	6.30E-05	3.30E-05	1.10E-05	6.70E-04	1.40E-04	4.00E-05	4.00E-05
Er	3.00E-04	2.20E-04	9.40E-05	3.30E-05	1.90E-03	4.20E-04	1.30E-04	1.40E-04
Tm	4.70E-05	3.60E-05	1.50E-05	5.70E-06	2.50E-04	5.60E-05	2.00E-05	2.20E-05
Yb	2.50E-04	2.20E-04	1.00E-04	3.80E-05	1.50E-03	3.40E-04	1.40E-04	1.60E-04
Lu	3.60E-05	2.90E-05	1.50E-05	6.10E-06	1.90E-04	4.40E-05	2.20E-05	2.40E-05
Ta	4.00E-05	4.00E-05	5.00E-05	1.50E-04	2.80E-04	5.00E-05	3.00E-05	4.00E-05
Pb	4.60E-03	2.00E-03	2.00E-03	3.70E-04	2.10E-02	3.20E-03	4.00E-03	9.60E-04
Th	5.70E-04	3.30E-04	5.40E-04	3.10E-04	1.50E-03	2.40E-04	3.90E-04	3.20E-04
U	2.00E-04	1.40E-04	2.10E-04	1.30E-04	9.00E-04	1.50E-04	1.60E-04	1.50E-04

	Oxic Half-Cycle II				Reducing Half-Cycle II			
	Bisley		Guaba Ridge		Bisley		Guaba Ridge	
	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous
Mn	1.03E+00	8.79E-01	3.28E-01	2.25E-01	3.57E+00	2.72E+00	6.76E-01	4.76E-01
Rb	5.40E-03	4.30E-03	3.40E-03	2.10E-03	4.20E-03	3.00E-03	2.40E-03	2.40E-03
Y	2.60E-03	2.31E-03	6.80E-04	4.14E-04	5.39E-03	3.33E-03	9.21E-04	1.43E-03
Zr	2.30E-03	1.60E-03	2.30E-03	1.10E-03	6.50E-03	2.10E-03	3.00E-03	8.70E-04
Nb	5.20E-05	5.50E-05	2.90E-04	1.00E-04	5.90E-05	1.80E-05	9.90E-05	6.30E-05
La	4.60E-04	5.90E-04	2.80E-04	4.80E-04	2.40E-03	7.20E-04	1.10E-03	3.30E-04
Ce	4.60E-03	7.10E-03	3.40E-03	1.70E-03	1.70E-02	9.70E-03	3.60E-03	6.60E-03
Pr	3.80E-04	6.00E-04	2.40E-04	1.20E-04	1.40E-03	8.20E-04	2.80E-04	4.30E-04
Nd	1.90E-03	3.00E-03	1.00E-03	5.20E-04	6.90E-03	4.20E-03	1.10E-03	2.00E-03
Sm	4.90E-04	7.80E-04	2.50E-04	1.30E-04	1.70E-03	1.00E-03	1.20E-04	4.60E-04
Eu	1.50E-04	2.20E-04	7.50E-05	4.00E-05	4.80E-04	2.80E-04	3.30E-05	1.30E-04
Gd	4.50E-04	7.10E-04	2.30E-04	1.20E-04	1.60E-03	9.70E-04	1.10E-04	4.60E-04
Tb	6.90E-05	1.10E-04	3.50E-05	1.80E-05	2.40E-04	1.40E-04	1.60E-05	6.50E-05
Dy	4.10E-04	6.50E-04	2.10E-04	1.10E-04	1.40E-03	8.20E-04	9.60E-05	3.80E-04
Ho	8.10E-05	1.30E-04	4.00E-05	2.30E-05	2.80E-04	1.70E-04	2.10E-05	8.00E-05
Er	2.30E-04	3.60E-04	1.20E-04	7.10E-05	8.00E-04	4.80E-04	6.30E-05	2.60E-04
Tm	3.20E-05	4.80E-05	1.90E-05	1.20E-05	1.10E-04	6.50E-05	9.60E-06	4.00E-05
Yb	2.00E-04	3.00E-04	1.40E-04	8.70E-05	6.50E-04	4.00E-04	6.70E-05	2.90E-04
Lu	2.60E-05	3.90E-05	2.00E-05	1.40E-05	8.50E-05	5.40E-05	1.10E-05	4.70E-05
Ta	4.00E-05	1.10E-04	1.90E-04	5.00E-05	1.40E-04	9.00E-05	2.50E-04	1.10E-04
Pb	6.00E-03	5.60E-03	2.60E-03	8.80E-04	1.10E-02	5.30E-03	1.70E-03	1.80E-03
Th	6.30E-04	6.50E-04	8.00E-04	3.40E-04	1.10E-03	5.20E-04	7.50E-04	5.00E-04
U	3.20E-04	2.70E-04	3.00E-04	1.50E-04	5.10E-04	3.20E-04	3.40E-04	2.90E-04

Table C.4: [X]_{Bisley}/[X]_{Guaba Ridge} for full suite of metals analyzed in experiments

	Bedrock		Bulk soil	Oxic half-cycle I		Reducing half-cycle I		Oxic half-cycle II		Reducing half-cycle II	
	Total		Total	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous	Solution	Aqueous
Al	1.0	1.2	1.2	1.5	0.8	7.2	1.3	0.6	2.1	9.1	0.4
Ti	1.1	1.8	1.8	1.4	1.3	7.0	1.2	1.4	1.2	6.6	6.6
Fe	1.0	3.6	3.6	1.6	0.8	4.1	1.0	0.9	1.4	1.9	1.2
Mo	0.8	1.3	1.3	1.4	1.3	7.0	1.2	1.2	2.5	2.6	2.0
Mn	2.4	0.7	0.7	11.6	3.6	10.5	6.3	3.1	3.9	5.3	5.7
Rb	--	1.1	1.1	1.5	2.2	1.7	2.1	1.6	2.0	1.8	1.3
Zr	0.9	0.6	0.6	0.9	2.0	7.3	1.6	1.0	1.5	2.2	2.4
Nb	1.0	0.9	0.9	0.3	3.0	0.6	0.3	0.2	0.6	0.6	0.3
La	1.3	2.0	2.0	4.5	1.0	12.7	2.8	1.6	1.2	2.2	2.2
Ce	1.2	1.4	1.4	2.3	5.7	14.3	2.6	1.4	4.2	4.7	1.5
Pr	1.8	1.8	1.8	2.8	5.3	15.7	3.1	1.6	5.0	5.0	1.9
Nd	2.0	2.5	2.5	3.1	5.5	17.4	3.3	1.9	5.8	6.3	2.1
Sm	2.4	2.6	2.6	3.2	5.3	17.7	3.3	2.0	6.0	14.2	2.2
Eu	2.3	4.0	4.0	3.3	5.3	16.4	3.1	2.0	5.5	14.5	2.2
Gd	2.4	3.3	3.3	3.2	4.8	18.1	3.5	2.0	5.9	14.5	2.1
Tb	2.0	2.0	2.0	3.3	10.3	18.4	3.6	2.0	6.1	15.0	2.2
Dy	2.0	3.7	3.7	3.1	5.2	18.4	3.6	2.0	5.9	14.6	2.2
Ho	2.0	2.0	2.0	3.0	5.7	16.8	3.5	2.0	5.7	13.3	2.1
Er	1.7	4.0	4.0	3.2	6.7	14.6	3.0	1.9	5.1	12.7	1.8
Tm	1.5	2.8	2.8	3.1	6.3	12.5	2.5	1.7	4.0	11.5	1.6
Yb	1.3	4.0	4.0	2.5	5.8	10.7	2.1	1.4	3.4	9.7	1.4
Lu	1.0	1.0	1.0	2.4	4.8	8.6	1.8	1.3	2.8	7.7	1.1
Ta	--	0.7	0.7	0.8	0.3	9.3	1.3	0.2	2.2	0.6	0.8
Pb	--	0.4	0.4	2.3	5.4	5.3	3.3	2.3	6.4	6.5	2.9
Th	0.9	2.0	2.0	1.1	1.1	3.8	0.8	0.8	1.9	1.5	1.0
U	1.2	1.3	1.3	1.0	1.1	5.6	1.0	1.1	1.8	1.5	1.1

Table C.5: Correlation matrix for Bisley(red) and Guaba Ridge (blue)

[illegible]

Table D.1. (continued)

Location	Sample	Zn ppb	As ppb	Sr ppb	Rb ppb	Y ppb	Zr ppb	Nb ppb	Ag ppb	Ba ppb	La ppb	Ce ppb	Pr ppb	Nd ppb	Sm ppb		
Big Island, Hawaii	Kona Region	PW1	4E+00	--	6E-02	4E+01	4E-03	--	3E-03	--	4E-01	--	--	--	--		
		PW3	1E+00	--	1E-01	5E+01	2E-03	--	4E-03	--	5E-01	--	--	--	--		
		PW4	--	--	--	4E+01	8E-04	--	4E-03	--	--	--	--	--	--		
		PW7	6E+00	--	8E-02	2E+01	2E-03	--	4E-03	--	1E+00	--	--	--	--		
		IW5	5E+00	--	4E-02	7E+01	1E-03	--	4E-03	--	9E-01	--	--	--	--		
		Puu Lani	6E+00	--	2E-01	7E+01	8E-03	--	3E-02	--	1E+00	--	--	--	--		
		Puu Waa Waa	7E+01	--	2E-01	4E+01	2E-03	--	3E-02	--	1E+00	--	--	--	--		
		Keei	3E+00	2E-01	--	3E+00	1E-03	5E-03	3E-04	3E-04	6E-01	--	--	--	--		
		Kalaoa	2E+00	3E-01	--	8E+00	7E-04	8E-03	2E-04	3E-04	7E-01	--	--	--	--		
		Honokuhua	2E+00	1E+00	--	5E+01	3E-03	2E-02	--	-1E-02	4E+00	--	--	--	--		
	Hilo-Hamakua Coast	Makahiloa	1E+00	2E-02	--	4E-01	6E-02	8E-01	3E-02	4E-03	4E-01	4E-02	1E-01	2E-02	7E-02	2E-02	
		Pahale	6E-01	1E-02	--	2E-01	6E-02	5E-01	2E-02	2E-03	2E-01	4E-02	9E-02	1E-02	7E-02	2E-02	
		Manoloa	8E-01	3E-02	--	3E-01	8E-02	1E+00	5E-02	5E-03	6E-01	4E-02	2E-01	2E-02	9E-02	3E-02	
		Manowaiopae	3E+00	3E-02	--	4E-01	8E-02	1E+00	5E-02	5E-03	5E-01	5E-02	2E-01	2E-02	1E-01	3E-02	
		Kapue	3E+00	1E-02	--	2E-01	8E-02	4E-01	7E-03	9E-03	8E-01	5E-02	1E-01	2E-02	8E-02	2E-02	
		Honolii	1E+00	2E-02	--	3E-01	7E-02	4E-01	1E-02	6E-03	5E-01	4E-02	9E-02	1E-02	6E-02	2E-02	
	Kohala Peninsula	Kolekole	5E+00	3E-02	--	1E+00	3E-01	9E-01	1E-02	0E+00	2E+00	2E-01	4E-01	6E-02	3E-01	6E-02	
		Pololu 1	9E+00	--	2E-01	1E+01	2E-02	--	1E-02	--	2E+00	--	--	--	--	--	
		Pololou 2	2E+00	--	2E-01	1E+01	3E-02	--	2E-02	--	1E+00	--	--	--	--	--	
		WP87	2E+00	--	1E-01	1E+01	3E-02	--	2E-02	--	3E+00	--	--	--	--	--	
	Waipio	2E+00	--	1E-01	3E+01	7E-02	--	2E-02	--	4E+00	--	--	--	--	--		
Maui, Hawaii	MCG site 3	--	--	--	--	--	--	--	--	--	--	--	--	--	--		
	MCG site 5	--	--	--	--	--	--	--	--	--	--	--	--	--	--		
	Kauai, Hawaii	Kokee Upstream	4E+00	2E-02	--	4E-01	3E-02	2E-01	1E-02	2E-03	2E+00	2E-02	8E-02	7E-03	3E-02	8E-03	
Kokee Downstream		9E-01	2E-02	--	3E-01	2E-02	1E-01	4E-03	1E-03	2E+00	7E-03	3E-02	3E-03	1E-02	3E-03		
Kokee Tributary		3E+00	6E-02	--	8E-01	2E-01	3E-01	4E-02	1E-02	3E+00	9E-02	2E-01	2E-02	1E-01	3E-02		
Waimea River, dam		2E+00	2E-02	--	7E-01	3E-01	2E-01	1E-02	6E-03	2E+00	1E-01	2E-01	3E-02	2E-01	4E-02		
Waimea River, Poo Koa		3E+00	2E-02	--	8E-01	3E-01	1E-01	6E-03	5E-03	2E+00	1E-01	1E-01	4E-02	2E-01	5E-02		
Waimea River, powerhouse		1E+00	2E-02	--	9E-01	3E-01	9E-02	3E-03	4E-03	2E+00	7E-02	8E-02	2E-02	1E-01	3E-02		
Waimea River, ford		2E+00	2E-02	--	7E-01	5E-01	4E-01	1E-02	1E-02	3E+00	1E-01	2E-01	5E-02	2E-01	7E-02		
Critical Zone Observatories (CZO)		Eel River	S. fork Eel/Angelo Coa	7E-01	1E-01	--	2E-01	--	1E-02	2E-03	2E-02	1E+01	--	--	--	--	
	Reynolds		Johnston Draw	2E+00	3E-01	--	4E-01	--	4E-01	2E-02	3E-03	6E+00	--	--	--	--	
	Intensely Managed Landscapes	Reynolds Mountain	4E+00	4E-01	--	3E+00	--	8E-01	3E-02	4E-03	8E+00	--	--	--	--		
		Clear Creek	--	--	--	--	--	--	--	3E-03	5E+00	--	--	--	--		
	Santa Catalina Mountains-Jemez River Basin	Marshall Gulch	4E+00	2E-01	--	1E+00	--	1E-01	1E-02	2E-03	1E+01	1E-02	2E-02	4E-03	2E-02	6E-03	
		Rose Hill	6E-01	8E-02	--	7E-01	--	4E-02	2E-03	7E-03	3E+01	2E-02	1E-02	5E-03	2E-02	4E-03	
	Susquehanna Shale Hills	Gordon Gulch	1E+00	7E-02	--	2E-01	--	3E-02	1E-03	3E-03	8E+00	5E-02	3E-02	1E-02	4E-02	8E-03	
		Boulder	Mamayas	9E-01	5E-02	--	5E-01	--	9E-02	6E-03	3E-03	6E+00	2E-02	5E-02	9E-03	4E-02	1E-02
	Luquillo	Icacos	2E+00	6E-02	--	1E+00	--	4E-01	1E-02	3E-03	8E+01	1E-01	2E-01	3E-02	1E-01	3E-02	
		Guaba Ridge	1E+00	3E-02	--	1E+00	--	8E-02	9E-03	7E-03	5E+00	4E-01	8E-01	1E-01	6E-01	1E-01	
	Southern Sierra	Providence Creek	4E-01	3E-02	--	2E-01	--	2E-02	8E-04	6E-03	4E+00	2E-01	4E-01	8E-02	4E-01	8E-02	
		Calhoun	Weir 3	5E+00	5E-02	--	1E+00	--	7E-02	1E-02	1E-03	1E+01	3E-01	2E-01	7E-02	3E-01	7E-02
		Weir 4	2E+00	5E-02	--	8E-01	--	5E-02	3E-03	1E-03	1E+01	3E-02	4E-02	9E-03	4E-02	8E-03	
		Holcomb	1E+00	4E-02	--	7E-01	--	6E-02	3E-03	--	--	--	--	--	--	--	

Table D.2: Subsurface soil Mo data for Hawaii

Duration of weathering	$\delta^{98}\text{Mo}$
kyr	‰
0.3	-0.20
10	-0.45
10	-0.26
10	-0.53
10	-0.63
10	-0.11
10	-0.19
10	-0.01
170	-0.2
410	-0.47
410	-0.53
410	-0.36
4100	-0.2

Table D.3: Compilation of global riverine Mo data

Citation	Sample	Sample Type	Discharge	Mo Discharge	Catchment Area	Mo	1/[Mo]	Mo	1/[Mo]	$\delta^{98}\text{Mo}$
			$\text{m}^3 \text{ s}^{-1}$	mol Mo yr^{-1}	km^2	ppb	ppb^{-1}	nM	nM^{-1}	‰
Archer and Vance, 2008										
	Itchen	river	2007	137345	400	0.46	2.15	4.84	0.21	0.89
	Kalix	river	2007	126586	23600	0.74	1.35	7.74	0.13	0.75
	Kalix	river	29400	15483545	23600	0.53	1.88	5.55	0.18	0.95
	Kalix	river	29400	15576261	23600	0.48	2.07	5.03	0.20	0.8
	Kalix	river	29400	16410704	23600	0.47	2.11	4.94	0.20	0.73
	Kalix	river	29400	15854409	23600	0.47	2.12	4.91	0.20	0.86
	Kalix	river	29400	14741819	23600	0.47	2.13	4.88	0.20	0.75
	Nile	river	16170	4574136	3254555	0.70	1.42	7.33	0.14	-0.08
	Nile	river	6.2	99130	3254555	0.43	2.34	4.45	0.22	0.53
	Nile	river	6.2	99326	3254555	1.07	0.94	11.11	0.09	0.13
	Nile	river	6.2	99912	3254555	1.74	0.58	18.11	0.06	0.19
	Nile	river	6.2	99130	3254555	1.28	0.78	13.31	0.08	0.23
	Nile	river	8059	1690088	3254555	0.48	2.10	4.96	0.20	0.95
	Nile	river	209000	28605044	3254555	0.34	2.90	3.59	0.28	1.15
	Nile	river	209000	28341403	3254555	0.77	1.30	7.99	0.13	-0.1
	Nile	river	2630	607948	3254555	0.68	1.47	7.07	0.14	0.23
	Volga	river	2630	369082	1410994	0.64	1.57	6.65	0.15	0.94
	Chang Jiang	river	2630	920630	1940000	1.60	0.62	16.71	0.06	0.7
	Chang Jiang	river	2630	1501208	1940000	1.61	0.62	16.81	0.06	0.4
	Chang Jiang	river	2630	1103098	1940000	1.70	0.59	17.71	0.06	0.64
	Chang Jiang	river	2630	411381	1940000	1.64	0.61	17.11	0.06	0.58
	Chang Jiang	river	2630	297753	1940000	1.53	0.66	15.91	0.06	0.65
	Ottawa	river	2630	662688	146301	0.21	4.80	2.17	0.46	2
	Ottawa	river	2630	586384	146301	0.19	5.21	2.00	0.50	2.15
	Clear Creek	river	289	70542	1489	48.67	0.02	#####	0.00	-0.01
	Clear Creek	river	289	50582	1489	48.77	0.02	#####	0.00	-0.02
	Clear Creek	river	289	45843	1489	49.06	0.02	#####	0.00	-0.01
	Clear Creek	river	289	45023	1489	48.67	0.02	#####	0.00	-0.02
	Brahmaputra	river	289	44749	1621000	0.86	1.16	8.98	0.11	0.49
	Amazon	river	289	44476	6144727	0.42	2.40	4.34	0.23	0.32
	Amazon	river	5.3	809	6144727	0.41	2.42	4.30	0.23	0.38
Pearce et al., 2010					103000					
	SE Iceland	river	175	14294	--	0.25	4.02	2.59	0.39	-0.38
	SE Iceland	river	175	42274	--	0.74	1.36	7.66	0.13	1.26
	SE Iceland	river	175	16225	--	0.28	3.54	2.94	0.34	-0.18
	SE Iceland	river	175	7174	--	0.12	8.01	1.30	0.77	-0.26
	SE Iceland	river	175	8609	--	0.15	6.68	1.56	0.64	0.24
	W Iceland	river	79.91	7107	--	0.27	3.69	2.82	0.35	0.7
	W Iceland	river	79.91	7107	--	0.27	3.69	2.82	0.35	0.7
	W Iceland	river	79.91	7938	--	0.30	3.31	3.15	0.32	0.65
	W Iceland	river	79.91	9954	--	0.38	2.64	3.95	0.25	0.71
	W Iceland	river	79.91	7989	--	0.30	3.29	3.17	0.32	0.75
	W Iceland	river	79.91	6678	--	0.25	3.93	2.65	0.38	0.35
	W Iceland	river	79.91	22428	--	0.85	1.17	8.91	0.11	0.19
	W Iceland	river	79.91	9324	--	0.36	2.82	3.70	0.27	0.46
	W Iceland	river	79.91	4687	--	0.18	5.60	1.86	0.54	0.14
	W Iceland	river	79.91	7686	--	0.29	3.42	3.05	0.33	0.38
	W Iceland	river	79.91	2016	--	0.08	13.02	0.80	1.25	1.52
	W Iceland	river	79.91	4385	--	0.17	5.99	1.74	0.57	0.85

Table D.3. (continued)

Citation	Sample	Sample Type	Discharge m ³ s ⁻¹	Mo Discharge mol Mo yr ⁻¹	Catchment Area km ²	Mo ppb	1/[Mo] ppb	Mo nM	1/[Mo] nM	$\delta^{18}\text{O}$ ‰
<i>Scheiderich et al., 2010</i>	Susquehanna	river	1100	97565	71225	0.27	3.70	2.81	0.36	0.90
<i>Neubert et al., 2011</i>	Entleuch	river	29400	8344426	500	0.17	5.82	1.79	0.56	0.21
	Entleuch	river	29400	12053059	500	0.11	9.38	1.11	0.90	0.11
	Entleuch	river	500	28225	500	0.16	6.31	1.65	0.61	0.1
	Entleuch	river	500	17502	500	0.09	11.57	0.90	1.11	-0.09
	Entleuch	river	500	26017	500	0.07	14.67	0.71	1.41	-0.11
	Entleuch	river	500	14191	500	0.05	19.65	0.53	1.89	0.049
	Entleuch	river	500	11195	500	0.28	3.53	2.95	0.34	1
	Entleuch	river	500	8357	500	0.24	4.25	2.45	0.41	1.25
	Entleuch	river	500	46516	500	0.26	3.84	2.71	0.37	1.04
	Entleuch	river	500	38632	500	0.26	3.87	2.69	0.37	1.35
	Entleuch	river	500	42731	500	0.19	5.29	1.97	0.51	0.84
	Entleuch	river	500	42416	500	0.22	4.45	2.34	0.43	0.76
	Entleuch	river	500	31063	500	0.24	4.18	2.49	0.40	0.96
	Aare	river	500	36897	500	0.49	2.05	5.09	0.20	0.97
	Aare	river	500	39262	500	0.55	1.83	5.69	0.18	0.88
	Aare	river	560	89890	500	0.56	1.79	5.82	0.17	1.09
	Aare	river	560	100486	500	0.67	1.50	6.94	0.14	0.79
	Aare	river	560	102782	500	0.69	1.45	7.18	0.14	0.8
	Aare	river	560	122562	500	0.88	1.14	9.13	0.11	0.65
	Aare	river	560	126800	500	0.20	5.01	2.08	0.48	1.65
	Sikkim	river	560	161061	12540	13.34	0.07	139.09	0.01	0.34
	Sikkim	river	560	36733	12540	4.13	0.24	43.03	0.02	0.31
	Sikkim	river	2510	11002595	12540	8.64	0.12	90.06	0.01	0.32
	Sikkim	river	2510	3403680	12540	4.22	0.24	44.03	0.02	0.41
	Chang Jiang	river	2510	7123982	1940000	0.86	1.16	9.01	0.11	0.97
	Chang Jiang	river	2510	3482836	1940000	1.25	0.80	13.01	0.08	0.86
<i>Voegelin et al., 2012</i>	Malaval	river	--	--	68	0.81	1.23	8.44	0.12	0.88
	Malaval	river	--	--	68	0.30	3.33	3.13	0.32	0.47
	Sejallieres	river	--	--	68	0.20	5.00	2.08	0.48	0.82
	Sejallieres	river	--	--	68	0.17	5.88	1.77	0.56	0.77
	Malaval	river	--	--	68	0.02	50.00	0.21	4.80	0.58
	Malaval	river	--	--	68	0.04	25.00	0.42	2.40	0.42
	Malaval	river	--	--	68	0.15	6.67	1.56	0.64	0.48
	Malaval	river	--	--	68	0.12	8.33	1.25	0.80	0.4
	Malaval	river	--	--	68	0.12	8.33	1.25	0.80	0.3
	Malaval	river	--	--	68	0.15	6.67	1.56	0.64	0.33
	Malaval	river	--	--	68	0.07	14.29	0.73	1.37	0.66
	Malaval	river	--	--	68	0.14	7.14	1.46	0.69	0.42
<i>Rahaman et al., 2014</i>	Narmada	river	1447	196220.1456	98796	0.41	2.42	4.30	0.23	0.19
	Tapi	river	489	94068.7344	65145	0.59	1.71	6.10	0.16	0.90
<i>Wang et al., 2015</i>	Xijang	river	168	49325	350000	0.89	1.12	9.32	0.11	1.09
	Xijang	river	226	74479	350000	1.00	1.00	10.46	0.10	1.04
	Xijang	river	860	215612	350000	0.76	1.31	7.95	0.13	1.18
	Xijang	river	14700	2002662	350000	0.41	2.41	4.32	0.23	1.3
	Xijang	river	960	169235	350000	0.54	1.86	5.59	0.18	1.31
	Xijang	river	1450	252871	350000	0.53	1.88	5.53	0.18	1.25
	Xijang	river	820	136538	350000	0.51	1.97	5.28	0.19	1.24
	Xijang	river	380	93353	350000	0.75	1.34	7.79	0.13	1.18
	Xijang	river	1450	345240	350000	0.72	1.38	7.55	0.13	1.17
	Xijang	river	390	83633	350000	0.65	1.53	6.80	0.15	1.24
	Xijang	river	210	48808	350000	0.71	1.41	7.37	0.14	1.27
	Xijang	river	860	203136	350000	0.72	1.39	7.49	0.13	1.14
	Xijang	river	270	62413	350000	0.70	1.42	7.33	0.14	1.14
	Xijang	river	236	54777	350000	0.71	1.42	7.36	0.14	1.16
	Xijang	river	265	62678	350000	0.72	1.39	7.50	0.13	1.24
	Xijang	river	265	61006	350000	0.70	1.43	7.30	0.14	1.17
	Xijang	river	560	123268	350000	0.67	1.49	6.98	0.14	1.22
	Huanghe	river	1586	4896576	752547	9.40	0.11	97.96	0.01	0.17
	Huanghe	river	381	1058541	752547	8.46	0.12	88.16	0.01	0.25
	Huanghe	river	799	2151846	752547	8.20	0.12	85.45	0.01	0.28
	Huanghe	river	413	1164378	752547	8.58	0.12	89.46	0.01	0.3
	Huanghe	river	477	1194388	752547	7.62	0.13	79.45	0.01	0.38
	Huanghe	river	716	2528935	752547	10.75	0.09	112.07	0.01	0.24
	Huanghe	river	244	84643	752547	1.06	0.95	11.01	0.09	0.37
	Huanghe	river	204	615028	752547	9.18	0.11	95.66	0.01	0.36
	Huanghe	river	278	781140	752547	8.55	0.12	89.16	0.01	0.35
	Huanghe	river	1130	3285610	752547	8.85	0.11	92.26	0.01	0.22
	Huanghe	river	840	3099358	752547	11.23	0.09	117.07	0.01	0.28
	Huanghe	river	1580	6128706	752547	11.81	0.08	123.08	0.01	0.09
	Huanghe	river	313	1085784	752547	10.56	0.09	110.07	0.01	0.12
	Huanghe	river	218	694360	752547	9.70	0.10	101.06	0.01	0.15
	Huanghe	river	--	--	752547	7.96	0.13	82.95	0.01	0.29

^aNIST normalized

Appendix E. Methodology details

E.1. Reducible pool (SRO Fe- and Mn-) (oxyhydr)oxides associated) extraction for soil Mo isotopes

Based on Wiederhold et al., 2007 (and Filguerias et al., 2002) targeting the reducible pool for Fe isotopes

Equipment

- 50 mL centrifuge tubes (acid washed)
- 10 g soil (moist)
- 40 mL 0.5 M HCl
- Shaking table
- 10 mL pipette and pipette tips
- Centrifuge
- 0.45 μm filter

Procedure

1. Weigh 10 g soil into 50 mL centrifuge tubes
2. Add 40 mL of ultrapure 0.5 M HCl (to prevent trace metal contamination)
3. Shake tubes at room temperature for 24 hours
4. Centrifuge (3400 rpm for 15 min)
5. Filter supernatant with 0.45 μm filter
6. Evaporate in Teflon
7. Oxidize with HNO_3 and H_2O_2 to destroy OM

E.2. Oxidizable pool (organic matter associated) extraction for soil Mo isotopes

Equipment

- 10 g soil
- Milli-Q water
- Shaking table
- 20% Ammonium Hydroxide (NH_4OH)*
- 30% Hydrogen Peroxide (H_2O_2) *
- 99% (Glacial) Acetic Acid (CH_3COOH aka HOAc) *
- Centrifuge

Procedure

1. Using 10g of field-moist sample, mix soil and 20 - 80mL MQ water in an Erlenmeyer flask – you will be adding water to the centrifuge tubes from the reducible extraction until all soil is transferred to flask
2. Add 15mL 0.02 M HNO_3 and 25mL 30% H_2O_2 (adjusted to pH 2)
3. Suspend sample in solution by manual shaking
4. Let set over-night
5. Place flask in a heated water bath at 85°C for ~3 hours with intermittent agitation.
6. Add 10mL of 30% H_2O_2 (adjusted to pH 2) every ~45 minutes until effervescence ceases and soils become visibly lighter
7. Remove flasks from heat and add an additional 25mL of 30% H_2O_2
8. Total volume of H_2O_2 (adjusted to pH 2) added should be about 80mL
9. Allow solution to cool
10. Add 25mL of 3.2 M NH_4OAc in 20% HNO_3
11. Set overnight
12. Transfer soil and extractant into a 250mL bottle
13. Use MQ water to rinse Inside of E-flask into bottle until tube is full (50mL)
14. Vortex soil/extractant/MQ slurry
15. Centrifuge at 3000 rpm for 20 minutes
 - a. Remove supernatant
16. Decanting supernatant into pre-acid washed 250mL bottle.
17. Rinse each sample with an additional 20mL of Milli-Q water
18. Vortex soil/extractant/MQ slurry
19. Centrifuge at 3000 rpm for 20 minutes
20. Decant rinse water to store with supernatant
21. Filtration – 0.45 μm filter

E.3. Molybdenum column chemistry

Table E.1: Column chemistry

AG1 - X8 anion exchange resin 200 - 400 mesh in 1M HCl	
Vegetation / soil / bedrock digests (100 ng Mo) in 1M HF - 0.5M HCl	
Load resin in 1M HCl	2 mL
1M HCl	150 mL
7M HNO ₃	10 mL
6M HCl	10 mL
1M HCl	30 mL
1M HF - 0.5M HCl	4 mL
SAMPLE w/ 200 µL H ₂ O ₂	6-10 mL
1M HF - 0.5M HCl	6 x 2 mL
4M HCl	8 mL
1M HCl (ELUTE)	30 mL

E.4. Column wash justification

A total of 950 ng Mo was rinsed off the AG1 X-8 resin in 200 mL of 1 M HCl prior to conditioning and loading of sample.

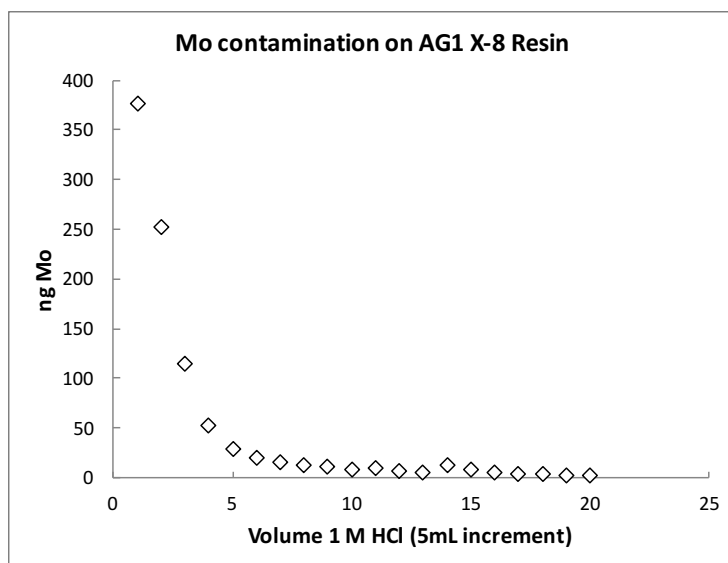


Figure E.1: Mo contamination on AG1 X-8 resin

Table E.2: Mo column efficiency

Sample	Initial (ng Mo)	Final (ng Mo)	Yield (%)
BHVO-a	354.7	326.2	92
BHVO-b	274.3	247.1	90
BHVO-c	100	94.8	94.8

E.5. Nu parameters

Table E.3: Nu instrument settings

Nu Instrument Settings	
RF Power	1300 W
Argon gas flow rate	
Coolant	13 L min ⁻¹
Auxillary	0.8 L min ⁻¹
Nebulizer Pressure	0 psi
Sensitivity	250 V ppm ⁻¹

Table E.4: Nu Faraday Cup configuration

Faraday Cup											
H6	H5	H4	H3	H2	H1	Ax	L1	L2	L3	L4	L5
¹⁰⁰ Mo		⁹⁸ Mo		⁹⁷ Mo		⁹⁶ Mo		⁹⁵ Mo	⁹⁴ Mo		⁹² Mo

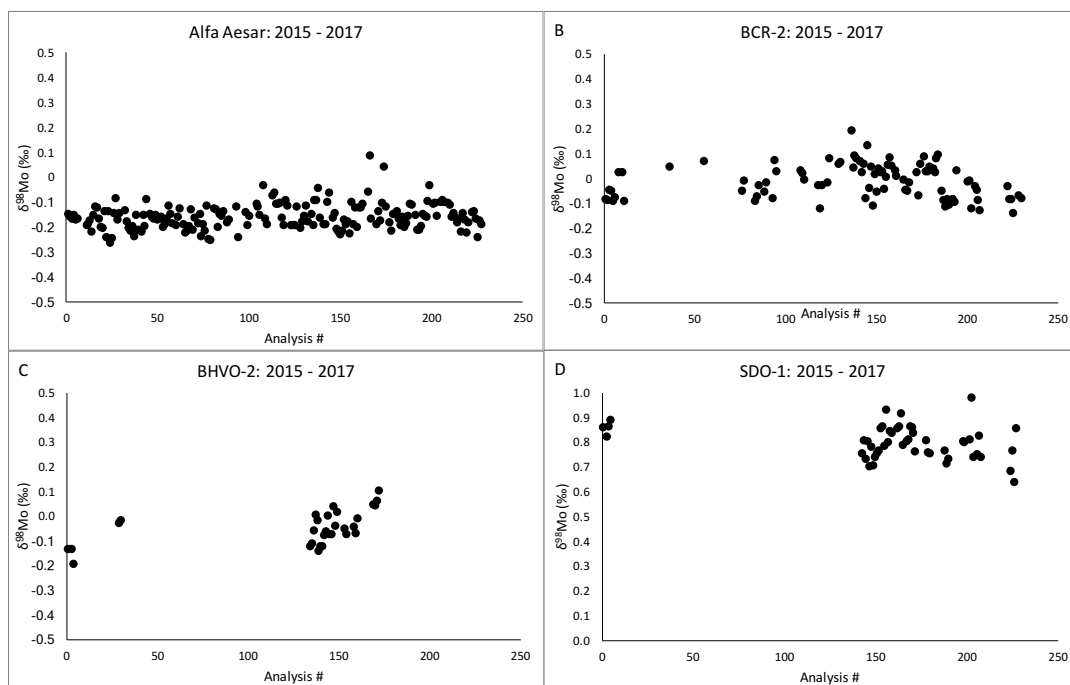


Figure E.2: Nu standard reproducibility for A) Alfa Aesar, B) BCR-2, C) BHVO-2, and D) SDO-1 standards.

Alfa Aesar in-house standard is used to monitor external reproducibility. Analyses measured over 33 separate sessions from 2015 – 2017.

E.5.1. Mo double spike NICE code

' Iterative routine for reduction of molybdenum isotopes using a 100/97 Mo double spike

' Written by Liz King: November 2014 (eking@coas.oregonstate.edu)

'Declare Variables:

' standards

Dim Rsta9598, Rsta9798, Rsta10098, Rsta9698, Rsta9498, Rsta9298

' spike

Dim Rspike9598, Rspike9798, Rspike10098, Rspike9698, Rspike9498, Rspike9298

' Intensities

Dim Mo92, Mo94, Mo95, Mo96, Mo97, Mo98, Mo100

' Masses

Dim amu92, amu94, amu95, amu96, amu97, amu98, amu100

' Fractionation factors

Dim FRAC, NFRAC, FRAC1, FRAC2, FRAC3, FRAC4, FRAC5, FRAC6, NFRAC1, NFRAC2, NFRAC3, NFRAC4, NFRAC5, NFRAC6

' Raw ratios

Dim ratio9298, ratio9498, ratio9598, ratio9698, ratio9798, ratio10098

' Defining planes and lines

Dim RX1, RY1, RZ1, RX2, RY2, RZ2, RX3, RY3, RZ3, MX1, MY1, MZ1, MX2, MY2, MZ2, MX3, MY3, MZ3, PA, PB, PC, PD, PE, PF, PG, ND, NE, NF, NG, NA, NB, NC, PBUP, PBDN, PAUP, PADN, NBUP, NBDN, NAUP, NADN, INX1, INY1, INZ1, INX2, INY2, INZ2

'ICP fractionation correction

Dim corr9798, corr9698, corr9598, corr9498, corr9298

'Delta

Dim delta9895, delta9896, delta9894, delta9892, Q98, SAM9698, SAM9498,
SAM9298

,

' Define masses:

amu92 = 91.905985
amu94 = 93.905085
amu95 = 94.905840
amu96 = 95.904678
amu97 = 96.906020
amu98 = 97.905406
amu100 = 99.907477

' Standard (04/22/15)

Rsta9598 = 0.6614302141427
Rsta9798 = 0.396051406063
Rsta10098 = 0.397905494973
'Rsta9698 = 0.69169
'Rsta9498 = 0.38432
'Rsta9298 = 0.61892

' Spike (8/17/2016 --> Solver fine-tuned because new spike and higher sensitivity)

Rspike9598 = 0.07555624833372
Rspike9798 = 15.25190203847
Rspike10098 = 15.07626504089
'Rspike9698 = 0.17145
'Rspike9498 = 0.03578
'Rspike9298 = 0.04049

' First subtract zero from all beams to get intensities

Mo100 = Mass(1, 0) - Zero(1, 0)
Mo98 = Mass(1, 2) - Zero(1, 2)
Mo97 = Mass(1, 4) - Zero(1, 4)
Mo96 = Mass(1, 6) - Zero(1, 6)
Mo95 = Mass(1, 8) - Zero(1, 8)

Mo94 = Mass(1, 10) - Zero(1, 10)
 Mo92 = Mass(1, 14) - Zero(1, 14)

' Define raw ratios:

ratio9298 = Mo92 / Mo98
 ratio9498 = Mo94 / Mo98
 ratio9598 = Mo95 / Mo98
 ratio9698 = Mo96 / Mo98
 ratio9798 = Mo97 / Mo98
 ratio10098 = Mo100 / Mo98

' Initial fractionation assumptions:

FRAC = 2
 NFRAC = 0.1

' Three-dimensional fractionation correction:

' Natural fractionation (line 1 , plane 1):

' Standard (ST):

RX1 = Rsta9598
 RY1 = Rsta9798
 RZ1 = Rsta10098

' Corrected for NFRAC (SA):

RX2 = Rsta9598 * (amu95 / amu98) ^ NFRAC
 RY2 = Rsta9798 * (amu97 / amu98) ^ NFRAC
 RZ2 = Rsta10098 * (amu100 / amu98) ^ NFRAC

' Spike (SP):

RX3 = Rspike9598
 RY3 = Rspike9798
 RZ3 = Rspike10098

' Instrumental fractionation (line 2, plane 2):

' SA-SP mixture (MS):

MX1 = ratio9598

MY1 = ratio9798
MZ1 = ratio10098

' Corrected for FRAC (MT):

MX2 = ratio9598 * (amu98 / amu95) ^ FRAC
MY2 = ratio9798 * (amu98 / amu97) ^ FRAC
MZ2 = ratio10098 * (amu98 / amu100) ^ FRAC

' Spike (SP):

MX3 = Rspike9598
MY3 = Rspike9798
MZ3 = Rspike10098

' Subroutines:

' NOTE: M and N prefix refers to line 2 and plane 2 (defined by fractionation)
and P and R prefix refers to plane 1 and line 1 (defined by natural fractionation)

' Make lines and planes:

' Z = DX + E (LINE)

' Z = FY + G (LINE)

' Z = AX + BY + C (PLANE)

' Line 1:

PD = (RZ1 - RZ2) / (RX1 - RX2)

PE = RZ1 - RX1 * PD

PF = (RZ1 - RZ2) / (RY1 - RY2)

PG = RZ1 - RY1 * PF

' Plane 1:

PBUP = (RX1 * (RZ2 - RZ3)) + (RX2 * (RZ3 - RZ1)) + (RX3 * (RZ1 - RZ2))

PBDN = (RX1 * (RY2 - RY3)) + (RX2 * (RY3 - RY1)) + (RX3 * (RY1 - RY2))

PB = PBUP / PBDN

PAUP = (RY1 * (RZ2 - RZ3)) + (RY2 * (RZ3 - RZ1)) + (RY3 * (RZ1 - RZ2))

$$PADN = (RY1 * (RX2 - RX3)) + (RY2 * (RX3 - RX1)) + (RY3 * (RX1 - RX2))$$

$$PA = PAUP / PADN$$

$$PC = RZ1 - (PA * RX1) - (PB * RY1)$$

' Line 2:

$$ND = (MZ1 - MZ2) / (MX1 - MX2)$$

$$NE = MZ1 - MX1 * ND$$

$$NF = (MZ1 - MZ2) / (MY1 - MY2)$$

$$NG = MZ1 - MY1 * NF$$

' Plane 2:

$$NBUP = (MX1 * (MZ2 - MZ3)) + (MX2 * (MZ3 - MZ1)) + (MX3 * (MZ1 - MZ2))$$

$$NBDN = (MX1 * (MY2 - MY3)) + (MX2 * (MY3 - MY1)) + (MX3 * (MY1 - MY2))$$

$$NB = NBUP / NBDN$$

$$NAUP = (MY1 * (MZ2 - MZ3)) + (MY2 * (MZ3 - MZ1)) + (MY3 * (MZ1 - MZ2))$$

$$NADN = (MY1 * (MX2 - MX3)) + (MY2 * (MX3 - MX1)) + (MY3 * (MX1 - MX2))$$

$$NA = NAUP / NADN$$

$$NC = MZ1 - (NA * MX1) - (NB * MY1)$$

' Make intercept between a line and a plane:

' line 2 (ND, NE, NF, NG) , plane 1 (PA, PB, PC) = INX1, INY1, INY1:

$$INX1 = ((PB * NG) - (PB * NE) + (NE * NF) - (PC * NF)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$\text{INY1} = ((\text{PA} * \text{NE}) - (\text{PA} * \text{NG}) + (\text{ND} * \text{NG}) - (\text{PC} * \text{ND})) / ((\text{PA} * \text{NF}) + (\text{PB} * \text{ND}) - (\text{ND} * \text{NF}))$$

$$\text{INZ1} = (\text{PA} * \text{INX1}) + (\text{PB} * \text{INY1}) + \text{PC}$$

' line 1 (PD, PE, PF, PG) , plane 2 (NA, NB, NC) = INX2, INY2, INZ2:

$$\text{INX2} = ((\text{NB} * \text{PG}) - (\text{NB} * \text{PE}) + (\text{PE} * \text{PF}) - (\text{NC} * \text{PF})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INY2} = ((\text{NA} * \text{PE}) - (\text{NA} * \text{PG}) + (\text{PD} * \text{PG}) - (\text{NC} * \text{PD})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INZ2} = (\text{NA} * \text{INX2}) + (\text{NB} * \text{INY2}) + \text{NC}$$

' Fractionation:

$$\text{FRAC1} = (\text{Log}(\text{ratio9598} / \text{INX1})) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 2$$

$$\text{NFRAC1} = (\text{Log}(\text{INX2} / \text{Rsta9598})) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 0.1$$

'

'LOOPING#1

' Three-dimensional fractionation correction:

' Natural fractionation (line 1 , plane 1):

' Standard (ST):

$$\text{RX1} = \text{Rsta9598}$$

$$\text{RY1} = \text{Rsta9798}$$

$$\text{RZ1} = \text{Rsta10098}$$

' Corrected for NFRAC (SA):

$$\text{RX2} = \text{Rsta9598} * (\text{amu95} / \text{amu98}) ^ \text{NFRAC1}$$

$$\text{RY2} = \text{Rsta9798} * (\text{amu97} / \text{amu98}) ^ \text{NFRAC1}$$

$$\text{RZ2} = \text{Rsta10098} * (\text{amu100} / \text{amu98}) ^ \text{NFRAC1}$$

' Spike (SP):

RX3 = Rspike9598
 RY3 = Rspike9798
 RZ3 = Rspike10098

' Instrumental fractionation (line 2, plane 2):

' SA-SP mixture (MS):

MX1 = ratio9598
 MY1 = ratio9798
 MZ1 = ratio10098

' Corrected for FRAC (MT):

MX2 = ratio9598 * (amu98 / amu95) ^ FRAC1
 MY2 = ratio9798 * (amu98 / amu97) ^ FRAC1
 MZ2 = ratio10098 * (amu98 / amu100) ^ FRAC1

' Spike (SP):

MX3 = Rspike9598
 MY3 = Rspike9798
 MZ3 = Rspike10098

' Subroutines:

' NOTE: M and N prefix refers to line 2 and plane 2 (defined by fractionation)
 and P and R prefix refers to plane 1 and line 1 (defined by natural fractionation)

' Make lines and planes:

' Z = DX + E (LINE)

' Z = FY + G (LINE)

' Z = AX + BY + C (PLANE)

' Line 1:

PD = (RZ1 - RZ2) / (RX1 - RX2)

PE = RZ1 - RX1 * PD

PF = (RZ1 - RZ2) / (RY1 - RY2)

$$PG = RZ1 - RY1 * PF$$

' Plane 1:

$$PBUP = (RX1 * (RZ2 - RZ3)) + (RX2 * (RZ3 - RZ1)) + (RX3 * (RZ1 - RZ2))$$

$$PBDN = (RX1 * (RY2 - RY3)) + (RX2 * (RY3 - RY1)) + (RX3 * (RY1 - RY2))$$

$$PB = PBUP / PBDN$$

$$PAUP = (RY1 * (RZ2 - RZ3)) + (RY2 * (RZ3 - RZ1)) + (RY3 * (RZ1 - RZ2))$$

$$PADN = (RY1 * (RX2 - RX3)) + (RY2 * (RX3 - RX1)) + (RY3 * (RX1 - RX2))$$

$$PA = PAUP / PADN$$

$$PC = RZ1 - (PA * RX1) - (PB * RY1)$$

' Line 2:

$$ND = (MZ1 - MZ2) / (MX1 - MX2)$$

$$NE = MZ1 - MX1 * ND$$

$$NF = (MZ1 - MZ2) / (MY1 - MY2)$$

$$NG = MZ1 - MY1 * NF$$

' Plane 2:

$$NBUP = (MX1 * (MZ2 - MZ3)) + (MX2 * (MZ3 - MZ1)) + (MX3 * (MZ1 - MZ2))$$

$$NBDN = (MX1 * (MY2 - MY3)) + (MX2 * (MY3 - MY1)) + (MX3 * (MY1 - MY2))$$

$$NB = NBUP / NBDN$$

$$NAUP = (MY1 * (MZ2 - MZ3)) + (MY2 * (MZ3 - MZ1)) + (MY3 * (MZ1 - MZ2))$$

$$NADN = (MY1 * (MX2 - MX3)) + (MY2 * (MX3 - MX1)) + (MY3 * (MX1 - MX2))$$

$$NA = NAUP / NADN$$

$$NC = MZ1 - (NA * MX1) - (NB * MY1)$$

' Make intercept between a line and a plane:

' line 2 (ND, NE, NF, NG) , plane 1 (PA, PB, PC) = INX1, INY1, INY1:

$$INX1 = ((PB * NG) - (PB * NE) + (NE * NF) - (PC * NF)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$INY1 = ((PA * NE) - (PA * NG) + (ND * NG) - (PC * ND)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$INZ1 = (PA * INX1) + (PB * INY1) + PC$$

' line 1 (PD, PE, PF, PG) , plane 2 (NA, NB, NC) = INX2, INY2, INY2:

$$INX2 = ((NB * PG) - (NB * PE) + (PE * PF) - (NC * PF)) / ((NA * PF) + (NB * PD) - (PD * PF))$$

$$INY2 = ((NA * PE) - (NA * PG) + (PD * PG) - (NC * PD)) / ((NA * PF) + (NB * PD) - (PD * PF))$$

$$INZ2 = (NA * INX2) + (NB * INY2) + NC$$

' Fractionation:

$$FRAC2 = (\text{Log}(\text{ratio9598} / INX1)) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 2$$

$$NFRAC2 = (\text{Log}(INX2 / Rsta9598)) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 0.1$$

,

'LOOPING#2

' Three-dimensional fractionation correction:

' Natural fractionation (line 1 , plane 1):

' Standard (ST):

RX1 = Rsta9598
 RY1 = Rsta9798
 RZ1 = Rsta10098

' Corrected for NFRAC (SA):

$RX2 = Rsta9598 * (amu95 / amu98) ^ NFRAC2$
 $RY2 = Rsta9798 * (amu97 / amu98) ^ NFRAC2$
 $RZ2 = Rsta10098 * (amu100 / amu98) ^ NFRAC2$

' Spike (SP):

RX3 = Rspike9598
 RY3 = Rspike9798
 RZ3 = Rspike10098

' Instrumental fractionation (line 2, plane 2):

' SA-SP mixture (MS):

MX1 = ratio9598
 MY1 = ratio9798
 MZ1 = ratio10098

' Corrected for FRAC (MT):

$MX2 = ratio9598 * (amu98 / amu95) ^ FRAC2$
 $MY2 = ratio9798 * (amu98 / amu97) ^ FRAC2$
 $MZ2 = ratio10098 * (amu98 / amu100) ^ FRAC2$

' Spike (SP):

MX3 = Rspike9598
 MY3 = Rspike9798
 MZ3 = Rspike10098

' Subroutines:

' NOTE: M and N prefix refers to line 2 and plane 2 (defined by fractionation)
 and P and R prefix refers to plane 1 and line 1 (defined by natural fractionation)

' Make lines and planes:

' $Z = DX + E$ (LINE)

' $Z = FY + G$ (LINE)

' $Z = AX + BY + C$ (PLANE)

' Line 1:

$$PD = (RZ1 - RZ2) / (RX1 - RX2)$$

$$PE = RZ1 - RX1 * PD$$

$$PF = (RZ1 - RZ2) / (RY1 - RY2)$$

$$PG = RZ1 - RY1 * PF$$

' Plane 1:

$$PBUP = (RX1 * (RZ2 - RZ3)) + (RX2 * (RZ3 - RZ1)) + (RX3 * (RZ1 - RZ2))$$

$$PBDN = (RX1 * (RY2 - RY3)) + (RX2 * (RY3 - RY1)) + (RX3 * (RY1 - RY2))$$

$$PB = PBUP / PBDN$$

$$PAUP = (RY1 * (RZ2 - RZ3)) + (RY2 * (RZ3 - RZ1)) + (RY3 * (RZ1 - RZ2))$$

$$PADN = (RY1 * (RX2 - RX3)) + (RY2 * (RX3 - RX1)) + (RY3 * (RX1 - RX2))$$

$$PA = PAUP / PADN$$

$$PC = RZ1 - (PA * RX1) - (PB * RY1)$$

' Line 2:

$$ND = (MZ1 - MZ2) / (MX1 - MX2)$$

$$NE = MZ1 - MX1 * ND$$

$$NF = (MZ1 - MZ2) / (MY1 - MY2)$$

$$NG = MZ1 - MY1 * NF$$

' Plane 2:

$$\text{NBUP} = (\text{MX1} * (\text{MZ2} - \text{MZ3})) + (\text{MX2} * (\text{MZ3} - \text{MZ1})) + (\text{MX3} * (\text{MZ1} - \text{MZ2}))$$

$$\text{NBDN} = (\text{MX1} * (\text{MY2} - \text{MY3})) + (\text{MX2} * (\text{MY3} - \text{MY1})) + (\text{MX3} * (\text{MY1} - \text{MY2}))$$

$$\text{NB} = \text{NBUP} / \text{NBDN}$$

$$\text{NAUP} = (\text{MY1} * (\text{MZ2} - \text{MZ3})) + (\text{MY2} * (\text{MZ3} - \text{MZ1})) + (\text{MY3} * (\text{MZ1} - \text{MZ2}))$$

$$\text{NADN} = (\text{MY1} * (\text{MX2} - \text{MX3})) + (\text{MY2} * (\text{MX3} - \text{MX1})) + (\text{MY3} * (\text{MX1} - \text{MX2}))$$

$$\text{NA} = \text{NAUP} / \text{NADN}$$

$$\text{NC} = \text{MZ1} - (\text{NA} * \text{MX1}) - (\text{NB} * \text{MY1})$$

' Make intercept between a line and a plane:

' line 2 (ND, NE, NF, NG) , plane 1 (PA, PB, PC) = INX1, INY1, INY1:

$$\text{INX1} = ((\text{PB} * \text{NG}) - (\text{PB} * \text{NE}) + (\text{NE} * \text{NF}) - (\text{PC} * \text{NF})) / ((\text{PA} * \text{NF}) + (\text{PB} * \text{ND}) - (\text{ND} * \text{NF}))$$

$$\text{INY1} = ((\text{PA} * \text{NE}) - (\text{PA} * \text{NG}) + (\text{ND} * \text{NG}) - (\text{PC} * \text{ND})) / ((\text{PA} * \text{NF}) + (\text{PB} * \text{ND}) - (\text{ND} * \text{NF}))$$

$$\text{INZ1} = (\text{PA} * \text{INX1}) + (\text{PB} * \text{INY1}) + \text{PC}$$

' line 1 (PD, PE, PF, PG) , plane 2 (NA, NB, NC) = INX2, INY2, INY2:

$$\text{INX2} = ((\text{NB} * \text{PG}) - (\text{NB} * \text{PE}) + (\text{PE} * \text{PF}) - (\text{NC} * \text{PF})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INY2} = ((\text{NA} * \text{PE}) - (\text{NA} * \text{PG}) + (\text{PD} * \text{PG}) - (\text{NC} * \text{PD})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INZ2} = (\text{NA} * \text{INX2}) + (\text{NB} * \text{INY2}) + \text{NC}$$

' Fractionation:

$$\text{FRAC3} = (\text{Log}(\text{ratio9598} / \text{INX1})) / (\text{Log}(\text{amu95} / \text{amu98}))$$

2

NFRAC3 = (Log(INX2 / Rsta9598)) / (Log(amu95 / amu98)) ' should be close to
0.1

```
'
*****
*****
```

'LOOPING#3

' Three-dimensional fractionation correction:

' Natural fractionation (line 1 , plane 1):

' Standard (ST):

```
RX1 = Rsta9598
RY1 = Rsta9798
RZ1 = Rsta10098
```

' Corrected for NFRAC (SA):

```
RX2 = Rsta9598 * (amu95 / amu98) ^ NFRAC3
RY2 = Rsta9798 * (amu97 / amu98) ^ NFRAC3
RZ2 = Rsta10098 * (amu100 / amu98) ^ NFRAC3
```

' Spike (SP):

```
RX3 = Rspike9598
RY3 = Rspike9798
RZ3 = Rspike10098
```

' Instrumental fractionation (line 2, plane 2):

' SA-SP mixture (MS):

```
MX1 = ratio9598
MY1 = ratio9798
MZ1 = ratio10098
```

' Corrected for FRAC (MT):

```
MX2 = ratio9598 * (amu98 / amu95) ^ FRAC3
MY2 = ratio9798 * (amu98 / amu97) ^ FRAC3
```

$$MZ2 = \text{ratio10098} * (\text{amu98} / \text{amu100}) ^ \text{FRAC3}$$

' Spike (SP):

$$MX3 = \text{Rspike9598}$$

$$MY3 = \text{Rspike9798}$$

$$MZ3 = \text{Rspike10098}$$

' Subroutines:

' NOTE: M and N prefix refers to line 2 and plane 2 (defined by fractionation)
and P and R prefix refers to plane 1 and line 1 (defined by natural fractionation)

' Make lines and planes:

$$' Z = DX + E \text{ (LINE)}$$

$$' Z = FY + G \text{ (LINE)}$$

$$' Z = AX + BY + C \text{ (PLANE)}$$

' Line 1:

$$PD = (RZ1 - RZ2) / (RX1 - RX2)$$

$$PE = RZ1 - RX1 * PD$$

$$PF = (RZ1 - RZ2) / (RY1 - RY2)$$

$$PG = RZ1 - RY1 * PF$$

' Plane 1:

$$PBUP = (RX1 * (RZ2 - RZ3)) + (RX2 * (RZ3 - RZ1)) + (RX3 * (RZ1 - RZ2))$$

$$PBDN = (RX1 * (RY2 - RY3)) + (RX2 * (RY3 - RY1)) + (RX3 * (RY1 - RY2))$$

$$PB = PBUP / PBDN$$

$$PAUP = (RY1 * (RZ2 - RZ3)) + (RY2 * (RZ3 - RZ1)) + (RY3 * (RZ1 - RZ2))$$

$$PADN = (RY1 * (RX2 - RX3)) + (RY2 * (RX3 - RX1)) + (RY3 * (RX1 - RX2))$$

$$PA = PAUP / PADN$$

$$PC = RZ1 - (PA * RX1) - (PB * RY1)$$

' Line 2:

$$ND = (MZ1 - MZ2) / (MX1 - MX2)$$

$$NE = MZ1 - MX1 * ND$$

$$NF = (MZ1 - MZ2) / (MY1 - MY2)$$

$$NG = MZ1 - MY1 * NF$$

' Plane 2:

$$NBUP = (MX1 * (MZ2 - MZ3)) + (MX2 * (MZ3 - MZ1)) + (MX3 * (MZ1 - MZ2))$$

$$NBDN = (MX1 * (MY2 - MY3)) + (MX2 * (MY3 - MY1)) + (MX3 * (MY1 - MY2))$$

$$NB = NBUP / NBDN$$

$$NAUP = (MY1 * (MZ2 - MZ3)) + (MY2 * (MZ3 - MZ1)) + (MY3 * (MZ1 - MZ2))$$

$$NADN = (MY1 * (MX2 - MX3)) + (MY2 * (MX3 - MX1)) + (MY3 * (MX1 - MX2))$$

$$NA = NAUP / NADN$$

$$NC = MZ1 - (NA * MX1) - (NB * MY1)$$

' Make intercept between a line and a plane:

' line 2 (ND, NE, NF, NG) , plane 1 (PA, PB, PC) = INX1, INY1, INY1:

$$INX1 = ((PB * NG) - (PB * NE) + (NE * NF) - (PC * NF)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$INY1 = ((PA * NE) - (PA * NG) + (ND * NG) - (PC * ND)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$INZ1 = (PA * INX1) + (PB * INY1) + PC$$

' line 1 (PD, PE, PF, PG) , plane 2 (NA, NB, NC) = INX2, INY2, INY2:

$$\text{INX2} = ((\text{NB} * \text{PG}) - (\text{NB} * \text{PE}) + (\text{PE} * \text{PF}) - (\text{NC} * \text{PF})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INY2} = ((\text{NA} * \text{PE}) - (\text{NA} * \text{PG}) + (\text{PD} * \text{PG}) - (\text{NC} * \text{PD})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INZ2} = (\text{NA} * \text{INX2}) + (\text{NB} * \text{INY2}) + \text{NC}$$

' Fractionation:

$$\text{FRAC4} = (\text{Log}(\text{ratio9598} / \text{INX1})) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 2$$

$$\text{NFRAC4} = (\text{Log}(\text{INX2} / \text{Rsta9598})) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 0.1$$

'

'LOOPING#4

' Three-dimensional fractionation correction:

' Natural fractionation (line 1 , plane 1):

' Standard (ST):

$$\begin{aligned} \text{RX1} &= \text{Rsta9598} \\ \text{RY1} &= \text{Rsta9798} \\ \text{RZ1} &= \text{Rsta10098} \end{aligned}$$

' Corrected for NFRAC (SA):

$$\begin{aligned} \text{RX2} &= \text{Rsta9598} * (\text{amu95} / \text{amu98}) ^ \text{NFRAC4} \\ \text{RY2} &= \text{Rsta9798} * (\text{amu97} / \text{amu98}) ^ \text{NFRAC4} \\ \text{RZ2} &= \text{Rsta10098} * (\text{amu100} / \text{amu98}) ^ \text{NFRAC4} \end{aligned}$$

' Spike (SP):

$$\begin{aligned} \text{RX3} &= \text{Rspike9598} \\ \text{RY3} &= \text{Rspike9798} \\ \text{RZ3} &= \text{Rspike10098} \end{aligned}$$

' Instrumental fractionation (line 2, plane 2):

' SA-SP mixture (MS):

MX1 = ratio9598
 MY1 = ratio9798
 MZ1 = ratio10098

' Corrected for FRAC (MT):

MX2 = ratio9598 * (amu98 / amu95) ^ FRAC4
 MY2 = ratio9798 * (amu98 / amu97) ^ FRAC4
 MZ2 = ratio10098 * (amu98 / amu100) ^ FRAC4

' Spike (SP):

MX3 = Rspike9598
 MY3 = Rspike9798
 MZ3 = Rspike10098

' Subroutines:

' NOTE: M and N prefix refers to line 2 and plane 2 (defined by fractionation)
 and P and R prefix refers to plane 1 and line 1 (defined by natural
 fractionation)

' Make lines and planes:

' Z = DX + E (LINE)

' Z = FY + G (LINE)

' Z = AX + BY + C (PLANE)

' Line 1:

PD = (RZ1 - RZ2) / (RX1 - RX2)

PE = RZ1 - RX1 * PD

PF = (RZ1 - RZ2) / (RY1 - RY2)

PG = RZ1 - RY1 * PF

' Plane 1:

PBUP = (RX1 * (RZ2 - RZ3)) + (RX2 * (RZ3 - RZ1)) + (RX3 * (RZ1 - RZ2))

$$PBDN = (RX1 * (RY2 - RY3)) + (RX2 * (RY3 - RY1)) + (RX3 * (RY1 - RY2))$$

$$PB = PBUP / PBDN$$

$$PAUP = (RY1 * (RZ2 - RZ3)) + (RY2 * (RZ3 - RZ1)) + (RY3 * (RZ1 - RZ2))$$

$$PADN = (RY1 * (RX2 - RX3)) + (RY2 * (RX3 - RX1)) + (RY3 * (RX1 - RX2))$$

$$PA = PAUP / PADN$$

$$PC = RZ1 - (PA * RX1) - (PB * RY1)$$

' Line 2:

$$ND = (MZ1 - MZ2) / (MX1 - MX2)$$

$$NE = MZ1 - MX1 * ND$$

$$NF = (MZ1 - MZ2) / (MY1 - MY2)$$

$$NG = MZ1 - MY1 * NF$$

' Plane 2:

$$NBUP = (MX1 * (MZ2 - MZ3)) + (MX2 * (MZ3 - MZ1)) + (MX3 * (MZ1 - MZ2))$$

$$NBDN = (MX1 * (MY2 - MY3)) + (MX2 * (MY3 - MY1)) + (MX3 * (MY1 - MY2))$$

$$NB = NBUP / NBDN$$

$$NAUP = (MY1 * (MZ2 - MZ3)) + (MY2 * (MZ3 - MZ1)) + (MY3 * (MZ1 - MZ2))$$

$$NADN = (MY1 * (MX2 - MX3)) + (MY2 * (MX3 - MX1)) + (MY3 * (MX1 - MX2))$$

$$NA = NAUP / NADN$$

$$NC = MZ1 - (NA * MX1) - (NB * MY1)$$

' Make intercept between a line and a plane:

' line 2 (ND, NE, NF, NG) , plane 1 (PA, PB, PC) = INX1, INY1, INY1:

$$INX1 = ((PB * NG) - (PB * NE) + (NE * NF) - (PC * NF)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$INY1 = ((PA * NE) - (PA * NG) + (ND * NG) - (PC * ND)) / ((PA * NF) + (PB * ND) - (ND * NF))$$

$$INZ1 = (PA * INX1) + (PB * INY1) + PC$$

' line 1 (PD, PE, PF, PG) , plane 2 (NA, NB, NC) = INX2, INY2, INY2:

$$INX2 = ((NB * PG) - (NB * PE) + (PE * PF) - (NC * PF)) / ((NA * PF) + (NB * PD) - (PD * PF))$$

$$INY2 = ((NA * PE) - (NA * PG) + (PD * PG) - (NC * PD)) / ((NA * PF) + (NB * PD) - (PD * PF))$$

$$INZ2 = (NA * INX2) + (NB * INY2) + NC$$

' Fractionation:

$$FRAC5 = (\text{Log}(\text{ratio9598} / INX1)) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 2$$

$$NFRAC5 = (\text{Log}(INX2 / Rsta9598)) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 0.1$$

'

'LOOPING#5

' Three-dimensional fractionation correction:

' Natural fractionation (line 1 , plane 1):

' Standard (ST):

$$RX1 = Rsta9598$$

$$RY1 = Rsta9798$$

$$RZ1 = Rsta10098$$

' Corrected for NFRAC (SA):

$$\begin{aligned}RX2 &= Rsta9598 * (amu95 / amu98) ^ NFRAC5 \\RY2 &= Rsta9798 * (amu97 / amu98) ^ NFRAC5 \\RZ2 &= Rsta10098 * (amu100 / amu98) ^ NFRAC5\end{aligned}$$

' Spike (SP):

$$\begin{aligned}RX3 &= Rspike9598 \\RY3 &= Rspike9798 \\RZ3 &= Rspike10098\end{aligned}$$

' Instrumental fractionation (line 2, plane 2):

' SA-SP mixture (MS):

$$\begin{aligned}MX1 &= ratio9598 \\MY1 &= ratio9798 \\MZ1 &= ratio10098\end{aligned}$$

' Corrected for FRAC (MT):

$$\begin{aligned}MX2 &= ratio9598 * (amu98 / amu95) ^ FRAC5 \\MY2 &= ratio9798 * (amu98 / amu97) ^ FRAC5 \\MZ2 &= ratio10098 * (amu98 / amu100) ^ FRAC5\end{aligned}$$

' Spike (SP):

$$\begin{aligned}MX3 &= Rspike9598 \\MY3 &= Rspike9798 \\MZ3 &= Rspike10098\end{aligned}$$

' Subroutines:

' NOTE: M and N prefix refers to line 2 and plane 2 (defined by fractionation)
and P and R prefix refers to plane 1 and line 1 (defined by natural fractionation)

' Make lines and planes:

' Z = DX + E (LINE)

' Z = FY + G (LINE)

' Z = AX + BY + C (PLANE)

' Line 1:

$$PD = (RZ1 - RZ2) / (RX1 - RX2)$$

$$PE = RZ1 - RX1 * PD$$

$$PF = (RZ1 - RZ2) / (RY1 - RY2)$$

$$PG = RZ1 - RY1 * PF$$

' Plane 1:

$$PBUP = (RX1 * (RZ2 - RZ3)) + (RX2 * (RZ3 - RZ1)) + (RX3 * (RZ1 - RZ2))$$

$$PBDN = (RX1 * (RY2 - RY3)) + (RX2 * (RY3 - RY1)) + (RX3 * (RY1 - RY2))$$

$$PB = PBUP / PBDN$$

$$PAUP = (RY1 * (RZ2 - RZ3)) + (RY2 * (RZ3 - RZ1)) + (RY3 * (RZ1 - RZ2))$$

$$PADN = (RY1 * (RX2 - RX3)) + (RY2 * (RX3 - RX1)) + (RY3 * (RX1 - RX2))$$

$$PA = PAUP / PADN$$

$$PC = RZ1 - (PA * RX1) - (PB * RY1)$$

' Line 2:

$$ND = (MZ1 - MZ2) / (MX1 - MX2)$$

$$NE = MZ1 - MX1 * ND$$

$$NF = (MZ1 - MZ2) / (MY1 - MY2)$$

$$NG = MZ1 - MY1 * NF$$

' Plane 2:

$$NBUP = (MX1 * (MZ2 - MZ3)) + (MX2 * (MZ3 - MZ1)) + (MX3 * (MZ1 - MZ2))$$

$$NBDN = (MX1 * (MY2 - MY3)) + (MX2 * (MY3 - MY1)) + (MX3 * (MY1 - MY2))$$

$$NB = NBUP / NBDN$$

$$\text{NAUP} = (\text{MY1} * (\text{MZ2} - \text{MZ3})) + (\text{MY2} * (\text{MZ3} - \text{MZ1})) + (\text{MY3} * (\text{MZ1} - \text{MZ2}))$$

$$\text{NADN} = (\text{MY1} * (\text{MX2} - \text{MX3})) + (\text{MY2} * (\text{MX3} - \text{MX1})) + (\text{MY3} * (\text{MX1} - \text{MX2}))$$

$$\text{NA} = \text{NAUP} / \text{NADN}$$

$$\text{NC} = \text{MZ1} - (\text{NA} * \text{MX1}) - (\text{NB} * \text{MY1})$$

' Make intercept between a line and a plane:

' line 2 (ND, NE, NF, NG) , plane 1 (PA, PB, PC) = INX1, INY1, INZ1:

$$\text{INX1} = ((\text{PB} * \text{NG}) - (\text{PB} * \text{NE}) + (\text{NE} * \text{NF}) - (\text{PC} * \text{NF})) / ((\text{PA} * \text{NF}) + (\text{PB} * \text{ND}) - (\text{ND} * \text{NF}))$$

$$\text{INY1} = ((\text{PA} * \text{NE}) - (\text{PA} * \text{NG}) + (\text{ND} * \text{NG}) - (\text{PC} * \text{ND})) / ((\text{PA} * \text{NF}) + (\text{PB} * \text{ND}) - (\text{ND} * \text{NF}))$$

$$\text{INZ1} = (\text{PA} * \text{INX1}) + (\text{PB} * \text{INY1}) + \text{PC}$$

' line 1 (PD, PE, PF, PG) , plane 2 (NA, NB, NC) = INX2, INY2, INZ2:

$$\text{INX2} = ((\text{NB} * \text{PG}) - (\text{NB} * \text{PE}) + (\text{PE} * \text{PF}) - (\text{NC} * \text{PF})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INY2} = ((\text{NA} * \text{PE}) - (\text{NA} * \text{PG}) + (\text{PD} * \text{PG}) - (\text{NC} * \text{PD})) / ((\text{NA} * \text{PF}) + (\text{NB} * \text{PD}) - (\text{PD} * \text{PF}))$$

$$\text{INZ2} = (\text{NA} * \text{INX2}) + (\text{NB} * \text{INY2}) + \text{NC}$$

' Fractionation:

$$\text{FRAC6} = (\text{Log}(\text{ratio9598} / \text{INX1})) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 2$$

$$\text{NFRAC6} = (\text{Log}(\text{INX2} / \text{Rsta9598})) / (\text{Log}(\text{amu95} / \text{amu98})) \text{ ' should be close to } 0.1$$

,

' ICP Fractionation Correction:

$$\text{corr9798} = \text{ratio9798} / (\text{amu97} / \text{amu98}) ^ \text{FRAC6}$$

$$\text{corr9698} = \text{ratio9698} / (\text{amu96} / \text{amu98}) ^ \text{FRAC6}$$

$$\text{corr9598} = \text{ratio9598} / (\text{amu95} / \text{amu98}) ^ \text{FRAC6}$$

$$\text{corr9498} = \text{ratio9498} / (\text{amu94} / \text{amu98}) ^ \text{FRAC6}$$

$$\text{corr9298} = \text{ratio9298} / (\text{amu92} / \text{amu98}) ^ \text{FRAC6}$$

' Make delta value 98/95:

$$\text{delta9895} = (((1 / \text{INX2}) - (1 / \text{Rsta9598})) / (1 / \text{Rsta9598})) * 1000$$

' define Q98 based on 97Mo / 98Mo: (calculates a factor for the amount of spike in the sample and then uses the calibrated spike ratios to subtract the spike from all other isotopes)

$$\text{Q98} = (\text{Rspike9798} - \text{corr9798}) / (\text{corr9798} - \text{INX2})$$

'More deltas:

$$\text{'SAM9698} = ((\text{corr9698} * (\text{Q98} + 1) - \text{Rspike9698})) / \text{Q98}$$

$$\text{'delta9896} = (((1 / \text{SAM9698}) / (1 / \text{Rsta9698})) - 1) * 1000$$

$$\text{'SAM9498} = ((\text{corr9498} * (\text{Q98} + 1) - \text{Rspike9498})) / \text{Q98}$$

$$\text{'delta9894} = (((1 / \text{SAM9498}) / (1 / \text{Rsta9498})) - 1) * 1000$$

$$\text{'SAM9298} = ((\text{corr9298} * (\text{Q98} + 1) - \text{Rspike9298})) / \text{Q98}$$

$$\text{'delta9892} = (((1 / \text{SAM9298}) / (1 / \text{Rsta9298})) - 1) * 1000$$

$$\text{Result}(0) = \text{Mo92}$$

$$\text{Result}(1) = \text{Mo94}$$

$$\text{Result}(2) = \text{Mo95}$$

$$\text{Result}(3) = \text{Mo96}$$

$$\text{Result}(4) = \text{Mo97}$$

$$\text{Result}(5) = \text{Mo98}$$

Result(6) = Mo100
Result(7) = ratio9298
Result(8) = ratio9498
Result(9) = ratio9598
Result(10) = ratio9698
Result(11) = ratio9798
Result(12) = ratio10098
Result(13) = FRAC6
Result(14) = NFRAC6
Result(15) = INX2 '(true 95 / 98)
Result(16) = INY2 '(true 97 / 98)
Result(17) = Q98
Result(18) = corr9598
Result(19) = delta9895

