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Deciphering isotope signatures of Earth Surface and Critical Zone processes

Fang-Zhen Teng [a,*], Lin Ma [b]

[a] Isotope Laboratory, Department of Earth and Space Sciences, University of Washington, Seattle, WA 98195
[b] Center for Earth and Environmental Isotope Research, Department of Geological Sciences, University of Texas at El Paso, El Paso, TX 79968

Earth's Critical Zone is the thin outer layer of our planet from the top of the tree canopy to the bottom of groundwater aquifers, and supports almost all human activities (e.g. Brantley et al. 2007, 2011). Understanding, predicting and managing the evolution, functions and services of the Critical Zone is the focus of international Critical Zone research of the 21st century (Banwart et al. 2013). Concerted efforts have been made recently to understand geochemical processes such as weathering, soil formation, erosion, riverine transport, element mobility, and environmental pathways in both natural and managed systems. A variety of traditional and non-traditional isotope systematics, with elements from light to heavy mass on the periodic table, has been developed and used in the geochemical community. In December of 2014, we convened a special session at the Fall AGU conference in San Francisco, CA on "Deciphering isotope signatures of Earth Surface and Critical Zone processes". The 16 papers in this volume result from work presented in that session, as well as contributions from scientists who were unable to attend. The topics covered by these papers range widely from low temperature geochemical and biological processes in natural environments such as rivers, soils, and catchments, to experimental calibration and modeling of the isotope fractionation factors and element partitioning during low-temperature fluid-rock interactions. The isotope systematics include both stable (C, N), non-traditional stable (Li, Mg, Ca, Cu, Zn, Mo) and radiogenic (Ar, Sr, U-series) isotopes.

1. Element and isotope fractionations during weathering and soil formation

Understanding the isotope fractionation mechanisms during Earth surface processes is the prerequisite for using isotopes to study the Critical Zone. Eight papers in this volume are dedicated to this topic.

To constrain the connection of groundwaters and hydrothermal springs to surface waters, Pogge von Strandmann et al. (2016) measured Li isotopes for cold ground waters and hydrothermal springs that feed the Lake Myvatn, Iceland. They found that Li isotopic compositions of cold springs, in contrast to high-temperature springs, are highly variable and correlate with temperature and total dissolved solids, suggesting similar processes that control Li isotope fractionation during continental weathering also operate in springs. Furthermore, Li isotopes, different from Si isotopes, are not affected by phytoplankton or plant growth as indicated by the lack of seasonal variations, which makes Li isotopes an ideal tracer for continental weathering.

Magnesium isotopic compositions of dolostone can potentially be used as tracers of seawater evolution, paleoclimate change and origins of dolostone. However, dolostone can be easily weathered and the effects of dolostone weathering on Mg isotope geochemistry need be evaluated first. Gao et al. (2016) measured Mg and Sr isotopes for a dolostone weathering profile from Hubei, China. They found large Mg isotope fractionation during dolostone weathering, with the direction and degree of Mg isotope fractionation controlled by the dissolution and recrystallization of carbonate minerals. The important implication of this study is that step-leaching experiments are required to reveal the pristine Mg isotopic compositions of dolostone.

To characterize the behaviors of Cu and Zn isotopes in black shales during weathering, Lv et al. (2016) systematically studied Cu and Zn concentrations and isotopic compositions of unweathered and weathered shales and cherts from the Maokou Formation in central China. The Cu and Zn isotopic compositions vary greatly in weathered shales and cherts and are overall lighter than the unweathered protoliths. These results suggest a preferential release of heavy Cu and Zn isotopes into fluids during shale weathering, which should be considered for studies of global cycling of Cu and Zn in the ocean.

Vance et al. (2016) comprehensively studied Cu and Zn isotopes in two weathering profiles developed on granitoids in Scotland and basalts in Hawaii. They found Cu and Zn in both profiles are mobile but only Cu isotopes are significantly fractionated, with the heavy Cu isotopes preferring fluids to soils. The complicated and contrasting Cu and Zn behaviors reflect multiple processes in controlling metal budget and isotope compositions including mineral dissolution, change of redox conditions, organic ligands and atmospheric additions.

King et al. (2016) investigated behaviors of Mo isotopes during early states of soil development along a basaltic weathering profile in Hawaii. The Mo isotopic compositions of the weathered residue, different from the underlying basaltic protolith, vary as a function of rainfall gradient, with the lightest at the dry sites and evolving heavier with increasing precipitation. The large isotopic variation reflects a combination of precipitation, volcanic fog and potentially anthropogenic inputs as well as Mo-organic matter interactions. This study illustrates the potential application of Mo as a tracer for atmospheric inputs and pedogenic processes.

* Corresponding author.
E-mail address: fteng@u.washington.edu (F.-Z. Teng).

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Uranium-series isotopes are emerging as a tool to characterize weathering and soil forming processes in the Critical Zone. To understand behaviors of U-series isotopes in a semi-arid and lithologically complex volcanic terrain, Huckle et al (2016) presented a comprehensive dataset of U-series isotopes in bedrock, soils, dust, soil sequential extracts, soil pore water, spring water, and stream water from the Jemez River Basin Critical Zone Observatory (CZO) in New Mexico, USA. Their results showed evidence of past episodic mixing of volcanic ash in these soils and suggested that modeling of soil formation using a mass balance approach without considering possible atmospheric inputs is problematic. Huckle et al. (2016) also showed systematical variations of ($^{234}U/^{238}U$) activity values in spring and stream waters of a headwater catchment during snowmelt and dry seasons, suggesting that the U-series isotopes are a promising tracer of water residence time and mixing of different water sources.

Meek et al. (2016) conducted a multi-tracer study using $^{87}Sr/^{86}Sr$, Ca/Sr, and Ge/Si ratios from soils, leaves, sap waters, soil pore waters, ground waters, and stream waters in a forest catchment underlying gray shale in temperate central Pennsylvania (Susquehanna Shale Hills CZO). This study investigated effects of plant uptake, biological cycling, hydrological losses, atmospheric inputs and chemical weathering on sources and cycling of Ca, Sr, Ge, and Si in terrestrial ecosystems. These combined datasets reveal an important interaction of slower chemical weathering processes with more rapid, biologically driven cycling between soils and biomass in this watershed.

One of the best examples on using multiple isotopes to study Critical Zone processes (CZ-tope) is from the Susquehanna Shale Hills CZO. Sullivan et al. (2016) synthesized various isotope proxies to elucidate Critical Zone processes in this temperate forested landscape. Multiple isotopic measurements including U-series, meteoric ^{10}Be, H, B, C, O, S, Mg, Fe, Sr, Pb and Cs in soils, waters, vegetation samples, revealed complex interactions of geochemical, geomorphological, hydrological and biological processes together with anthropogenic influences in the Critical Zone across widely disparate time scales. The CZ-tope, the interpretation of multiple elements' isotopic ratios quantified for identical samples in one landscape, paints an emerging picture of Susquehanna Shale Hills CZO as a relatively fast-eroding but slow-weathering landscape in which: nutrients are tightly cycled by vegetation; soils move downslope largely by freeze-thaw; subsurface particle transport is an important flux for mass loss; mobile and immobile reservoirs act to fractionate water and cations into trees and stream water; the imprint of humans is manifested in the metal contents of the topsoil.

2. Experimental and theoretical studies of isotope fractionations during low-temperature fluid-rock interactions

Dissolution of primary minerals is often accompanied by precipitation of secondary phases during rock weathering. Laboratory and theoretical studies of isotope behaviors during both processes are thus important for understanding isotopic variations in natural samples. Three papers in this volume deal with this topic.

Schott et al. (2016) carried out theoretical and experimental studies on equilibrium partitioning of Mg isotopes between aqueous solutions and carbonates. Their results, together with previous studies on natural samples and laboratory experiments, provide a set of updated equilibrium Mg isotope fractionation factors related to carbonates, which lays the foundation for using Mg isotopes in carbonates to reconstruct paleoenvironmental changes with marine and terrestrial records.

Ryu et al. (2016) investigated Mg isotope fractionations during biotite dissolution through a series of leaching experiments and during clay formation (lizardite and kerolite). The leaching solutions are always enriched in light Mg isotopes, with their Mg isotopic compositions depending on a balance between the relative proportions of labile and structural Mg. By contrast, the synthetic clays are always enriched in heavy Mg isotopes. These experimental results are consistent with previous studies of other type of clays and natural samples, and help to better understand behaviors of Mg isotopes during continental weathering.

Zhu et al. (2016) used Si isotope doping method to measure albite dissolution rates while a secondary phase is forming. They found this new technique is very robust and provides higher precision for measuring albite dissolution rates at near equilibrium conditions, which helps to resolve the long-standing problem of the field-laboratory discrepancy in silicate dissolution rates.

3. Isotopic tracers of environmental pathways, erosion and riverine transport, sedimentary and soil records

The ultimate goal of characterizing the behaviors of elements and isotopes in surface environments is to use them to trace important geological, biological, and hydrological processes. The rest of the papers in this volume do just that.

Symbiotic mycorrhizal fungi can play a critical role in rock weathering by targeting minerals that contain required plant nutrients. Remiszewski et al. (2016) coupled field experiments with geochemical analyses and studied nutrient cycling (P, Mg, Ca) in forest landscapes dominated by arbuscular-mycorrhizal (AM) and ectomycorrhizal (EcM) fungi in Hubbard Brook Experimental Forest in New Hampshire, USA. In-growth bags containing different rock types of varying nutrient contents (granite, tonalite) were fabricated to create an in-situ geologic gradient. Only Ca concentrations in the exchangeable solution varied significantly between the two fungal types. Concentrations of other nutrients (Mg, P) and Pb and Sr isotopic compositions of the exchangeable and weathering solutions were not significantly different within lithology. Their results suggested that weathering fluxes in AM- and EcM-dominated forest stands may be more comparable than previously argued.

Soil erosion continuously redistributes soil and associated soil organic matter (SOM) on the Earth's surface, with important implications for biogeochemical cycling of essential elements and terrestrial carbon sequestration. McCorkle et al. (2016) used natural abundance levels of the stable and radioactive isotopes of C (^{13}C and ^{14}C) and stable isotope of nitrogen (^{15}N) to elucidate the origins of SOM eroded from low-order catchments along the western slopes of the Sierra Nevada of California, USA. Their results suggested that surface (sheet) erosion, as opposed to channeling through established streams and episodic mass wasting events, is likely the largest source of sediment exported out of these minimally disturbed, headwater catchments. The erosional export of sediments with a high concentration of C in the form of relatively undecomposed litter suggested that it is unlikely that soil erosion acts as a significant net sink for atmospheric CO_2.

The studies in soils are limited by the lack of reliable dating tools. Deng et al. (2016) conducted $^{40}Ar/^{39}Ar$ laser incremental heating analyses in potassium-bearing Mn-oxides from a weathering profile at the Zunyi manganese deposit, northern Guizhou Plateau, SW China. Their study constrains the timing and rate of chemical weathering in the Critical Zone and provides insights into paleoclimatic conditions for the formation of the weathering profile and associated Mn-oxides.

The travel time of siliciclastic sediments from continents to final deposition locations on the seafloor is an important parameter bearing on land–sea interactions and climate variability in marine sediment record. Li C. et al. (2016) measured ($^{234}U/^{238}U$) activity ratios of the lithogenic fraction from late Quaternary sediment deposited in the Okinawa Trough, East China Sea and calculated the comminution ages and transport times. Their study places an important constraint on time scale of sediment transport process in East Asia marginal sea, illustrating the potential of this U-series approach to decipher climate-related changes in the mode of supply of lithogenic sediment to marginal seas.

The “dolomite problem”, i.e., the lack of dolomite formation in the modern ocean in contrast to the massive dolomites in the deep time, is still puzzling geologists. Li F.-B. et al. (2016) measured Mg isotopic compositions of ribbon rock samples from the Ediacaran Doushantuo Formation in South China, with the aim to constrain ribbon rock dolomitization and to better understand the processes responsible for dolomite formation. They found these ribbon rocks have overall light Mg isotopic compositions, with marlstone layers enriched in heavy Mg isotopes than the limestone layers. These results suggest that the main source of Mg for dolomitization is seawater rather than clay minerals. Thus, Ribbon rock dolomitization provides a plausible mechanism for ancient dolomite formation in carbonate platform.

4. Concluding remarks

As the papers in this volume illustrate, the field of Critical Zone studies by isotopes is evolving rapidly. These and many previous isotopic studies have provided great insights into weathering, soil formation, erosion, riverine transport and environmental pathways in the Critical Zone. Yet, some fundamental questions in the Critical Zone research remain unanswered (e.g., see reviews of Brantley et al. 2011; Banwart et al. 2013). As the research in this field has brought together a wide range of multidisciplinary expertise, we believe that the isotope geochemical community can work even more closely with the Critical Zone community to provide a major international capability to deliver transformative science advances.

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References

Banwart, S.A., Chorover, J., Gaillardet, J., Sparks, D., White, T., Anderson, S., Aufdenkampe, A., Bernasconi, S., Brantley, S.L., Chadwick, O., Dietrich, W.E., Duffy, C., Goldhaber, M., Lehnert, K., Nikolaidis, N.P., Ragnarsdottir, K.V., 2013. Sustaining Earth's Critical Zone - Basic Science and Interdisciplinary Solutions for Global Challenges. The University of Sheffield, United Kingdom 48pp., ISBN: 978-0-9576890-0-8.

Brantley, S.L., White, T.S., Ragnardottir, K.V., 2007. The Critical Zone: where rock meets life. Elements 3 (5), 307–339.

Brantley, S.L., Megonigal, J.P., Scatena, F.N., Balogh-Brunstad, Z., Barnes, R.T., Bruns, M.A., Van Cappellen, P., Dontsova, K., Hartnett, H.E., Hartshorn, A.S., Heimsath, A., Herndon, E., Jin, L., Keller, C.K., Leake, J.R., McDowell, W.H., Meinzer, F.C., Mozdzer, T.J., Petsch, S., Pett-Ridge, J., Pregitzer, K.S., Raymond, P.A., Riebe, C.S., Shumaker, K., Sutton-Grier, A., Walter, R., Yoo, K., 2011. Twelve testable hypotheses on the geobiology of weathering. Geobiology 9 (2), 140–165.