



Originally published as:

von Blanckenburg, F., Schuessler, J. A. (2014): Element Cycling in the Critical Zone as Viewed by New Isotope Tools. - *Procedia earth and planetary science*, 10, p. 173-178.

DOI: <http://doi.org/10.1016/j.proeps.2014.08.053>



Geochemistry of the Earth's Surface meeting, GES-10

Element cycling in the Critical Zone as viewed by new isotope tools

Friedhelm von Blanckenburg^{a,b*}, Jan A. Schuessler^a

^a GFZ German Research Centre for Geosciences, Section 3.4 Earth Surface Geochemistry, Telegrafenberg, D-14473 Potsdam, Germany

^b Department of Earth Sciences, Institute of Geological Sciences, Freie Universität Berlin, Germany

Abstract

Isotope Geochemists are dedicating substantial effort at developing isotope ratio-based tools that are now beginning to provide detailed insights into the processes that cycle elements between the compartments of the weathering zone. The first group makes use of the metal and metalloid elements of which the stable isotope ratios shift mainly when a) secondary minerals are formed; b) elements are cycled through higher plants. Distinct stable isotope ratios emerge for a given cycled element as a function of the isotope fractionation factor of the process involved and of the elements' relative fluxes through these compartments (e.g. soil water, secondary minerals, plants, remaining primary minerals). A second tool provides absolute fluxes from the weathering zone: The ratio of the meteoric cosmogenic nuclide ^{10}Be ($T_{1/2} = 1.39$ My) to the stable isotope ^9Be combines a tracer of roughly known flux to the Earth's surface (over time scales characteristic of weathering) with one that depends on its release rate from rock by weathering. The resulting $^{10}\text{Be}/^9\text{Be}$ isotope ratio discloses both the Earth surfaces' denudation rate and its weathering intensity. For both tools, a set of steady state mass balance equations describe these systems from the scale of a soil column over the hillslope scale to an entire river basin.

© 2014 Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

Peer-review under responsibility of the Scientific Committee of GES-10

Keywords: Stable isotopes; mass fractionation; meteoric cosmogenic isotopes; weathering; erosion

1. Introduction

The formation of soil, the physically mobile material mantling much of the Earth's surface, entails massive geochemical transformations. Primary minerals contained in the unweathered substrate dissolve and the released solutes are available for discharge in groundwater, formation of secondary minerals, or utilization as nutrients by plants. These chemical weathering reactions generate a solute mass loss flux (W , Fig. 1). The remaining solid residue is eroded (E). The sum of all mass loss rates ($E + W$) is the total denudation rate (D) of a landscape. The

* Corresponding author. Tel.: +49-331-288 28 50
E-mail address: fvb@gfz-potsdam.de

principle processes are coupled to each other and are often repeated in multiple cycles. Significant progress towards understanding the couplings of these processes would be made if one were able to extract the ‘story’ and the ‘speed’ each particle or molecule experienced during its unique history of dissolution, uptake, and transport. The opportunity to extract this information is now offered in the form of new isotope methods^{1,2}.

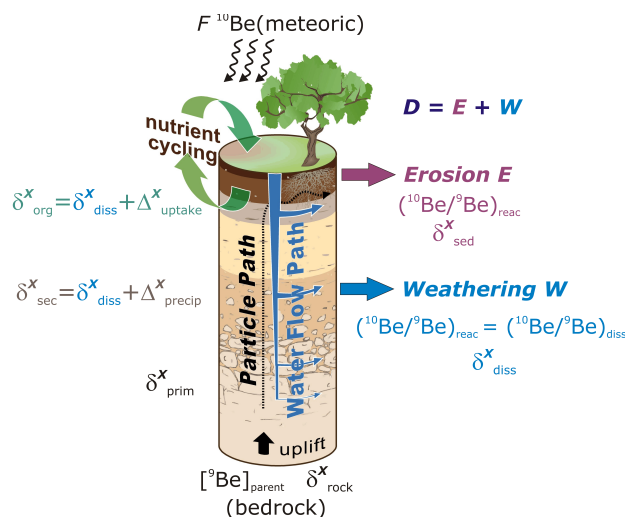


Fig. 1. Pathways of elemental and isotopic fluxes in the Critical Zone. Elements are released from bedrock into the weathering zone in the dissolved and the particulate form. Stable isotopes are fractionated mainly by formation of or adsorption onto secondary minerals and uptake into plants. ^{10}Be from bedrock is mixed with meteoric ^{10}Be delivered from the atmosphere. These processes generate specific isotope signatures in the different Critical Zone compartments. These transformations are recorded once the elements have been exported in the dissolved form (weathering mass flux W , in $\text{kg m}^{-2} \text{yr}^{-1}$), or in particulate form (erosion mass flux E in $\text{kg m}^{-2} \text{yr}^{-1}$, containing primary minerals, secondary minerals and plant litter) into rivers.

First, minute shifts in the relative abundances of stable isotopes of elements that differ in their relative atomic mass occur through dissolution, adsorption/desorption, oxidation/reduction, uptake by plants, and changes in the ligand an element binds to. This effect, called *stable isotope fractionation*, has been known for many years to affect the lighter elements such as oxygen, hydrogen and carbon. Since about 15 years, analytical advances have accelerated new developments in stable isotope geochemistry and isotope variations have been detected for virtually all metals (e.g., Li, Mg, Ca, Fe, Sr, Mo) and metalloids (e.g., B, Si) that have more than one stable isotope. Geochemists are now exploring these isotope ratio shifts so that these novel stable isotopes can be attributed to distinct physico-chemical processes and the isotopic fingerprints they carry can be deciphered³.

Second, the meteoric variety of cosmogenic nuclides, *meteoric* ^{10}Be , offers widely unexploited potential, (1) being an excellent geochemical tracer of the way water from precipitation interacts with solid matter, and (2) being suitable for determining erosion rates of surfaces⁴. When used in conjunction with its stable counterpart ^9Be , released from rock by weathering, one combines the advantage of the meteoric ^{10}Be nuclide, delivered at known rates, and the ^9Be flux, being higher the more ^9Be is released by weathering². Thus, this ratio has been suggested to be a proxy for denudation⁵⁻⁷, but has never been tested as such in hillslope settings. Meteoric ^{10}Be has traditionally been used as a mono-isotopic fallout tracer⁴. Its application has now been extended to provide large-scale estimates from the $^{10}\text{Be}/^9\text{Be}$ ratio in seawater and authigenic sediment⁸.

This contribution summarizes conceptual models that have been recently developed by our group to convert the information that metal stable isotopes¹ and the $^{10}\text{Be}(\text{meteoric})/^9\text{Be}$ ratio² offer to decipher processes and fluxes of metals and metalloids in the Critical Zone. These models are based on a simple mass balance, the main assumption of which is that over some time scale, the fluxes in and out of the Critical Zone balance each other. The

development and application of these isotope systems is underpinned by analytical developments, for example by providing the ability to measure metal and metalloid stable isotope ratios at the micrometer scale⁹ and to extract distinct solid weathering zone compartments chemically¹⁰.

2. Metal stable isotopes in the Critical Zone

Mass-dependent isotope fractionation means (1) that a stable isotope ratio of a particular element changes based on the very small differences in the physico-chemical behaviour between these isotopes that depend on their relative mass difference, and (2) that this isotope fractionation gets apparent when an element is non-quantitatively transferred from one compartment into another (e.g., from water to mineral; from soil solution to plant cell). The magnitude of the isotopic ratio shift is controlled by the fractionation factor of the reaction and by the relative amount of the element transferred. To deconvolve these two effects, Bouchez et al.¹ designed a steady state, mixed throughflow reactor, mass balance model representing the weathering zone from the soil scale to the large river scale. We assume the main fractionating processes being formation of secondary precipitates such as clays, or adsorption onto their surface, and uptake by plants. The model shows that:

$$\delta_{diss}^X - \delta_{rock}^X = -\Delta^X \cdot \frac{E_{org+sec}^X}{S_{rock+prim}^X} \quad (1)$$

where δ_{diss}^X and δ_{rock}^X are the isotope composition of the element X in the dissolved load and in the source rock, respectively, Δ^X the flux-weighted combined isotope fractionation factor including the fractionations generated by secondary mineral formation and uptake by plants, respectively, $E_{org+sec}^X$ represents the export flux of X in isotopically fractionated solids (organics and secondary precipitates), and $S_{rock+prim}^X$ the release flux of X to water through primary mineral dissolution. The main predictions are: For very “soluble” elements (i.e., those with a low affinity for secondary precipitates and that these are easily redissolved from plant litter or secondary minerals), virtually no fractionated solid is exported, and δ_{diss}^X is likely to be close to the source rock, δ_{rock}^X . Therefore, such elements are not viable tracers of weathering processes. Equation (1) further predicts that the largest difference in isotope ratios can be observed between source rock and dissolved species, where the transfer of an element between the former compartments is not quantitative and when the export of element X is greatly in favour of either solid or dissolved export. Here, the measured difference in isotope ratios, $\delta_{diss}^X - \delta_{rock}^X$, is equal to the combined isotope fractionation factor of all processes at play in the weathering zone. The validity of these predictions are verified using an extensive database of measured water and rock isotope compositions and a compilation of experimentally determined isotope fractionation factors for Li, B, Mg, Si and Ca: It is observed that most $\delta_{diss}^X - \delta_{rock}^X$ data fall indeed between 0 (source rocks) and published isotope fractionation factors, $-\Delta^X$ for each of these elements¹. Only for Ca, most of the $\delta_{diss}^{Ca} - \delta_{rock}^{Ca}$ values are small compared to estimates of the fractionation factors $-\Delta^{Ca}$ of the potentially contributing reactions. The cause for the absence of expressed fractionation might be the high solubility of Ca, rendering its isotopes less suitable to trace weathering processes as all Ca might be partitioned into the dissolved compartment.

We can reduce this model to the comparison of relative isotope ratios only, that then become a function of the ratio of fluxes, without the need to know the involved fractionation factors. The relationship between the ratio of solid-to-dissolved export of X , E^X/W^X (or expressed as the non-dimensional fraction of X exported as dissolved species, $w^X = W^X/(W^X + E^X)$) and the isotope ratios in the weathering system compartments, can be obtained from¹:

$$\frac{\delta_{diss}^X - \delta_{rock}^X}{\delta_{sed}^X - \delta_{rock}^X} = -\frac{E^X}{W^X} = -\frac{1 - w^X}{w^X} \quad (2)$$

An example for the use of equation (2) in various Critical Zone settings is shown in Fig. 2 for Si in Puerto Rico, Mg in Greenland, Mg in the Azores, and Li in Iceland. The figure shows the fraction of an element that is exported in the dissolved form, and also the ratio at which it is eroded relative to its dissolved loss. Note that where the isotope

differences in equation (2) become small, the errors of this estimate are amplified.

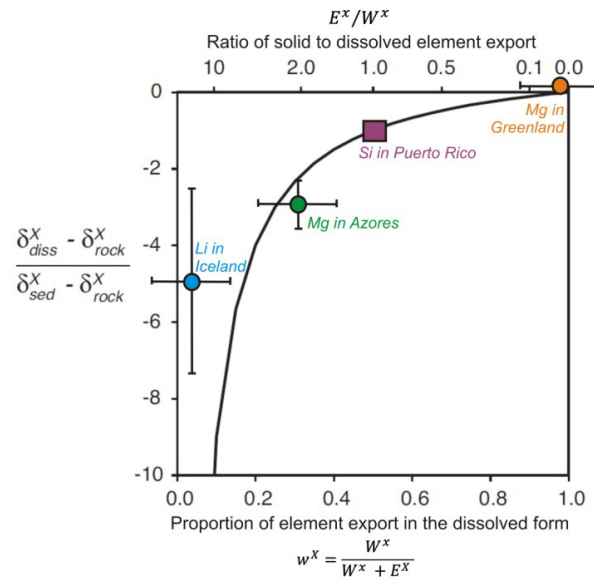


Fig. 2. The ratio of an element exported from the Critical Zone in the solid to that exported in the dissolved form (upper x-axis) and the fraction of elemental weathering export w^x (lower x-axis) as calculated from stable isotope ratios. This relationship from eq. 2 is shown by the black curve. Data points on the y-axis show isotope data that are from Ziegler et al.¹¹ for Si in Puerto Rico weathering zone materials. The other sites show isotopes from river suspended and dissolved loads and are from Pogge von Strandmann et al.¹² for Mg in Azores, Wimpenny et al.¹³ for Mg in Greenland, and Pogge von Strandmann et al.¹⁴ for Li in Iceland. Data points on the x-axis show an independent estimate from river loads, where the high errors of these estimates account for sorting effects. Only in Puerto Rico the independently derived Si flux ratios are from soil weathering estimates as calculated by White et al.¹⁵ that are not subject to sorting.

3. The $^{10}\text{Be}(\text{meteoric})/^{9}\text{Be}$ ratio

The $^{10}\text{Be}(\text{meteoric})/^{9}\text{Be}$ ratio combines a proxy for the Be flux deposited onto the Earth surface from the atmosphere at a known rate with a flux proxy depending on the release rate from the solid substrate during erosion/weathering. Meteoric ^{10}Be alone has been used to determine erosion rates from meteoric ^{10}Be adsorbed to bulk soil or sediment⁴. The erosion rate can be calculated following equation (3)²:

$$E = \frac{F_{\text{met}}^{10\text{Be}}}{[^{10}\text{Be}]_{\text{reac}}} - \frac{Q}{K_d} \quad (3)$$

where $F_{\text{met}}^{10\text{Be}}$ is the flux of meteoric ^{10}Be to the Earth's surface (in atoms $\text{m}^{-2} \text{yr}^{-1}$), E is the erosion flux (in $\text{kg m}^{-2} \text{yr}^{-1}$), and $[^{10}\text{Be}]_{\text{reac}}$ is the concentration of reactive (adsorbed and precipitated) ^{10}Be (in atoms kg^{-1}). However, the retention of $^{10}\text{Be}_{\text{reac}}$ depends on water discharge and the Be partition coefficient K_d (in L kg^{-1} , depending strongly on grain size) that links Be concentrations in the reactive and dissolved phases⁴. Accordingly, equation (3) has been complemented² to account for this loss into solution, where Q is the water flux out of the system (in $\text{m}^3 \text{m}^{-2} \text{yr}^{-1}$ or equivalently in m yr^{-1}). We ignore radioactive decay of ^{10}Be as the half life (1.39 My) is much longer than the mean residence time of ^{10}Be in the weathering zone in most natural settings.

Another way to cancel out the loss of ^{10}Be is to use the reference stable isotope ^9Be . ^9Be is typically present at concentrations of 2 to 3 ppm in silicate rocks (global felsic rock and clastic sediment average), is released and partitioned between a reactive phase (adsorbed to clay and hydroxide surfaces, given the high partition coefficients at intermediate pH), and into the dissolved phase (Fig. 1). The combined mass flux of both phases is defined by the weathering advance rate and a mineral dissolution rate – and is hence proportional to the chemical weathering rate

and the denudation rate. At the same time, the surface of the weathering zone is continuously exposed to fallout of meteoric ^{10}Be . This ^{10}Be percolates into the weathering zone where it mixes with dissolved ^9Be . Both isotopes may exchange with the adsorbed Be within a few days to weeks, so that the equilibration rate of Be is fast relative to soil residence times. Hence a $^{10}\text{Be}/^9\text{Be}(\text{reactive})$ ratio results from which the total denudation rate can be calculated. A prerequisite is that the flux of meteoric ^{10}Be is known from field experiments⁴ or from global production models¹⁶. In the terminology of von Blanckenburg et al.² $(^{10}\text{Be}/^9\text{Be})_{\text{diss}}$ is the isotope ratio of Be dissolved in river waters (Be_{diss}); and $(^{10}\text{Be}/^9\text{Be})_{\text{reac}}$ is the isotope ratio of reactive Be (Be_{reac}) adsorbed onto the particulate load of rivers and contained in Be-rich secondary phases, such as Fe-Mn oxihydroxides. This reactive compartment can be extracted chemically¹⁰. Provided the contact time between river water and river particles is sufficiently long, $(^{10}\text{Be}/^9\text{Be})_{\text{reac}}$ and $(^{10}\text{Be}/^9\text{Be})_{\text{diss}}$ equilibrate during riverine transport to a homogeneous ratio as shown previously². If we assume that the ^{10}Be and the ^9Be fluxes that enter the weathering zone balance those that leave the zone over some time scale, a steady state ratio can be calculated for a given river over this time scale:

$$\left(\frac{^{10}\text{Be}}{^9\text{Be}}\right)_{\text{reac}} = \left(\frac{^{10}\text{Be}}{^9\text{Be}}\right)_{\text{diss}} = \frac{F_{\text{met}}^{10\text{Be}}}{D \cdot [^9\text{Be}]_{\text{parent}} \cdot (f_{\text{reac}}^{9\text{Be}} + f_{\text{diss}}^{9\text{Be}})} \quad (4)$$

where D is the soil's or river basin's denudation rate that comprises both physical erosion and chemical weathering (in $\text{kg m}^{-2} \text{yr}^{-1}$), $[^9\text{Be}]_{\text{parent}}$ is the mean ^9Be concentration of the river basin's parent rock (in atoms kg^{-1} or mol kg^{-1}), and $f_{\text{reac}}^{9\text{Be}} + f_{\text{diss}}^{9\text{Be}}$ is the fraction of ^9Be released during weathering from the parent rock, i.e., the fraction of ^9Be that is ultimately available for mixing with dissolved ^{10}Be .

Figure 3 shows the results of a comparison of denudation rate D calculated from $^{10}\text{Be}/^9\text{Be}$ compiled from the literature, including both dissolved and reactive Be in global rivers, where D from meteoric $^{10}\text{Be}/^9\text{Be}$ was compared to an independent estimate of D from either river loads or *in situ*-produced cosmogenic ^{10}Be . The encouraging agreement between both estimates was obtained from fitting the meteoric-derived D by using a global $f_{\text{reac}}^{9\text{Be}} + f_{\text{diss}}^{9\text{Be}}$ of 0.2. Given that a large fraction of ^9Be resides in easily weatherable plagioclase and biotite¹⁷, this unexpectedly low fraction of ^9Be released by weathering presumably implies that the data includes a substantial proportion of shale-bearing catchments, in which the ^9Be is retained unweathered in illite or muscovite.

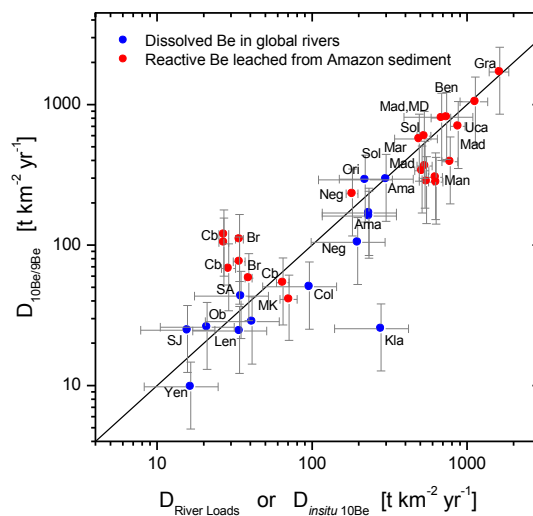


Fig. 3 Comparison of catchment-wide denudation rates D calculated from $^{10}\text{Be}/^9\text{Be}$ using eq. (4) (y-axis) (compilation in ²). Blue symbols represent D from dissolved Be in rivers; on the x-axis an independent estimate of D from river load gauging. Data with red symbols are derived from $^{10}\text{Be}/^9\text{Be}$ measured on the reactive (leached) Be on Amazon sediment, whereas D on the x-axis was independently determined from *in situ*-formed ^{10}Be in river quartz. D from $^{10}\text{Be}/^9\text{Be}$ was calculated using $[^9\text{Be}]_{\text{parent}}$ of 2.5 ppm, $F_{\text{met}}^{10\text{Be}}$ of 1×10^6 atoms $\text{cm}^{-2} \text{yr}^{-1}$, and $f_{\text{reac}}^{9\text{Be}} + f_{\text{diss}}^{9\text{Be}}$ of 0.2.

4. Conclusions

These results represent only a first (but encouraging) picture of these emerging isotopic tools. Important efforts to make these models more applicable are those that refine the separation techniques for isotope measurements to target specific compartments of the Critical Zone, to determine more stable isotope fractionation factors (mainly for plant uptake and secondary mineral formation), to explore how and where isotopes (of both stable metals and Be) exchange, and at what time scale, to explore over what spatial and what temporal scale the assumption of steady state of fluxes is actually valid, and whether transient effects should be rather represented by the Rayleigh fractionation equation. Finally, reactive transport models will be developed that explore these systems and the associated isotope fractionation as solutes are released at the weathering front and then move through porous media with fluid-solid interaction. However, this level of detail, while required to understand Critical Zone processes, is not available when isotope ratios are used as measured in the sedimentary record as proxies for past weathering and erosion processes. Already now, such models are available for use in authigenic seawater precipitates, such as for Li^{18} (remodelled¹) or the Be seawater record^{7,8}.

Acknowledgements

We are indebted to Julien Bouchez (formerly GFZ Potsdam) for his major contributions towards developing the mass balance models. Hella Wittmann is acknowledged for her contributions towards developing the $^{10}\text{Be}/^9\text{Be}$ proxy in large river basins, and Sue Brantley for a review of this article.

References

1. Bouchez J, von Blanckenburg F and Schuessler JA. Modeling novel stable isotope ratios in the weathering zone. *American Journal of Science*. 2013; 313: 267-308.
2. von Blanckenburg F, Bouchez J and Wittmann H. Earth surface erosion and weathering from the ^{10}Be (meteoric)/ ^9Be ratio. *Earth and Planetary Science Letters*. 2012; 351-352: 295-305.
3. Bullen T and Eisenhauer A. Metal stable isotopes in low-temperature systems: a primer. *Elements*. 2009; 5: 349-52.
4. Willenbring JK and von Blanckenburg F. Meteoric cosmogenic Beryllium-10 adsorbed to river sediment and soil: applications for Earth-surface dynamics. *Earth Science Reviews*. 2010; 98: 105-22.
5. Brown ET, Measures CI, Edmond JM, Bourles DL, Raisbeck GM and Yiou F. Continental inputs of Beryllium to the oceans. *Earth and Planetary Science Letters*. 1992; 114: 101-11.
6. von Blanckenburg F, O'Nions RK, Belshaw NS, Gibb A and Hein JR. Global distribution of Beryllium isotopes in deep ocean water as derived from Fe-Mn crusts. *Earth and Planetary Science Letters*. 1996; 141: 213-26.
7. Willenbring JK and von Blanckenburg F. Long-term stability of global erosion rates and weathering during late-Cenozoic cooling. *Nature*. 2010; 465: 211-4.
8. von Blanckenburg F and Bouchez J. River fluxes to the sea from the oceans $^{10}\text{Be}/^9\text{Be}$ ratio. *Earth and Planetary Science Letters*. 2014; 387: 34-43.
9. Schuessler JA and von Blanckenburg F. Testing the limits of micro-scale analyses of Si stable isotopes by femtosecond laser ablation multicollector inductively coupled plasma mass spectrometry with application to rock weathering. *Spectrochimica Acta Part B: Atomic Spectroscopy*. 2014; 98: 1-18.
10. Wittmann H, von Blanckenburg F, Bouchez J, et al. The dependence of meteoric ^{10}Be concentrations on particle size in Amazon River bed sediment and the extraction of reactive $^{10}\text{Be}/^9\text{Be}$ ratios. *Chemical Geology*. 2012; 318-319: 126-38.
11. Ziegler K, Chadwick OA, White AF and Brzezinski MA. $\delta^{30}\text{Si}$ systematics in a granitic saprolite, Puerto Rico. *Geology*. 2005; 33: 817-20.
12. Pogge von Strandmann PAE, Burton KW, James RH, van Calsteren P and Gislason SR. Assessing the role of climate on uranium and lithium isotope behaviour in rivers draining a basaltic terrain. *Chemical Geology*. 2010; 270: 227-39.
13. Wimpenny J, James RH, Burton KW, Gannoun A, Mokadem F and Gislason SR. Glacial effects on weathering processes: New insights from the elemental and lithium isotopic composition of West Greenland rivers. *Earth and Planetary Science Letters*. 2010; 290: 427-37.
14. Pogge von Strandmann PAE, Burton KW, James RH, van Calsteren P, Gislason SR and Mokadem F. Riverine behaviour of uranium and lithium isotopes in an actively glaciated basaltic terrain. *Earth and Planetary Science Letters*. 2006; 251: 134-47.
15. White AF, Blum AE, Schulz MS, et al. Chemical weathering in a tropical watershed, Luquillo mountains, Puerto Rico: I. Long-term versus short-term weathering fluxes. *Geochim Cosmochim Acta*. 1998; 62: 209-26.
16. Heikkilä U, Beer J, Abreu JA and Steinhilber F. On the Atmospheric Transport and Deposition of the Cosmogenic Radionuclides (Be-10): A Review. *Space Sci Rev*. 2013; 176: 321-32.
17. Grew ES. Beryllium in Metamorphic Environments (emphasis on aluminous compositions). *Reviews in Mineralogy and Geochemistry*. 2002; 50: 487-549.
18. Misra S and Froelich PN. Lithium Isotope History of Cenozoic Seawater: Changes in Silicate Weathering and Reverse Weathering. *Science*. 2012; 335: 818-23.