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# RPPR Final Report

## as of 09-Mar-2022

Agency Code: 21XD

Proposal Number: 69868EVSR

Agreement Number: W911NF-17-2-0028

### INVESTIGATOR(S):

**Name:** Program Manager Julia G. Barzyk

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**Phone Number:** 9195494379

**Principal:** Y

Organization: **University of North Carolina - Chapel Hill**

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DUNS Number: 608195277

EIN: 566001393

**Report Date:** 01-Feb-2022

Date Received: 08-Mar-2022

**Final Report** for Period Beginning 15-Feb-2017 and Ending 01-Nov-2021

**Title:** Isotopic fractionation of lithium and cerium by fluid-rock interactions on Earth's surface

**Begin Performance Period:** 15-Feb-2017

**End Performance Period:** 01-Nov-2021

**Report Term:** 0-Other

Submitted By: Program Manager Julia Barzyk

Email: julia.g.barzyk.civ@army.mil

Phone: (919) 549-4379

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

**STEM Degrees:** 2

**STEM Participants:** 1

**Major Goals:** The research will investigate isotopic fractionation of two elements, lithium and potassium, as well as rare earth element behavior in Earth's surface environment through complementary laboratory experiments and field studies. The rare earth elements and lithium isotopic system are better studied, but although a number of applications have been developed, systematic evaluation on fractionation by weathering has not been performed. Recently developed analytical methods indicate that measurement of potassium isotopic ratios is possible, and the potential of using K isotopes to determine paleo conditions has been explored. However, the use of K isotopes as tracers of other processes has not been considered. The proposed effort will gather foundational knowledge that is expected to serve as a starting point for a range of potential applications in environmental chemistry, paleoclimatology, and surface processes. The research will combine analysis of data from samples obtained on the island of San Cristobal in the Galapagos archipelago with those from laboratory experiments to determine fractionation of lithium and potassium between water and common clays, using known standards in a controlled setting and under conditions relevant to the surface environment. Although at the proposal stage we had anticipated also investigating cerium isotopic behavior, based on the analytical capabilities available and the many fruitful directions that resulted from analysis of Li, K and other trace elements, Ce analyses were not performed but may be by Prof. Liu in follow-on research.

**Accomplishments:** Please see .pdf attachment.

**Training Opportunities:** Undergraduate honor thesis student William Larsen received support from this award. He graduated with highest honors in the spring of 2018 and began graduate school at Rice University in the fall 2019. He authored a peer-reviewed publication on his senior thesis that was published in Applied Geochemistry in 2021. A 2021 web article from the UNC Center for Galapagos Studies provides a summary of his research (uploaded as 'other' product).

Wenshuai Li began his graduate studies in the fall of 2016 and received funding from this award. His research focused on Li and K sorption experiments onto kaolinite and other clays minerals, and he has authored numerous publications. He received his PhD in 2021 and has been awarded the Japan Society for the Promotion of Science Fellowship to conduct postdoctoral work at the University of Tokyo in 2022.

Heather Hanna started working towards her PhD in fall of 2016. Her work focused on the geochemistry of rocks and soils from the Galapagos, and she has submitted a manuscript on this work for publication. She received her PhD in 2021. She is former employee of the North Carolina Geological Survey, and she is continuing her career as an independent consultant in forensic geology, specializing in analysis of geologic and soil trace evidence.

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**Results Dissemination:** The products submitted include 2 PhD theses, 2 posters, 2 conference abstracts, 1 submitted manuscript, and the following 8 peer-reviewed publications:

Larsen W.&, Liu X-M., Riveros-Iregui, D. A. (2021) Rare earth element behavior in springs and streams on a basaltic island: San Cristóbal, Galápagos. *Applied Geochemistry*, 131:105004.

Li W.&, and Liu X-M. (2021) Systematic investigations on iron cycling in phosphorus/siderophore systems: synergism or antagonism? *Applied Geochemistry*, 124: 104796.

Li W.&, Liu X-M., Wang, K., and Koefoed, P. (2021) Lithium and potassium isotope fractionation during silicate rock dissolution: an experimental approach. *Chemical Geology*, 568: 120142.

Li W.& and Liu X-M. (2020) Experimental investigation of lithium isotope fractionation during kaolinite adsorption: Implications for chemical weathering. *Geochimica et Cosmochimica Acta*, 284:156-172.

Li, W.& and Liu X-M. (2020) Mobilization and partitioning of rare earth elements in the presence of humic acids and siderophores. *Chemosphere*, 254: 126801.

Hanna H.D.&, Liu X-M., Rudnick R.L., Park Y-R, and Kay S.M. (2020) Lithium isotopes may trace subducting slab signatures in Aleutian arc lavas and intrusions. *Geochimica et Cosmochimica Acta*, Special Issue: The Continents, 278: 322-339.

Liu X-M. and Li W.& (2019) Lithium isotopic analysis by quadrupole-ICP-MS: Optimization for geological samples. *Journal of Analytical Atomic Spectrometry*, 34: 1708-1717.

Li W.&, Liu X-M., and Godfrey L. (2019) Development of a matrix independent lithium chromatography and isotopic analysis in geostandards by MC-ICP-MS. *Geostandards and Geoanalytical Research*, 43: 261-276.

**Honors and Awards:** Xiao-Ming Liu was awarded an NSF Faculty Early CAREER Award (2019) and the Early Career Award from the Geological Society of America, Mineralogy, Geochemistry, Volcanology & Petrology Division (2021). She was awarded tenure and promoted to Associate Professor (2021).

Wenshuai Li received a Geological Society of America graduate student research grant (2020) and he won the Roy L. Ingram Research Award from the UNC Department of Geological Science for his excellence performance in his graduate students for his research productivity (2019 and 2020). He has been awarded the Japan Society for the Promotion of Science (JSPS) Fellowship to conduct postdoctoral work at the University of Tokyo starting in 2022.

### Protocol Activity Status:

**Technology Transfer:** Before beginning her PhD studies at UNC, Heather Hanna had a career as a geologist with the North Carolina Geological Survey. In that role, she worked with law enforcement and served as an expert witness in forensic geology. Having earned her PhD, she is continuing to work in forensic geology as an independent consultant. During her PhD work, she further developed her micro-analytical skills, and with these skills, the PhD credential, and many years of experience as a field geologist, she will continue working with law enforcement in North Carolina, and potentially beyond, as a pioneer in forensic geology.

### PARTICIPANTS:

**Participant Type:** Undergraduate Student

**Participant:** William Larsen

**Person Months Worked:** 2.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**Participant Type:** Graduate Student (research assistant)

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**Participant:** Wenshuai Li

**Person Months Worked:** 15.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**Participant Type:** Graduate Student (research assistant)

**Participant:** Heather Hanna

**Person Months Worked:** 15.00

Project Contribution:

National Academy Member: N

**Funding Support:**

**ARTICLES:**

**Publication Type:** Journal Article

Peer Reviewed: Y

**Publication Status:** 1-Published

**Journal:** Geochimica et Cosmochimica Acta

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.gca.2019.07.049

Volume: 278

Issue:

First Page #: 322

Date Submitted: 3/4/22 12:00AM

Date Published: 6/1/20 8:00AM

Publication Location:

**Article Title:** Lithium isotopes may trace subducting slab signatures in Aleutian arc lavas and intrusions

**Authors:** Heather D. Hanna, Xiao-Ming Liu, Young-Rok Park, Suzanne M. Kay, Roberta L. Rudnick

**Keywords:** Lithium isotopes; Aleutian arc; Slab signature

**Abstract:** We report [Li] and d7Li values for a well-characterized suite of 52 geographically (165–184W), compositionally (SiO<sub>2</sub> = 46–70 wt.%), and temporally (0–38 Ma) diverse lavas and intrusive samples. The d7Li in these rocks range from 0.7‰ to +14.2‰, with 32 of the 35 lavas and 12 of the 17 intrusive samples falling within the depleted mantle range (d7Li +1.6 to +5.6‰), as sampled by mid-ocean ridge basalts (MORB). The d7Li values of Aleutian lavas do not exhibit the spatial trends observed in other slab component tracers, nor do d7Li values correlate with any slab component indicators, such as radiogenic isotopes, oxygen isotopes, or trace element ratios such as Cs/La and Th/La. The d7Li values in Aleutian intrusions also do not exhibit temporal trends, however, an overall positive relationship exists between d7Li and Th/Nd. Mixing models for d7Li and 143Nd/144Nd values suggest that Aleutian samples within or above the MORB d7Li range can be explained by addition of less than 1–2% sedi...

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Geochimica et Cosmochimica Acta

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.gca.2020.06.025

Volume: 284

Issue:

First Page #: 156

Date Submitted: 3/7/22 12:00AM

Date Published: 9/1/20 4:00AM

Publication Location:

**Article Title:** Experimental investigation of lithium isotope fractionation during kaolinite adsorption: Implications for chemical weathering

**Authors:** Wenshuai Li, Xiao-Ming Liu

**Keywords:** Li isotope, Kaolinite, Clay, Adsorption, Incorporation, Weathering, Kinetic fractionation

**Abstract:** The feedback between CO<sub>2</sub> sources and sinks through chemical weathering is one of the important reasons why Earth has maintained a habitable climate for over four billion years. The lithium (Li) isotopic system is a promising tracer of silicate weathering, but the mechanisms causing its isotope fractionation during weathering remain ambiguous. Here, we performed batch experiments of Li adsorption to one of the common clay minerals - kaolinite in three sets, including the time-series, pH dependent, and concentration-control sets. Our results demonstrate that the liquid-solid Li isotope fractionation reaches up to 36‰, with up to 99% initial Li being adsorbed on kaolinite. The magnitudes of Li adsorption and isotope fractionation increase with reaction time, and reach the steady-state after ~1000 min. The magnitude of Li isotope fractionation increases with the adsorption ratio of Li, in positive relationships with solute pH and ionic strength. . .

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Applied Geochemistry

Publication Identifier Type: DOI

Publication Identifier: 10.1016/j.apgeochem.2020.104796

Volume: 124

Issue:

First Page #: 104796

Date Submitted: 3/7/22 12:00AM

Date Published: 1/1/21 5:00AM

Publication Location:

**Article Title:** Systematic investigations on iron cycling in phosphorus/siderophore systems: Synergism or antagonism?

**Authors:** Wenshuai Li, Xiao-Ming Liu

**Keywords:** Ferrihydrite, Phosphorus, Siderophores, Synergism, Antagonism, Ecology

**Abstract:** Synergisms between microbial exudates on Fe (hydr)oxide dissolution as an effective Fe acquisition pathway have been recently addressed and vigorously debated. However, Fe liberation mechanisms and where siderophores and phosphorus (P) coexist received little attentions. Current study systematically investigated ferrihydrite dissolution in the presence of desferrioxamine B (DFOB) (a kind of fungally-derived siderophores) and inorganic/organic phosphorus (orthophosphate, Pi; myo-inositol hexaphosphate, IHP), as a function of solute pH, reaction time and reagent content. Reacted solids were characterized by N<sub>2</sub>-BET adsorption, zeta (?) potential analysis, sequential extraction analysis (SEDEX), field emission scanning electron microscopy (FESEM), high-resolution transmission electron microscopy (HRTEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), micro Raman spectroscopy and attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR). . .

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Chemical Geology

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Volume: 568

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Date Published: 5/1/21 4:00AM

Publication Location:

**Article Title:** Lithium and potassium isotope fractionation during silicate rock dissolution: An experimental approach

**Authors:** Wenshuai Li, Xiao-Ming Liu, Kun Wang, Piers Koefoed

**Keywords:** Silicate rocks, Chemical weathering, Dissolution, Lithium, Potassium, Isotope

**Abstract:** This study experimentally investigates the isotopic behaviors of Li and K during the dissolution of silicate rocks (i.e., basalt and granite). Proton-driven dissolution (in 0.8 M HNO<sub>3</sub>) and ligand-driven dissolution (in 5 mM citric acid or oxalic acid) experiments were performed in batch-closed systems over 15 days. We provide a time-series interpretation of Li and K isotope fractionation during silicate dissolution in ultra-acidic (unidirectional) and near-natural (biologically affected) environments. As the reaction progressed, we measured large isotope fractionation between the liquid (l) phase and the pristine silicate (s) phase, ranging from ?? 10.3 to 0.1‰ (??Li<sub>l-s</sub>) and from ?? 1.01 to ?? 0.11‰ (??K<sub>l-s</sub>) through the early stage of dissolution (less than 24 h). The enrichment of lighter Li and K isotopes in the solutions rapidly diminished as rock dissolution continued and gradually approached equilibrium to the end of experiments . .

**Distribution Statement:** 1-Approved for public release; distribution is unlimited.

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 1-Published

**Journal:** Geostandards and Geoanalytical Research

Publication Identifier Type: DOI

Publication Identifier: 10.1111/ggr.12254

Volume: 43

Issue: 2

First Page #: 261

Date Submitted: 3/7/22 12:00AM

Date Published: 2/1/19 5:00AM

Publication Location:

**Article Title:** Optimisation of Lithium Chromatography for Isotopic Analysis in Geological Reference Materials by

**Authors:** Wenshuai Li, Xiao-Ming Liu, Linda V. Godfrey

**Keywords:** lithium, isotopes, matrix, dual-column, MC-ICP-MS, reference materials

**Abstract:** The lithium isotope system can be an important tracer for various geological processes, especially tracing continental weathering. The key to this application is the accurate and precise determination of lithium isotopic composition. However, some of the previously established column separation methods are not well behaved when applied to chemically diverse materials, due to the significant variations in matrix/lithium ratios in some materials. Here, we report a new dual-column system for lithium purification to achieve accurate and precise analysis of lithium isotopic compositions using a multicollector inductively coupled plasma-mass spectrometer (MC-ICP-MS). Compared with single-column systems, our dual column system yielded a consistent elution range of the lithium-bearing fraction (7–16 ml) for samples with a large range of lithium loads and matrix compositions, so that column re-calibration is not required.

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**Journal:** Journal of Analytical Atomic Spectrometry  
Publication Identifier Type: DOI      Publication Identifier: 10.1039/C9JA00175A  
Volume: 34      Issue: 8      First Page #: 1708  
Date Submitted: 3/7/22 12:00AM      Date Published:  
Publication Location:

**Article Title:** Optimization of lithium isotope analysis in geological materials by quadrupole ICP-MS

**Authors:** Xiao-Ming Liu, Wenshuai Li

**Keywords:** Quadrupole ICP-MS, Lithium

**Abstract:** This study develops and optimizes a new protocol to measure lithium isotope ratios using a single collector quadrupole inductively coupled plasma mass spectrometer (Q-ICP-MS) operated under hot plasma (1550 W) conditions with a sample–standard bracketing method. Our Q-ICP-MS method reduces sample consumption to 2.5 ng of Li and achieves a high long-term precision of 1.1% (2SD). This Q-ICP-MS method exhibits high matrix tolerance (Na/Li less than 100), suitable for ng-sized and high-matrix geological samples. We also developed a dual-column system for Li separation, with large loading capacity (29.6 meq), complete recovery (>100%) and satisfactory purification (Na/Li  $\text{m}^{-1}$  less than 1), as well as a fixed elution range for Li fractions (28–60 mL). This new chromatography method has been applied to chemically diverse materials, producing consistent results.

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**Publication Type:** Journal Article      Peer Reviewed: Y      **Publication Status:** 5-Submitted  
**Journal:** Applied Geochemistry  
Publication Identifier Type:      Publication Identifier:  
Volume:      Issue:      First Page #:  
Date Submitted: 3/7/22 12:00AM      Date Published:  
Publication Location:

**Article Title:** IMPACT OF WEATHERING AND MINERALOGY ON THE CHEMISTRY OF SOILS FROM SAN CRISTOBAL ISLAND, GALAPAGOS

**Authors:** Heather D. Hanna, Xiao Ming Liu, Julia G. Barzyk

**Keywords:** Chemical weathering, soil development, mineralogy, soil geochemistry, Galapagos

**Abstract:** Chemical weathering of basalt is important to global CO<sub>2</sub> consumption, soil fertility, and production of economic laterite deposits. However, while research has examined climatic influence on secondary mineral formation, the influence of changing climate on mineralogical control of elemental behavior remains unclear. This study presents the first systematic research of soil samples spanning different climate zones on San Cristóbal island, Galapagos, to examine how basalt weathering impacts mineralogical control on soil chemistry. The results suggest weathering of primary igneous minerals dominate elemental retention in minimally weathered basalt from dry climates. With increasing humidity and progressive primary mineral depletion, amorphous phases begin to play a prominent role in elemental retention, eventually giving way to gibbsite and its precursors under high humidity and Fe oxides and oxyhydroxides and their precursors at drier, older sites. . .

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### CONFERENCE PAPERS:

**Publication Type:** Conference Paper or Presentation      **Publication Status:** 1-Published  
**Conference Name:** Goldschmidt Conference  
Date Received: 07-Mar-2022      Conference Date: 13-Aug-2017      Date Published:  
Conference Location: Paris, France  
**Paper Title:** Are lithium isotopes good proxies of continental silicate weathering?  
**Authors:** XIAO-MING LIU  
Acknowledged Federal Support: N

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**Publication Type:** Conference Paper or Presentation **Publication Status:** 1-Published  
**Conference Name:** Goldschmidt Conference  
Date Received: 07-Mar-2022 Conference Date: 12-Aug-2018 Date Published:  
Conference Location: Boston, US  
**Paper Title:** Evaluating lithium isotopes as a tracer for subducting slab components in Aleutian arc lavas  
**Authors:** Heather D. Hanna, Xiao Ming Liu, Young Rock Park, Suzanne M. Kay, Roberta L. Rudnick  
Acknowledged Federal Support: **N**

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**Conference Name:** Goldschmidt Conference  
Date Received: 07-Mar-2022 Conference Date: 21-Jun-2020 Date Published:  
Conference Location: Virtual  
**Paper Title:** Potassium isotope fractionation during plant uptake in Hawaii  
**Authors:** Wenshuai Li, Xiao Ming Liu, Yan Hu, Fang Zhen Teng, Yongfeng Hu, Oliver A. Chadwick  
Acknowledged Federal Support: **N**

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**Conference Name:** Goldschmidt Conference  
Date Received: 07-Mar-2022 Conference Date: 21-Jun-2020 Date Published:  
Conference Location: Virtual  
**Paper Title:** Potassium isotope fractionation during chemical weathering: a Hawaiian example  
**Authors:** Xiao Ming Liu, Wenshuai Li, Yan Hu, Fang Zhen Teng, Yongfeng Hu, Oliver A. Chadwick  
Acknowledged Federal Support: **N**

**DISSERTATIONS:**

**Publication Type:** Thesis or Dissertation  
**Institution:** University of North Carolina, Chapel Hill  
Date Received: 04-Mar-2022 Completion Date: 6/1/21 8:15PM  
**Title:** Tracing Chemical Weathering Using Lithium and Potassium Isotopes  
**Authors:** Wenshuai Li  
Acknowledged Federal Support: **N**

**Publication Type:** Thesis or Dissertation  
**Institution:** University of North Carolina at Chapel Hill  
Date Received: 04-Mar-2022 Completion Date: 6/1/21 4:00AM  
**Title:** GEOCHEMICAL INVESTIGATION OF FLUID-ROCK INTERACTIONS DURING CHEMICAL WEATHERING AND SUBDUCTION  
**Authors:** Heather Dawn Hanna  
Acknowledged Federal Support: **Y**

**RPPR Final Report**  
as of 09-Mar-2022

**Partners**

,

I certify that the information in the report is complete and accurate:

Signature: Julia G. Barzyk

Signature Date: 3/8/22 10:54PM

## Final Report: Accomplished under Goals

During the grant period, using coordinated laboratory experiments and field-based studies, we have made contributions to environmental geochemistry, paleoclimatology, and surface processes, through the development and application of new methods for elemental and isotopic analysis of geological samples. The research area was San Cristobal Island, Galapagos, a natural laboratory for the study of chemical weathering, owing to its uniform lithology and topography, as described below.

All results from the research have been published or submitted for publication. (Prepublication results were submitted in Interim Progress Reports.) This section of the Final Report provides an overview of the major contributions, in the context of the publications and their implications, and is divided into two sections: The first section on Li and K sorption, chromatography, and microanalysis reports on the development and adaptation of laboratory methods for analysis of geological materials to account for their complex matrices and to enable measurements using relatively common laboratory instrumentation. The second section on the investigation of chemical weathering on San Cristobal Island, Galapagos, reports on geochemical analyses on water, soil and rock samples and how these results contribute to our understanding of chemical weathering and the Galapagos paleoclimate.

### **Li and K sorption, chromatography, and microanalysis**

The first component of the research was to design and conduct laboratory experiments, and to adapt or refine the associated analytical techniques, on the fractionation of Li between water and common clay minerals, simulating continental weathering processes. Determination of Li behavior using these clay standards in a controlled environment, under earth-surface-like conditions, was necessary groundwork for the field-based studies. In addition to establishing the methods for the studies on the Galapagos samples, these methods have been applied in the analysis of samples collected by co-PI Liu and student Li during the grant period on Hawaii, another basaltic ocean island chain. (The fieldwork to Hawaii was not supported by the ARO grant.) These methods and the resulting characterization of isotopic fractionation are being used to inform studies on weathering processes in range of surface environments, with the 2021 *Chemical Geology* paper having already been cited 10 times.

#### **1. Development of a chromatography method to separate Li from geological samples**

A new method to separate Li from geological materials was developed to achieve higher accuracy and precision than was possible using existing procedures. The aim was to develop a method that could be used on chemically diverse materials, in anticipation of the rock and soil samples to be collected. A dual-column system was developed to prepare samples for multi-collector inductively coupled plasma-mass spectrometer (MC-ICP-MS) analysis. Compared with single-column systems, the new dual-column system yields more consistent results for samples with a wide range of Li loads and matrix compositions, eliminating the need for column re-calibration. As part of this work, high-precision measurements were made of Li isotopic compositions in 12 chemically diverse materials including seawater, silicates, carbonates, manganese nodules and clays.

Li W., Liu X-M., and Godfrey L. (2019) Development of a matrix independent lithium chromatography and isotopic analysis in geostandards by MC-ICP-MS. <i>Geostandards and Geoanalytical Research</i> , 43: 261-276.
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## 2. Optimization of measurement of Li isotope relative abundances by mass spectrometry

Once the separation method was established, a single-collector quadrupole ICP-MS protocol to measure the relative abundances of Li isotopes was optimized for geological samples, for use in conjunction with sample prepared by the chromatography method described above. Compared with existing methods (thermal ionization mass spectrometry (TIMS) with multiple detectors has conventionally been used), this protocol has the advantages of reduced sample consumption and consistent performance with high-matrix geological samples. When combined with dual-column separation, increased washing time (180 s) over previous methods during the digestion phase of sample preparation reduced memory effects, instrumental mass bias and matrix effects. The new method also creates potential for more researchers to work with Li isotopes because single-collector ICP-MS instruments, being commercially available and relatively affordable, are much more common than multi-collector instruments like TIMS, in geoscience departments, especially as the method performs very well for high-matrix samples such as geological samples, seawater and brines.

Liu X-M. and Li W. (2019) Lithium isotopic analysis by quadrupole-ICP-MS: Optimization for geological samples. *Journal of Analytical Atomic Spectrometry*, 34: 1708-1717.

## 3. Laboratory experiments of Li fractionation during simulated chemical weathering

Chemical weathering starts with the breakdown of silicate rocks, which results in the formation of clays, and then clays undergo their own weathering processes. The first laboratory experiments were designed and conducted to characterize the adsorption of Li onto clays and the resulting isotopic fractionation. Although Li isotopes have been used in previous studies to trace chemical weathering and inform paleoclimate research, little was known about their fractionation during the soil formation process. The clay mineral kaolinite was used, pH was varied, and Li concentration was controlled for periods of up to 15 days, at ambient temperature and a range of Li concentrations. The adsorption experiments were followed by a set of desorption experiments. Changes in Li complexation on kaolinite surfaces were determined by infrared spectroscopy and elemental and Li isotopic analyses by ICP-MS. Results indicated that Li was removed from solution by inner-sphere/outersphere surface complexation, which is likely followed by lattice occupation, and that Li isotope fractionation during kaolinite uptake is best described using a closed-system Rayleigh distillation model, a result consistent with the theoretical calculations and measurements from rivers worldwide. These results suggest that kinetic isotope fractionation is responsible for the wide ranges of Li isotopic signatures on Earth's surfaces. The finding is significant because it implies that the soil formation process may be the main driver for pronounced Li isotope fractionation, particularly in transport-limited weathering regions and, by extension, the continental-marine Li isotopic fluctuations during weathering over geological timescales.

Li W., and Liu X-M. (2020) Experimental investigation of lithium isotope fractionation during kaolinite adsorption: Implications for chemical weathering. *Geochimica et Cosmochimica Acta*, 284:156-172.

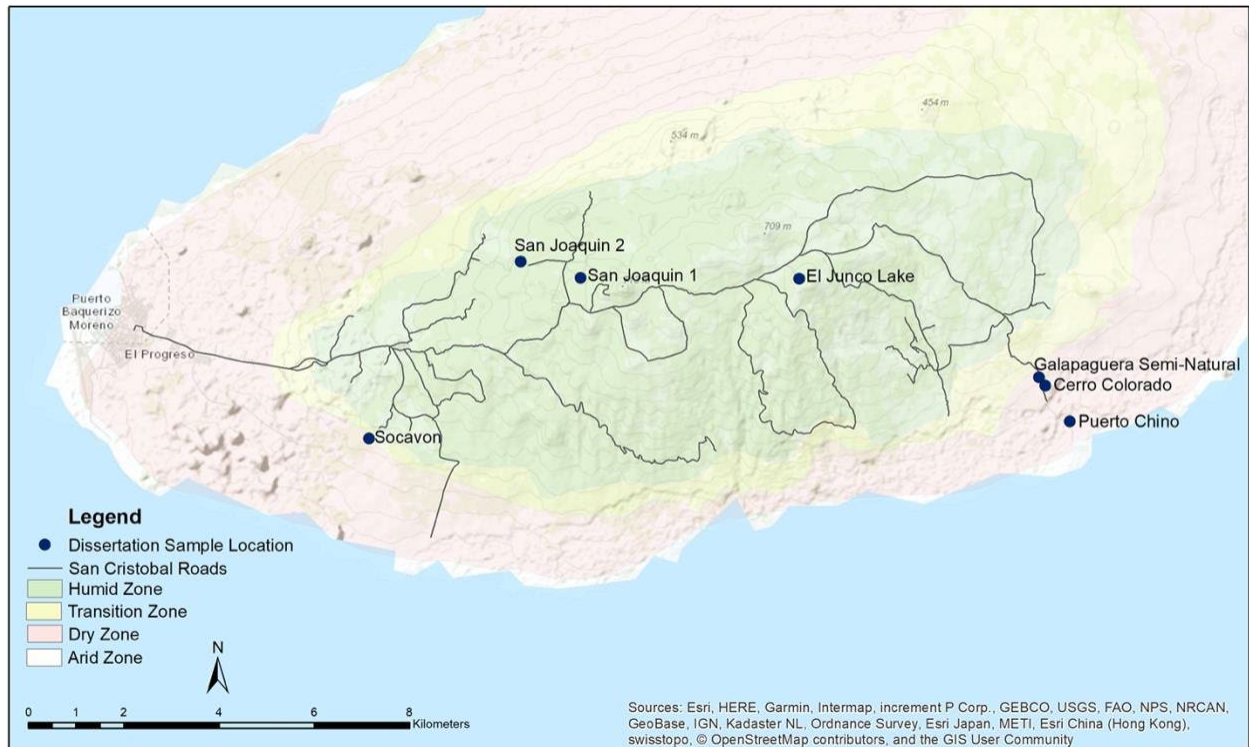
To investigate the second potential chemical weather fractionation process, the experimental methods were adapted to investigate the direction and magnitude of Li and K isotopic fractionation during dissolution of silicate rocks (basalt and granite) through a similar time series. The investigation was extended to K because the  $^{39}\text{K}/^{41}\text{K}$  ratio can also be used as a tracer of continental weathering and could therefore aid in interpretation of Li results. On pre- and post-treatment samples, elemental analyses were performed by x-ray fluorescence, and minerals were identified by x-ray diffraction. Following chromatography, isotopic analyses were performed by ICP-MS. The results of this work were somewhat unexpected and are described in detail in the resulting publication; in sum, it was found that the exchange of metals and isotopes during dissolution likely occurs in multiple steps: (i) kinetic loss of ions from silicate minerals in rocks into fluids, (ii) the breakdown of primary silicates and (iii) back-reactions (adsorption and/or precipitation). These results may indicate that the signature of kinetic isotope fractionation may be recorded in incomplete or unidirectional reactions with substantial undersaturation and that this process affects the fractionation of Li more than it does K. If this is the case, K isotopes may be a better weathering proxy.

Li W., Liu X-M., Wang, K., and Koefoed, P. (2021) Lithium and potassium isotope fractionation during silicate rock dissolution: an experimental approach. *Chemical Geology*, 568: 120142.

The foundational work in method development and proof of concept in experiments on natural samples provided the preliminary data that co-PI Liu used to prepare the proposal *Understanding chemical weathering using lithium and potassium isotopes* to NSF, which was funded as an NSF CAREER award.

### **Investigation of chemical weathering on San Cristobal Island, Galapagos**

Concurrent with the development of the above methods, a coordinated field campaign was conducted to collect water, soil and rock samples across a topographic gradient (representing different climate zones and therefore degrees of weathering) on San Cristobal Island, in the Galapagos Archipelago, Ecuador. Like the Hawaiian Islands, the Galapagos were formed by a mantle hotspot and therefore have a uniform lithology, ocean island basalt. The site was chosen as a natural laboratory in which to study continental weathering, an important process, as the chemical weathering of crustal silicate rocks affects the fluxes of nutrients to the ocean and regulates  $\text{CO}_2$ . Chemical weathering of basalt, in particular, is responsible for 30-35% of global  $\text{CO}_2$  consumption, despite basalt being only ~8% of exposed silicate rock. Laterites, important iron ores, are formed by basalt weathering, and progressive weathering of basalt results in elemental loss, impacting soil fertility. (See references within Heather Hanna's dissertation.) We aimed to characterize the complexities of basalt weathering, using new and improved geochemical methods, to provide a foundation for further insight into a range of Earth surface processes.



Map showing climate zones and sample collection sites on San Cristobal.

#### 4. Rare Earth element (REE) fractionation mechanisms in freshwater environments

In this component of the research, the fractionation of dissolved REEs in freshwater environments was assessed in laboratory experiments conducted using water samples that were collected from 8 groundwater springs and 8 streams on San Cristobal Island. Because the island is a single rock type (ocean island basalt) and exhibits a steep precipitation gradient on the windward slope over a short spatial extent, it provides an excellent setting from which to investigate primary controls of REE fractionation at a range of regolith weathering intensities and without the influence of varying lithology. Measurements of pH, temperature, and total dissolved solids were taken on-site, and after filtration, samples were returned to UNC, where REE concentrations were measured by ICP-MS.

Results suggest that two mechanisms are responsible for the observed REE fractionation in the catchment: pH-driven changes in aqueous complex stability by organic or anionic complexes and the preferential adsorption of heavy rare earth elements (HREE) onto Fe- and Mn-oxyhydroxides at low pH, contrasting with moderate enrichment of light rare earth elements (LREE) observed at higher pH. These results suggest that several proposed REE fractionation mechanisms established previously in laboratory experiments (e.g., a positive Ce anomaly associated with HREE enrichment in low pH waters) are observable in a natural watershed system, despite being obscured by mixing in larger world rivers. The results support the idea that the homogenous lithology and strong climate gradient of San Cristobal Island provide an excellent natural laboratory for weathering studies.

Larsen W., Liu X-M., Riveros-Iregui, D. A. (2021) Rare earth element behavior in springs and streams on a basaltic island: San Cristóbal, Galápagos. *Applied Geochemistry*, 131:105004.

Related research on REEs in natural organic matter that was not part of the planned project scope is reported here because the work was performed by co-PI Liu and student Li during the period that they were supported by the award. This work demonstrates how biogeochemical weathering, which occurs in surface environments where natural organic matter is present, influences the behavior of REEs, largely due to elemental differences in interaction between REE-bearing materials and iron oxides.

Li, W<sup>§</sup> and Liu X-M. (2020) Mobilization and partitioning of rare earth elements in the presence of humic acids and siderophores. *Chemosphere*, 254: 126801.

Li W., and Liu X-M. (2021) Systematic investigations on iron cycling in phosphorus/siderophore systems: synergism or antagonism? *Applied Geochemistry*, 124: 104796

## 5. The impact of weathering and mineralogy on soil chemistry

This research is the first systematic study of soil formation on San Cristobal Island and involved the collection of water, soil and rock samples from 6 sites, selected to represent the full range of climate zones and extents of weathering. The broad goal was to determine how the weathering of basalt impacts the resulting soil mineralogy and chemistry. After collection in the field and baking in the Galapagos Science Center laboratory on the island, samples were returned to UNC Chapel Hill. Powdered soil, saprolite, and rock samples were dissolved in preparation for elemental analysis, using the methods adapted from those described in the publications reported above, and reported in detail in the manuscript referenced below. The elemental analysis and Nd and Sr isotope ratio measurements were performed by ICP-MS. To determine mineralogy, aliquots of select powdered soil, saprolite, and rock samples were analyzed by x-ray diffraction at the Chapel Hill Analytical and Nanofabrication Lab (CHANL) at UNC Chapel Hill.

The data and a discussion of the implications are reported and discussed in the manuscript. A selection of findings is as follows:

- When age is held constant to examine the impact of climate, congruent weathering of olivine appears to dominate elemental retention in minimally weathered basalt in dry climates, with ferrihydrite formation and incongruent weathering of plagioclase playing a lesser role.
- As humidity and weathering intensity begin to increase, the importance of primary igneous minerals becomes secondary to the role of amorphous phases in controlling elemental retention.

- As weathering progresses over time in drier climates, Fe oxides and oxyhydroxides, and/or their amorphous precursors, become the dominant mineralogical control on elemental retention, while kaolin minerals play a less significant role.
- At multiple sites, radiogenic isotopic ratios  $^{87}\text{Sr}/^{88}\text{Sr}$  and  $^{143}\text{Nd}/^{144}\text{Nd}$  indicate parent basalt weathering is not the only contributor to soils.
- Mixing models suggest that Nd ratios can be explained by a ~35% contribution from ash of a similar composition to that of the pre-caldera phase of the Chacana volcano and/or a ~10% input from South American Eolian deposits. These results suggest that South American mainland sources alone can explain observed Nd isotope signatures in San Cristobal soils, without need for northern hemisphere and Australian dust deposition in the Eastern Equatorial Pacific.

In sum, the results suggest that weathering of primary igneous minerals dominates elemental retention in minimally weathered basalt from dry climates. With increasing humidity and progressive primary mineral depletion, amorphous phases begin to play a prominent role in elemental retention, eventually giving way to gibbsite and its precursors under high humidity and Fe oxides and oxyhydroxides and their precursors at drier, older sites. Strontium and Nd isotope ratios give insight into the influence of marine aerosols and dust/volcanic ash on San Cristobal profiles. Neodymium isotope models suggesting South American mainland dust and/or volcanic ash alone can account for isotopic signatures in study samples without need for an Asian or Australian dust influence.

Hanna H.D., Liu X-M., and Barzyk, J.G. (submitted 2021) Impact of weathering and mineralogy on the chemistry of soils from San Cristobal Island, Galapagos. *Applied Geochemistry*.

## 6. Li isotopes as tracers of magmatic and tectonic processes

The research reported in one additional peer-reviewed publication was supported by the award and involved collection of Li isotope data combined with previously collected geochemical data from intrusive and extrusive rock samples from the Aleutian Islands. Li isotope fractionation was studied in magmatic systems as a tracer of subduction processes. Student Heather Hanna performed this work when she was first beginning her graduate studies as an introduction to the Li isotope system and associated analytical methods.

Hanna H.D.<sup>‡</sup>, Liu X-M., Rudnick R.L., Park Y-R, and Kay S.M. (2020) Lithium isotopes may trace subducting slab signatures in Aleutian arc lavas and intrusions. *Geochimica et Cosmochimica Acta, Special Issue: The Continents*, 278: 322-339.