

Using Rare Earth Elements as an Indicator of Soil Formation.

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Abstract: *Rare earth elements (REE) total concentration in soils are impacted by successive soil forming processes. So it can be used as indicator of soil development. Iron oxides and OM are known to have strong affinities with REE, and to play an important role in transfer and immobilization of REE. The ones available in the literature indicate that the release of REE induced by weathering and subsequent leaching in percolating water are the main pathways determining the REE fate in soils. Show that the REE content is strongly correlated to the general loss of elements and mineral weathering. In the redistribution of the elements resulting from weathering, the mobility of these elements and the geochemical changes at the end of the washing appear as the main determining factors. Weathering rate of soils is a fundamental approach to understanding and revealing the development processes of soils.*

Key Word : *Rare earth elements , Soil formation , Soil development*

1. INTRODUCTION

Trace elements, especially rare earth elements (REE), are used extensively in the geochemical separation and characterization of soils and rocks and in the investigation of soil weathering processes. In the past REE was thought to be immobile throughout the weathering. However, studies on this subject have shown that REE is also mobile at various rates within the weathering processes (Balashov et al., 1964; Ronov et al., 1967; Nesbitt, 1979; Boulouge et al., 1990; Braun et al., 1990).

It is known that the soil's REE concentration is influenced by sequential soil processes during pedogenesis (REE), REE is affected by a series of processes leading to internal degradation, such as solubility, oxidation, reduction, precipitation (Babechuk et al., 2014 ; ALSalam et al., 2020). In addition, the fractionation of REE and Eu and Ce are used extensively to reveal the severity of the weathering in the parent material and the characteristics of the weathering environment. (Chang et al., 2000; Nath et al., 2000; Worrall and Pearson, 2001; Cao et al., 2001; Chiarenzelli et al., 2001; Xiong et al., 2002; Das and Haake, 2003; Egashira et al. et al., 2004; Honda et al., 2004). The distribution of rare earth elements in soils is closely controlled by soil weathering (Caspari et al., 2006). Especially in polygenic soils, studies on soil genetics and origin, using easily leached and resistant to leaching rare earth elements give very good results. REE is also closely associated with minerals the soil (Braun and Pagel, 1994).

The group of rare earth elements (REE) consists of 14 elements (Saatz et al., 2015; Vermeire et al., 2016). It forms a series that behaves geochemically coherently owing to the small but steady decrease in ionic radius with increase in atomic number (Henderson, 1984; Panahi et al., 2000; Yusoff et al., 2013). They are considered as promising tracers in pedogenesis. During pedogenesis, REE signature is affected by a variety of processes (dissolution, oxydo-reduction, precipitation and complexation). These processes induce internal fractionations and anomalies related to REE mass or different oxidation states for Ce and Eu.

LREE (La-Nd) – (La, Ce, Pr, Nd).

MREE (Sm-Ho) – (Sm, Eu, Gd, Tb, Dy, Ho).

HREE (Er-Lu) – (Er, Tm, Yb, Lu).

Ce, Eu – (Eu/Eu*) and (Ce/Ce*)

Therefore REE losses are linked to an increase of the weathering stage. Feldspars and quartz are known to contain negligible amounts of REE with the exception of Eu in feldspars (Towell et al., 1969; Condie et al., 1995; Compton et al., 2003). Amphiboles can contain high concentrations in REEs and negative anomalies in Eu (Skublov and Drugova, 2003). The heavy minerals are rather stable through weathering (Nickel, 1973), the REEs included in these minerals are expected to accumulate in the weathered horizons. Therefore, this study aims to use the geochemical approach of rare earth elements as an indicator for soil formation.

Geochemical transformations in soil

Soils are formed as a result of the joint effect of soil formation factors (Jeny, 1941). Soil changes vary considerably depending on the time it takes for soil formation. These changes include issues such as mineral fragmentation and geochemical changes of elements and their cycles in the soil plant water system. The weathering rates of soils are very variable due to changes in soil properties and differences in environmental conditions. The time taken for soil formation affects the properties of soils and determines their rate of weathering. This effect occurs with events such as the change of physical, chemical and mineralogical properties over time or different numbers of horizon differentiation. In the early stages of formation, the chemical structure of soils is controlled by the parent material, while the chemical properties of mature soils reflect the effects of the weathering environment. Soil composition differs from the parent material with the pedogenic processes that occur with the effect of vegetation, topography and especially the climate over time. This differentiation initially occurs as the redistribution of elements in the soil profile and horizontalization, and finally as the differentiation of soil types depending on this distribution in the landscape. (Jenkins and Jones, 1980). However, even if the time taken for soil formation is the same, soil morphology and physico-chemical properties may differ with the effect of other soil-forming factors. There are different effects on the mobilization or redistribution of elements during weathering. Each element is affected differently by pedogenic processes such as dissolution of primary minerals, formation of secondary minerals, equilibrium processes, material transport, ion exchange. In the redistribution of the elements resulting from weathering, the mobility of these elements and the geochemical changes at the end of the washing appear as the main determining factors. Determining the age or weathering rate of soils is a fundamental approach to understanding and revealing the development processes of soils (Phillips, 1993; Schoetzl et al. 1994). Chemical weathering of rocks is the main geological process in the geological cycle of elements and change of the earth's surface. Therefore, the distribution and

fractionation of rare earth elements in different natural environments gives us information on this subject (Aiuppa et al., 2000; Phillips and Rojstaczer, 2001).

Rare earth elements in soil

The rare earth elements, or REE for short, include a group of yttrium and scandium elements together with the lanthanides. Lanthanides are a group of chemically similar elements with atomic numbers from 57 to 71. Yttrium with atomic number 39 and scandium with atomic number 21 are also included in rare earth elements with similar chemical properties to lanthanides. They got this name because it is thought that they are not found more than other minerals in the earth's crust. Lanthanides are divided into two groups as Light Rare Earth Elements (LREE) and Heavy Rare Earth Elements (HREE).

Minerals containing Rare Earth Elements, Chemical Formulas and Metal Oxide contents are included in a wide range of minerals including REE, halides, carbonates, oxide and phosphate. REE is largely found in rock-forming minerals, where they are mainly replaced by ions. In order for them to form their own minerals, REE concentrations must be higher. The distribution of rare earth elements in soils is closely controlled by soil weathering (Caspari et al., 2006).

REE is also closely related to accessory minerals in the soil (Braun and Pagel, 1994) and is composed of 14 elements known as lanthanides (La-Lu) with atomic weights ranging from 57 to 71. Those with atomic weights between 57 and 62 are called light rare earth elements (LREE), and those with relatively higher atomic weights between 63 and 71 are called heavy rare earth elements (HREE). The medium heavy rare earth elements (MREE) group is also used. Rare earth elements are not easily affected by weathering except in very rainy and hot climates. There are two elements that do not fit this situation. Europium is the only lanthanide that usually happens in a divalent oxidation state and whose behavior is strongly influenced by plagioclase. This results in the potential for Eu to fractionate from the other lanthanides during weathering, since plagioclase is one of the most susceptible minerals to chemical dissolution. The loss of Eu, measured with the Eu anomaly (Eu/Eu^*) is highly correlated with Ca and Na loss from plagioclase (Babechuk et al., 2014 ; ALSalam et al., 2020). Cerium can track redox-related transformations during pedogenesis in weathering profiles as a result of the potential oxidation of Ce^{3+} to Ce^{4+} (Middelburg et al., 1988; Mongelli, 1993; Gallet et al., 1996; Murakami et al., 2001; Patino et al., 2003; Dengiz et al., 2013; Babechuk et al., 2014). The relative abundance of these two elements is used to evaluate the redox behavior of the environment during the efficiency of geochemical processes. By comparing these elements with other lanthanides, the enrichment and washing rates are determined, and the chemical and geochemical behaviors accelerated by the changed charge balance are revealed. Lanthanides (REE) are elements found in very low amounts in the soil. Lanthanides take place in the structure of phosphate and silicate minerals in the soil. Many lanthanides are in close association with Fe minerals. The lanthanides form trivalent complexes with humic compounds, oxalic acid, and other electronegative ligands. Another indicator of weathering in soils is the presence of heavy (HREE) or light rare earth elements (LREE) enrichment. LREE is closely related to the amount and movement of clay in the soil. Because LREE is kept within the clays to a significant extent. In this context, $\text{La(N)}/\text{Yb(N)}$ values, which are an indicator of LREE/HREE in soils. The change in the amount of REE in the sediments or soil provides information about the provenance studies of the sediments as well as the deposition processes depending on the weathering (Taylor and McLennan, 1985;

Last and Smol, 2001). The normalized REE distribution is used to express the degree of weathering of soils (Rollinson, 1993; McLennan, 1989). Fractionation of the REE (Sm/Nd, Eu/Eu*, Ce/Ce*) is evident during weathering soil. The loss of Eu is linked with that of Sr, Ca, and Na and thus associated with plagioclase dissolution during the stages of incipient to intermediate weathering (Babechuk et al., 2014).

The variety of factor that can impact the REE:

First, various compositions and solubility of minerals present in the soil parent material can partly govern the REE released with weathering.

Secondly, the type of OM present in solution can play a role in the process of REE complexation, and consequently in the REE mobilized with the organic carrier within the soil profile.

The LREE are known to be preferentially bound to carboxylic groups, whereas the HREE are preferentially bound to carboxy-phenolic and phenolic groups (Marsac et al., 2011; Gangloff et al., 2014). The type of chemical bonds with organic molecules and the resulting size of the organo-REE complexes can therefore impact the fractionation of REE during weathering and as such the signature of the REE leached from the soil profile. Finally, the physico-chemical conditions of the solution (e.g. the pH) and the other elements present in solution can have an impact on the mobility of REE and interfere with the complexation of REE by OM. Al and Fe may compete with REE in forming organic complexes, and an increase in concentrations of these cations can cause a decrease in the amount of REE bound to dissolved OM (Tang and Johannesson, 2003; Pourret et al., 2007a; Cidu et al., 2013).

The most important studies conducted about rare earth elements and their relationship to soil development, including:

Babechuk et al., (2014). In India, In this study, the chemical compositions of two profiles developed on Deccan Trap basalt are examined. One is sub-Recent and has only progressed to a moderate degree of alteration (Chhindwara profile), whereas the other is ancient (Paleocene) and the degree of alteration is extreme (Bidar laterite). Major element chemical variations, as expressed by weathering indices, are used to relate the extent of weathering with the behaviour of trace elements in the profiles. Fractionation of the REE (Sm/Nd, Eu/Eu*, Ce/Ce*) is evident during weathering of the basalt. The loss of Eu is linked with that of Sr, Ca, and Na and thus associated with plagioclase dissolution during the stages of incipient to intermediate weathering. The fractionation of Sm/Nd suggests that basaltic weathering products may not always preserve their parent rock ratio and, consequently, their Nd isotope composition over time.

Vermeire et al. (2016) , Results show that the REE content is strongly correlated to the general loss of elements and mineral weathering. Furthermore, the accumulation of secondary OM, Al and Fe-bearing phases does not impact the REE signature of the bulk soil. Results and the ones available in the literature indicate that the release of REE induced by weathering and subsequent leaching in percolating water are the main pathways determining the REE fate in Podzols.

ALsalam et al., (2020). In Turkey, this study was conducted in mountainous regions. Four representative profiles were dug at different elevations. The transect of four soils formed in elevation from 1139 to 1809 m, and soil samples were taken from each horizon for morphological, chemical, physical, geochemical and mineralogical analyzes. The low

negative Eu/Eu* ratio for the values of all the soil profiles studied was found to be related to the intensity of the increased weathering. This study indicated that soil properties and processes were strongly related to elevation and climatic conditions, both of which determine the leaching regime and weathering rates.

Nickel, E., (1973). Experimental dissolution of light and heavy minerals in comparison with weathering and intrastratal solution. *Contrib. Sedimentol.* 1, 1–68.

Land et al. (1999) investigated the fractionation of rare earth elements in a podzol profile in northern Sweden and reported that they were fractionated during various REE weathering, and the leaching tendency decreased with increasing atomic number of the elements.

Compton et al., (2003). Investigated the behavior of rare earth elements in soils located on a granitic terrace in semi-arid conditions in South Africa and reported that Ce, Eu and heavy rare earth elements were washed out in the granite rock with initial weathering and REE enrichment in the soil.

Kazansu et al., (2008). Carried out geochemical studies to investigate the origin and sources of rock weathering in clastic sediments in Tanzania, they stated that the soils of the region were moderately weathered from the major element geochemistry, the light REE was enriched, the heavy REE was washed away, and the soils showed negative Eu anomaly.

Ji et al., (2004). Reported in their study on REE mobility during weathering that although a weathered profile represents a reservoir for the elements, REE enrichment can only occur under favorable conditions such as low erosion, long-term rapid weathering.

Munksgaard et al., (2003). Used REE as markers of origin in marine sediments in northern Australia and reported that they could easily distinguish the five areas they examined by using Eu anomaly and light and heavy REE enrichment for this purpose, according to these ratios.

Mourier et al., (2008). Conducted studies on separating the subalpine soil types distribution using extractable Al, Fe and REE geochemistry and the rare earth element analyzes showed that the soils are composed of relatively homogeneous material, light rare earth elements increase on the surface compared to the C horizon, the normalized REE distribution undergoes a strong transport in Podzols. They reported that REE behaviors were clearly associated with soil weathering.

Zhang, Pan et al., (2007). Conducted a study on the geochemical properties of soils developed on different basalts in Hainan Island, China. It has been reported that REE content is related to soil age and shows soil development.

Singh and Rajamani, (2001). Investigated the sedimentation formation and dissociations of the sediments of the Kaveri Plain in Southern India, and the geochemistry of trace elements in the soil. Accordingly, they detected Eu anomaly in the sediment and determined that this determination was caused by the decomposition index of the parent material, the sediment and the accumulation of minerals.

Lee, Kim et al., (2008). Investigated the geochemical characteristics of REE in the drainage basin of the Han River. No difference was observed between the amount of REE and the main rock in the soil where granite and gneiss belonging to the sediments were decomposed. The Eu abnormality was found to be positive in soils with coarse fractions and negative in soils with fine fractions.

Jäger et al., (2015). Studied the effects of major and minor compounds on soil formation in marshy areas in the Swiss Alps. Differentiate the rare earth elements from each

other and studied the changes in soil development over time. Erosion was intense during the Leistocene and Holocene transition in soil formation. Elemental changes were detected along the slope.

2. CONCLUSIONS

Soil forming factors, such as vegetation and parent material composition can influence soil physico-chemical properties that in turn play a key role in the fractionation of REE during weathering. These observations indicate that LREE is more complex than HREE and richer than the weathering products of Phyllosilicates, and that of LREE remains in the clay, and LREE is retained in clay so that it is richer than Phyllosilicates' weathering products.

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