Determination of chemical weathering rates from U series nuclides in soils and weathering profiles: Principles, applications and limitations

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A B S T R A C T
The development of U-series nuclides for investigating weathering processes has been significantly stimulated by the analytical improvement made over the last decades in measuring the 238U series with intermediate half-lives (i.e., 234U–230Th–226Ra). It is proposed in this paper to present principles and methods that are now being developed to determine weathering rates from the study of U-series nuclides in soils and weathering profiles. Mathematical approaches, developed to calculate such rates, are based on some implicit assumptions that are also presented and must be kept in mind if one wants to correctly interpret the obtained ages.

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1. Introduction

By the 1960s it was recognized that U-series nuclides have great potential for study of weathering processes and rates (Rosholt et al., 1966; Hansen and Stout, 1968). This is because the nuclides are fractionated during water–rock interaction and have radioactive decay half-lives of the same order of magnitude as the time constants of many weathering processes (e.g. Ivanovich and Harmon, 1992; Chabaux et al., 2003a, 2008). Recent developments in this field of research are clearly related to the analytical improvements made during the past decades in measuring 238U series nuclides with intermediate half-lives (i.e., 234U–230Th–226Ra) (e.g., in Bourdon et al., 2003). In contrast to cosmogenic nuclides, or the U–Th/He chronometer, which provide information on denudation rates, U-series nuclides in soils relate directly to production rates of regolith (soils, weathering profiles). Applying both types of chronometers to the same weathering system should allow significant progress in understanding the coupling between weathering and erosion processes (Ma et al., 2010). In this paper principles and methods that are now being developed to determine weathering rates from the study of U-series nuclides in soils and weathering profiles are presented, and some of their limitations discussed.

2. Fractionation among U-series nuclides in soils and weathering profiles

Determining weathering front propagation rates in regolith with U-series nuclides is based on the assumption that fractionation among nuclides from the same radioactive decay series is controlled by weathering processes. The earliest studies showed that U-series disequilibrium across a weathering profile cannot often be described by a simple scheme in which fractionation occurs at the base of the profile and the U–Th system subsequently returns to secular equilibrium in the overlying horizons (e.g., Rosholt et al., 1966; Boulad et al., 1977; Rosholt, 1982; Mathieu et al., 1995; Dequincey et al., 1999). One example of a system with such simple behavior is a basaltic clast from an alluvial terrace in Costa Rica (Pelt et al., 2008). In that system, U–Th were fractionated at the transition between the fresh basalt and the weathering rind (marked by an U enrichment) and no further fractionation occurred within the rind itself. All other studies show that U–Th fractionations extend into weathering profiles above the base of the regolith (Dequincey et al., 2002; Dosseto et al., 2008; Blaes et al., 2009; Ma et al., 2010).

Interpreting (and hence modeling) U–Th disequilibria in weathering profiles, therefore, requires a complete understanding of the fractionation of U–Th and the relevant daughter isotopes. Such information can be retrieved by the comparison of U-series data with mineralogical and/or other geochemical data (major and trace element concentrations, Sr isotope ratios, etc.) (Dequincey et al., 2002; Chabaux et al., 2003a; Pelt et al., 2008; Ma et al., 2010; Blaes et al., 2009). These studies show that, in contrast to earlier assumptions, U–Th fractionation in weathering profiles cannot only be

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described in terms of U leaching/loss processes but also by U gain. Such scenarios involving gain and loss of U easily explain, for instance, the occurrence of \((^{234}\text{U}/^{238}\text{U})\) activity ratios > 1 with \((^{230}\text{Th}/^{238}\text{U})\) ratios < 1 within the same regolith sample, which is otherwise hard to reconcile with simple U leaching (Chabaux et al., 2008). Several of these studies have also shown that Th, often supposed to be immobile during weathering, can be mobilized (e.g., Ma et al., 2010; Chabaux et al., 2008). Analogous to U, Th mobilization can occur by Th complexation with inorganic (phosphates, fluorides, Fe-Al oxy-hydroxides) and organic (humic, fulvic acids) ligands and more generally by Th adsorption on colloidal soil phases including clays. The modeling of U-Th fractionalation in soil and weathering profiles can, therefore, no longer be solely explained by U gain and loss processes, but must also involves Th mobility.

The enrichment of U and probably of Th in soils might have multiple origins. In the African (Kaya) lateritic toposequence, U–Th disequilibrium in the saprolite can be related to the downward migration of U originating from the breakdown of the uppermost iron cap; in this case the U enrichments in specific soil levels result from local redistributions of U within the regolith profile (Dequeney et al., 2002, 2006; Chabaux et al., 2003b). This is also illustrated in the U–Th study of the Shale Hill Critical Zone observatory in Pennsylvania (Ma et al., 2010). Uranium-enrichments recorded in those profiles/toposequences thus do not require any external (e.g., atmospheric) contribution. This is consistent with studies suggesting that the impact of atmospheric U input onto the U river budget is generally negligible (Riotte and Chabaux, 1999; Chabaux et al., 2005). Nevertheless, the generalization of such a conclusion is probably not justified. Pett-Ridge et al. (2007) have shown that dry deposition contributes significantly to the U budget of Hawaiian soils. Similarly, isotope ratios in two basaltic soil profiles developed on Mount Cameroon point to an African eolian dust contribution of about 10% in the U and Th budget (Pelt, 2007). Future studies, including the analysis of atmospheric deposits along with soil toposequences, are needed to constrain the contribution of atmospheric deposits to the U and Th budgets of soils and weathering profiles.

3. Modeling U-series nuclides mobility within weathering profiles

Interpretation of the U-series radioactive disequilibria within soils and weathering profiles requires understanding migration mechanisms of U-series nuclides during loss or gain of the radionuclides. The mathematical formalism of this dual process is obviously not unique. However, given the nature of the soil formation processes and the radioactive decay of the nuclides, these data can often be interpreted in terms of continuous processes (e.g., Dequeney et al., 2002). Moreover, given the limited knowledge of the precise mechanisms controlling the mobility of these nuclides within weathering profiles, it seems premature to model these processes by overly complex mechanistic laws. Therefore, simple mathematical models are used where the loss processes are represented by first-order and the gain processes by zero-order kinetic rate laws. The general equations controlling these dual processes are given below for the parental nuclide \(p\) and an intermediary nuclide \(i\) of a radioactive decay series:

\[
\frac{dN^p}{dt} = F_p - k_p N^p - \lambda_p N^p \quad (1)
\]

\[
\frac{dN^i}{dt} = F_i - k_i N^i - \lambda_i N^i + \lambda_{i-1} N^{i-1} \quad (2)
\]

where \(N^i\) and \(N^p\) represents the number of nuclides \(i\) and \(p\) respectively, \(\lambda_i\) \((\lambda_p)\) is the decay constant of nuclide \(i\) \((p)\), \(k_i\) and \(k_p\) are the first-order rate constants describing the loss of nuclides \(i\) and \(p\), and \(F_i\) \((F_p)\) is the input flux of nuclide \(i\) \((p)\) gained by the regolith sample \((i-1\) is the parent nuclide of nuclide \(i)\).

Such equations have been applied in all recent studies to calculate regolith formation rates from \(^{238}\text{U}–^{234}\text{U}–^{230}\text{Th}\) disequilibria (Dosseto et al., 2008; Pelt et al., 2008; Ma et al., 2010; Blaes et al., 2009), and also, in some studies, to estimate the transfer time of sediments in an alluvial plain (Granet et al., 2007, 2010). They can be generalized for any other nuclide of the \(^{238}\text{U}\)-series, especially for \(^{226}\text{Ra}\) (Blaes et al., 2009), or the short half-life nuclides from the \(^{232}\text{Th}\) series.

4. Solutions to the mathematical equations

Usually the determination of a production rate from U-series disequilibrium in soils and weathering profiles relies on simplistic reasoning: it is assumed that weathering advances into underlying protolith in one direction, and samples collected along this direction are «dated» by U–Th disequilibrium chronometry (the age of the sample corresponds to the time when the sample became part of the weathering zone). Age variations along the weathering direction can then be used to determine the mean production rate of the regolith (i.e., the weathering advance rate). In most of the studies, it has been implicitly supposed that the principal weathering direction is vertical, and hence the production rate of a profile is determined by using age variations of soil samples from the base to the top of the profile. Usually, for such calculations the weathering advance rate is assumed to be constant in time along the weathering direction, which in turn implies the weathering to be isovolumetric (see also discussion in Ma et al. (2010)).

Generally speaking, the weathering parameters in the above equations (leaching and input parameters) are not known, and the measurement of radioactive disequilibrium of a single soil sample is not sufficient for the determination of its age. For instance, in the case of the \(^{238}\text{U}–^{234}\text{U}–^{230}\text{Th}\) chronometry, the three associated equations contain six unknown parameters (leaching and gain parameters) and one variable (time). The analysis of \(^{238}\text{U}–^{234}\text{U}–^{230}\text{Th}\) disequilibrium in one sample yields only two independent data \(\left(\frac{^{234}\text{U}/^{238}\text{U}}{}\right.\) and \(\frac{^{230}\text{Th}/^{234}\text{U}}{}\) activity ratios\), which are not enough to determine the age of the sample.

A first approach to solve the equations and to obtain ages of the soil samples and hence the production rate of the regolith is to consider the model parameters to be constant in the whole or in parts of the weathering profile (e.g. the Shale Hill study; Ma et al., 2010). In this case, the determination of the weathering rate necessitates the determination of the \(^{238}\text{U}–^{234}\text{U}–^{230}\text{Th}\) disequilibria in only four samples collected at different depths from a weathering profile. The sample number necessary for modeling decreases if other constraints can be introduced in the model: e.g., Th immobility during weathering, as reported for instance in the case of a lateritic profile in central Amazonia (Manaus, Brazil) (Pelt, 2007), reduces the parameter number to 4 (mobility coefficients) and allows the determination of weathering rates from \(^{238}\text{U}–^{234}\text{U}–^{230}\text{Th}\) analysis of only three samples. For the weathering rind of the basaltic cliff from the Costa Rica Terrace (Pelt et al., 2008), the analysis of only two rind sub-samples would be sufficient in theory to determine the rind formation rate since the U and Th isotopes were thought to be immobile. In all of those cases, zones within the weathering profiles were identified where the nuclide mobility parameters were constant: in other words, more than the required minimum number of samples were analyzed and the isotopic variations were consistent with the trends predicted by the model.

If there is no zone with constant mobility parameters, the above equation system is under-constrained. The age calculation of a soil sample is in this case only possible using an “inverse method”;
which necessitates a priori assumptions of model parameters. Solving the model equations involves an iterative procedure until convergence, at which point the solution yields a set of parameter values that satisfy the equations. Today, inverse methods often involve Monte Carlo randomized algorithms, which, with sensitivity analysis, help pinpoint the parameters that are the most influential in the model (Fajraoui et al., 2011). To the authors’ knowledge, inverse approaches have been rarely involved for the determination of weathering rates in soils. In a first attempt, it was applied in the U–Th study of the African Kaya lateritic profile (Chabaux et al., 2003b). This approach yielded time information about U redistribution after the breakdown of the iron cap in this weathering profile and revealed information relating U migration to climatic changes during the Quaternary.

5. Limits in the models

The weathering rates obtained from the U-series nuclides clearly depend on the model parameters; this is common in modeling and does not diminish the interest of the method. It only means that before using the model, its applicability to the studied case has to be verified/validated.

For instance, the kinetic laws used in the model equations for describing the radionuclide leaching (−kN terms in Eqs. (1) and (2), with k leaching kinetic constant of the nuclide N from the sample) implies that all the nuclides of the analyzed sample are mobile. When a fraction (z_{\text{mobile}}) of a nuclide N is not mobilizable, the kinetic law to be utilized should be: −k′N with k′ = k_0 (1 − z_{\text{mobile}}).

Similarly, if the nuclide N is carried by different mineral phases, each characterized by a specific leaching coefficient (the classical case of differential weathering), then the mean leaching coefficient used in Eqs. (1) and (2) should be written as follows: k = Σ[k_i], where k_i is the leaching coefficient of the nuclide N out of the mineral i and z_i the fraction of the nuclide N of the whole sample contained in the mineral i. In this case, except in some specific conditions, the mean k′ leaching coefficient of the nuclide N in the whole sample cannot be considered as constant over time. The consequence for such a weathering system is that the results derived from model equations, which assume the leaching coefficients to be constant over a part of the profile, have to be used with caution, i.e. not applied without validation.

Another point that has to be considered is the way to describe the ejection of a radioactive series nuclide from the solid grain due to alpha recoil. During an alpha radioactive decay, the nuclide recoil can be sufficient to induce an ejection of the daughter nuclide into solution (Kigoshi, 1971; Fleischer, 1988 and ref. therein), which occurs in addition to direct leaching of the nuclide from the rock. The content of an intermediary nuclide i of a radioactive decay series in a dissolving solid thus depends both on leaching and recoil alpha ejection whose intensity is proportional to the amount of the parent nuclide i − 1. The content of any intermediary nuclide of a radioactive series in a dissolving solid is, therefore, described by the equation:

\[
\frac{dN_i}{dt} = -k_iN_i - k_0N_i + \Delta_i(1 - f_i)N_{i-1}
\]

(3)

with f_i being the α-recoil loss fraction. This value is a function of the grain radius and the surface area, and k_i is the leaching coefficient of the nuclide N_i (the leaching process again approximated by first-order kinetic laws). From a mathematical point of view, this equation is not equivalent to the equation given in (2). This would only be the case if the ejection by alpha recoil were negligible compared to mobilization by leaching, or if the parent − daughter system remained close to secular equilibrium (i.e., \(\Delta_iN_i \approx \Delta_iN_{i-1}\)).

In conclusion, it is important to stress here that within the discussed limitations the mathematical approach developed to calculate weathering rates is based on some implicit model assumptions. These must be kept in mind and validated if one wants to correctly interpret the obtained ages. Further studies on physical–chemical parameters controlling absorption, desorption, complexation, etc. are needed in order to better constrain the processes and hence the models, controlling the mobility of radionuclides in the environment.

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References

Mathieu, D., Bernat, M., Nahon, D., 1995. Short-lived U and Th isotope distribution in a tropical laterite derived from Granite (Pitinga river basin, Amazonia,