

Weathering features of a remineralizer in soil under different land uses




Abstract – The objective of this work was to analyze the mineralogical, morphological, and compositional modifications resulting from the weathering of diabase grains buried into soil under different land uses for up to 378 days. Samples of comminuted diabase were put into polyester bags and buried into soil under corn crop, elephant grass, and woods, being unburied and evaluated after four time periods. The samples of the remineralizer (RM) were analyzed by X-ray diffractometry, total chemical analysis, scanning electron microscopy, and Al (Al_d and Al_o) and Fe (Fe_d and Fe_o) contents extracted by sodium dithionite-citrate-bicarbonate (DCB) and ammonium oxalate (AAO) solutions. Plagioclases and pyroxenes were the most weathered minerals in all three land uses and showed the same pattern of elemental gains and losses. The characterization of Fe and Al solubility in DCB and AAO showed that the greatest change in these elements was from the lithogenic and crystalline to the pedogenic and amorphous phase, when compared with their total content. Plagioclases and pyroxenes were the most weathered minerals, and Fe and Al show a great transfer from the crystalline to the amorphous phase, with values up to 26 and 175, respectively, for the ratios between bags with RM/ Fe_o and RM-control and bags with RM/ Al_o and RM-control.

Index terms: enhanced weathering, mineral dissolution, rock powder.

Características de intemperismo de um remineralizador em solo sob diferentes usos da terra

Resumo – O objetivo deste trabalho foi analisar as modificações mineralógicas, morfológicas e composicionais resultantes do intemperismo de grãos de diabásio enterrados em solo sob diferentes usos da terra por até 378 dias. Amostras de diabásio cominuído foram colocadas em sacos de poliéster e enterradas em solo sob cultivo de milho, capim-elefante e floresta, tendo sido desenterradas e avaliadas após quatro períodos. As amostras do remineralizador (RM) foram analisadas por difratometria de raios X, análise química total, microscopia eletrônica de varredura, e teores de Al (Al_d e Al_o) e Fe (Fe_d e Fe_o) extraídos com soluções de ditionito-citrato-bicarbonato (DCB) e amônio oxalato (AAO). Os plagioclásios e os piroxênios intemperizaram mais rápido nos três tipos de uso da terra, e mostraram o mesmo padrão de ganhos e perdas no balanço de massa de elementos. A caracterização das formas de Fe e Al em DCB e AAO mostrou que a maior mudança destes elementos foi da fase litogênica e cristalina para a secundária e amorfa, em comparação aos seus teores totais. Os plagioclásios e os piroxênios foram os minerais mais alterados, e Fe e Al apresentam grande transferência entre a fase cristalina e amorfa, com valores de até 26 e 175, respectivamente, para as razões entre sacos com RM/ Fe_o e RM-controle e sacos com RM/ Al_o e RM-controle.


Termos para indexação: intemperismo acelerado, dissolução mineral, pó de rocha.

Rafael Cipriano da Silva⁽¹⁾ ,
Edilene Pereira Ferreira⁽²⁾ ,
Antonio Carlos de Azevedo⁽³⁾ 

⁽¹⁾ Fundação Cearense de Meteorologia e Recursos Hídricos, Avenida Rui Barbosa, nº 1.246, CEP 60115-221 Fortaleza, CE, Brazil. E-mail: ciprorafael@gmail.com

⁽²⁾ Faculdade da Amazônia, Rua Walisson José Arrigo, nº 2.043, Cristo Rei, CEP 76983-496 Vilhena, RO, Brazil. E-mail: edilene_agro@yahoo.com.br

⁽³⁾ Universidade de São Paulo, Escola Superior de Agricultura Luiz de Queiroz, Avenida Pádua Dias, nº 11, CEP 13418-900 Piracicaba, SP, Brazil. E-mail: aazevedo@usp.br

 Corresponding author

Received
January 28, 2020

Accepted
September 03, 2021

How to cite

SILVA, R.C. da; FERREIRA, E.P.; AZEVEDO, A.C. de. Weathering features of a remineralizer in soil under different land uses. *Pesquisa Agropecuária Brasileira*, v.56, e01442, 2021. DOI: <https://doi.org/10.1590/S1678-3921.pab2021.v56.01442>.

Introduction

Remineralization, the application of powdered rocks into soils, is an agricultural practice to improve edaphic properties and increase biomass productivity (Harley & Gilkes, 2000; Leonardos et al., 2000; Van Straaten, 2006; Manning, 2010; Silva et al., 2017). It is also a low-cost technology to sequester atmospheric carbon through enhanced weathering and, potentially, lead to carbon mineralization (Manning et al., 2013). The effect of remineralizers (RMs) varies according to several factors, but, ultimately, it is related to the dissolution rate of their minerals (Manning, 2010; Ramos et al., 2015).

Mineral dissolution is a complex phenomenon. Its characterization by standard chemical parameters, such as thermodynamic stability constants and dissolution rates, is determined in laboratory conditions (Garrels & Christ, 1965; Palandri & Kharaka, 2004), which is very useful as a starting point, but may deviate from the dissolution rate in field conditions by a factor as great as 10^2 (White & Brantley, 2003; Yokoyama & Matsukura, 2006; Ganor et al., 2007). This is so because variables as the mineral:solution ratio, bioweathering, and seasonal variations in moisture and temperature, among others, greatly diverge from those in laboratory conditions (Benedetti et al., 1994; Yokoyama & Matsukura, 2006; Ganor et al., 2007). Therefore, to properly evaluate and manage the use of RMs in soils, the dissolution of these rocks in field conditions must be well understood and parametrized.

Daval et al. (2018), when analyzing feldspar grains buried into soil for 4 years and comparing the results with those found for minerals weathered under controlled conditions in a laboratory, reported a smaller dissolution rate in the field, which was attributed to the formation of amorphous silica surface layers. Despite this interesting result, the authors did not detail the release of elements from the feldspar nor the formation of secondary phases, possibly because their work was carried out with a single mineral. Gill (2014) also concluded that feldspars of the plagioclase group and pyroxenes are the major minerals in basalts and diabases, and that their dissolution in soil increases pH and cation exchange capacity, but decreases exchangeable Al, depending on the applied rate and particle size (Anda et al., 2015).

Grains of the diabase RM are basic rocks rich in plagioclases and pyroxenes, minerals that weather fast when compared with other ones such K-feldspars

and muscovite (White et al., 1990). In Brazil, those grains are abundant in the Paraná basin, being a potential source of silicon, iron, aluminum, calcium, magnesium, and potassium, particularly in the western region of the state of São Paulo.

The objective of this work was to analyze the mineralogical, morphological, and compositional modifications resulting from the weathering of diabase grains buried into soil under different land uses for up to 378 days.

Materials and Methods

The used RM is a diabase mined from the Limeira sill, located in the state of São Paulo, Brazil (22°36'31.2"S, 47°21'45.7"W). The most abundant minerals found were plagioclases and pyroxenes (Figure 1) as expected (Gill, 2014). Faria (2008) describes the Na-Ca solid solution in these plagioclases as An_{19} at the edges and An_{40} into the core, i.e., as more sodic and more calcic, respectively. Other minerals – ilmenite, magnetite, k-feldspar, and apatite – were also identified, but in smaller amounts.

For the experiment, polyester bags of 0.15x0.15 m were made using a 200 mesh cloth and then filled with 300 g RM. The particle-size distribution of the RM was: 30 g kg^{-1} greater than 2.00 mm, 258 g kg^{-1} from 2.00 to 1.00 mm, 270 g kg^{-1} from 1.00 to 0.50 mm, 143 g kg^{-1} from 0.50 to 0.25 mm, 166 g kg^{-1} from 0.25 to 0.125 mm, 77 g kg^{-1} from 0.053 to 0.002 mm, and 56 g kg^{-1} smaller than 0.002.

In January 30, 2014, the bags were buried in a farm in the municipality of Pirassununga, in the state of São Paulo (21°58'52.32"S, 47°22'44.27"W). The climate of the region is tropical seasonal, of the Cwa type, with dry winters from June to August and hot and rainy summers from October to March (Alvares et al., 2013). The annual rainfall is 1,410 mm, and the average annual temperature is 22°C, with a maximum and a minimum average of 30.8 and 10.6°C, respectively. Data were obtained from the weather station at the campus of Universidade de São Paulo, also located in the municipality of Pirassununga, in the state of São Paulo.

The experimental areas had the same soil type, classified as a Latossolo Vermelho ácido típico according to the Brazilian system of soil classification (Santos et al., 2018a), which is equivalent to an Anionic Acrudox (Soil Survey Staff, 2014). However, the areas had three contiguous land uses, less than 1,000 m

apart: corn (*Zea mays* L.) fields cultivated under a no-tillage system since 2009 and before that with passion fruit (*Passiflora edulis* Sims); elephant grass (*Pennisetum purpureum* Schumach), cultivated as a protective barrier for the field for at least 10 years; and a conservation area, with a forest fragment (woods). In each land use, four bags were buried horizontally, at 0.10 m depth, totaling 12 bags, with the greater axis of the bag parallel to the soil surface.

In the corn field, the bags with the RM (RM-corn) were buried approximately 1.0 m apart from each other and 0.10 m from the corn stalks, being unburied 59, 86,

119, and 154 days later. In the elephant grass site, the bags with the RM (RM-grass) were buried at about 0.10 m from the tussocks and 2.0 m apart from each other. In the woods site, the distribution of the bags with the RM (RM-woods) was random, depending on the distribution and location of the tree trunks, ensuring equidistance from the trees around each bag. In both the grass and woods areas, the bags were unburied after 86, 182, 274, and 378 days, differing from the unburying times for corn due to the crop's cycle.

Soil samples were collected in each area, at 0.0–0.2 m depth, to characterize soil fertility (Table 1) using

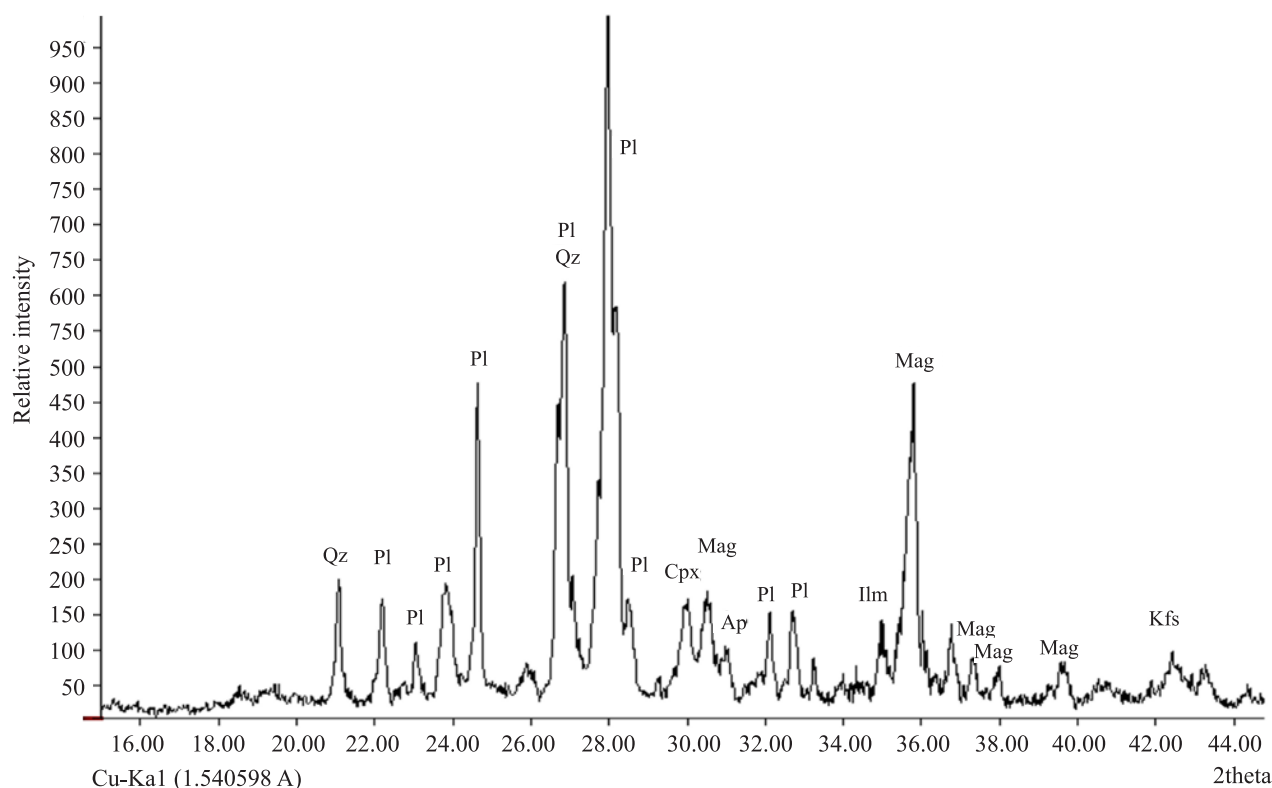


Figure 1. X-ray diffraction patterns of the remineralizer used as the control. Qz, quartz; Pl, plagioclase; Cpx, clinopyroxene; Mag, magnetite; Ap, apatite; Ilm, ilmenite; and Kfs, K-feldspar.

Table 1. Chemical attributes of soil samples collected at 0.0–0.2 m depth from the experimental areas under corn (*Zea mays*) crop, elephant grass (*Pennisetum purpureum*), and woods.

Land use	pH _{water}	Ca	Mg	K	Al	H+Al	SB ⁽¹⁾	CTC ⁽²⁾	P	Si	Fe	Fe _d ⁽³⁾	Fe _o ⁽⁴⁾
		----- (mmol _c dm ⁻³)-----								----- (mg dm ⁻³)-----		---- (g kg ⁻¹)----	
Corn	4.8	14	6	3.2	0	31	23.4	54.1	92	12.0	33	18.9	0.5
Grass	4.2	7	3	1.2	1	64	10.8	75.2	26	8.0	37	15.8	0.3
Woods	3.9	10	5	1.6	4	31	16.4	47.1	11	7.8	109	24.9	0.6

⁽¹⁾Sum of bases (Ca + Mg + K). ⁽²⁾Cation exchange capacity (sum of bases + H + Al). ⁽³⁾Iron determined in dithionite-citrate-bicarbonate solution. ⁽⁴⁾Iron determined in oxalate ammonium acid solution.

the standard methods of the state of São Paulo (Raij et al., 2001). In both the unburied samples and in the pristine RM (RM-control), pedogenic iron oxides and amorphous metal oxides were solubilized, respectively, in sodium-dithionite-citrate-bicarbonate (DCB) (Mehra & Jackson, 1958) and in acid ammonium oxalate (AAO) (McKeague, 1978) solutions; the Fe and Al in the extracts were measured by atomic absorption spectroscopy.

Aliquots of 5 g from the last unburied bags – at 154 days for the corn site and 378 days for the grass and woods sites – were dry-sieved into: coarse sand (from 1.0 to 0.5 mm), fine sand (from 0.25 to 0.125 mm), and silt (smaller than 0.05 mm), ground until passing through a 60 mesh sieve, then powder mounted and irradiated into the Miniflex II benchtop X-ray diffractometer (XRD, Rigaku Corporation, Tokyo, Japan), with a $\text{CuK}\alpha$ radiation of 0.154056 nm, operated at 30 kV and 15 mA, with a graphite monochromator and Ni filter. The angular range was 3 to 60 $^{\circ}2\theta$, at 0.02 $^{\circ}2\theta$ step, and 1 s per step. The XRD patterns were interpreted using the Match! 2.1 software (Crystal Impact, Bonn, Germany).

Total chemical composition was determined only for the longest buried RM and the RM-control, comprising Al_2O_3 , BaO , CaO , Cr_2O_3 , Fe_2O_3 , MgO , MnO , P_2O_5 , K_2O , SiO_2 , Na_2O , SrO , and TiO_2 . Aliquots were fused in $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$, at 1,000 $^{\circ}\text{C}$, cooled, and then dissolved in a solution of 4% nitric acid + 2% hydrochloric acid. The extract was analyzed by atomic emission spectrometry using inductively coupled plasma (ICP-AES); solution readings were sent to a commercial laboratory, which is why the used equipment has not been disclosed.

Based on the obtained results, the elemental mass balance (EMB) was calculated with the equation:

$$\text{EMB} = [(\text{RM-corn or RM-grass or RM-woods}) - (\text{RM-control}) / (\text{RM-control})] \times 100$$

Negative values imply loss of elements in the weathered RM, and positive values imply accumulation.

The RM samples were also fixed on an adhesive carbon metallic support coated with gold film and observed under the LEO 435 VP scanning electron microscope (Carl Zeiss Industrielle Messtechnik GmbH, Oberkochen, Germany), in order to determine the fine and coarse sand fractions. The grains were not subjected to cleaning procedures, so that weathering

features and biological attachments were preserved on grain surface.

Results and Discussion

The evaluated RM was composed by 52.10% SiO_2 , 14.45% Fe_2O_3 , 11.90% Al_2O_3 , 6.94% CaO , 3.45% MgO , 3.27% TiO_2 , 3.06% Na_2O , 1.59% K_2O , 0.24% MnO , and 0.75% P_2O_5 , as expected for a basic igneous rock (Gill, 2014).

Regarding grain morphology, plain surfaces and strait edges, associated with the cleavage of minerals, were frequently observed in the fine and coarse sand fractions of the RM-control (Figure 2 A and B), as well as occasional features of mechanical stress resulting from the comminution process (Figure 2 C and D). In general, etch pits and corroded depressions were identified in the buried grains (Figure 2 E and F), which are associated with the initial stages of weathering (Heindel et al., 2018). Filamentous material resembling fine roots or fungal hyphae were also frequent (Figure 2 D and F). During unburying, it was common to observe roots wrapping around the bags, particularly in the grass land use. Biological corrosion was inferred from some images (Figure 2 F), and similar structures were found in gneiss saprolites in the state of Pernambuco, Brazil (Santos et al., 2018b). Some grains seemed intensely dissolved, as inferred by the lack of sharp edges, when comparing the RM-control with the RM-woods after 378 days of being buried (Figure 2 B and E). However, at this point, it was not possible to conclude that such morphology is the result of weathering into the soil only. Krah et al. (2020) cultivated corn seedlings in pure basalt during 315 days and did not report any changes in rock grain morphology; however, the pH of the pots in their experiment was close to 9, while that of the soil used in the present study was between 4 and 5.

Changes in the intensity of diffracted X-rays are influenced by several factors (Moore & Reynolds, 1997), including the amount of the diffracting phase in the sample. The changes in the relative XRD intensities of plagioclases (0.425, 0.344, and 0.321 nm peaks) and pyroxenes (0.299, 0.294, 0.289, and 0.257 nm peaks) suggest that these are the most weathered phases in the coarse and fine sand fractions, when compared with the RM-control of each fraction (Figures 3, 4, and 5). Krah et al. (2020) also noted that diopside (pyroxene) and andesine (plagioclase) samples were

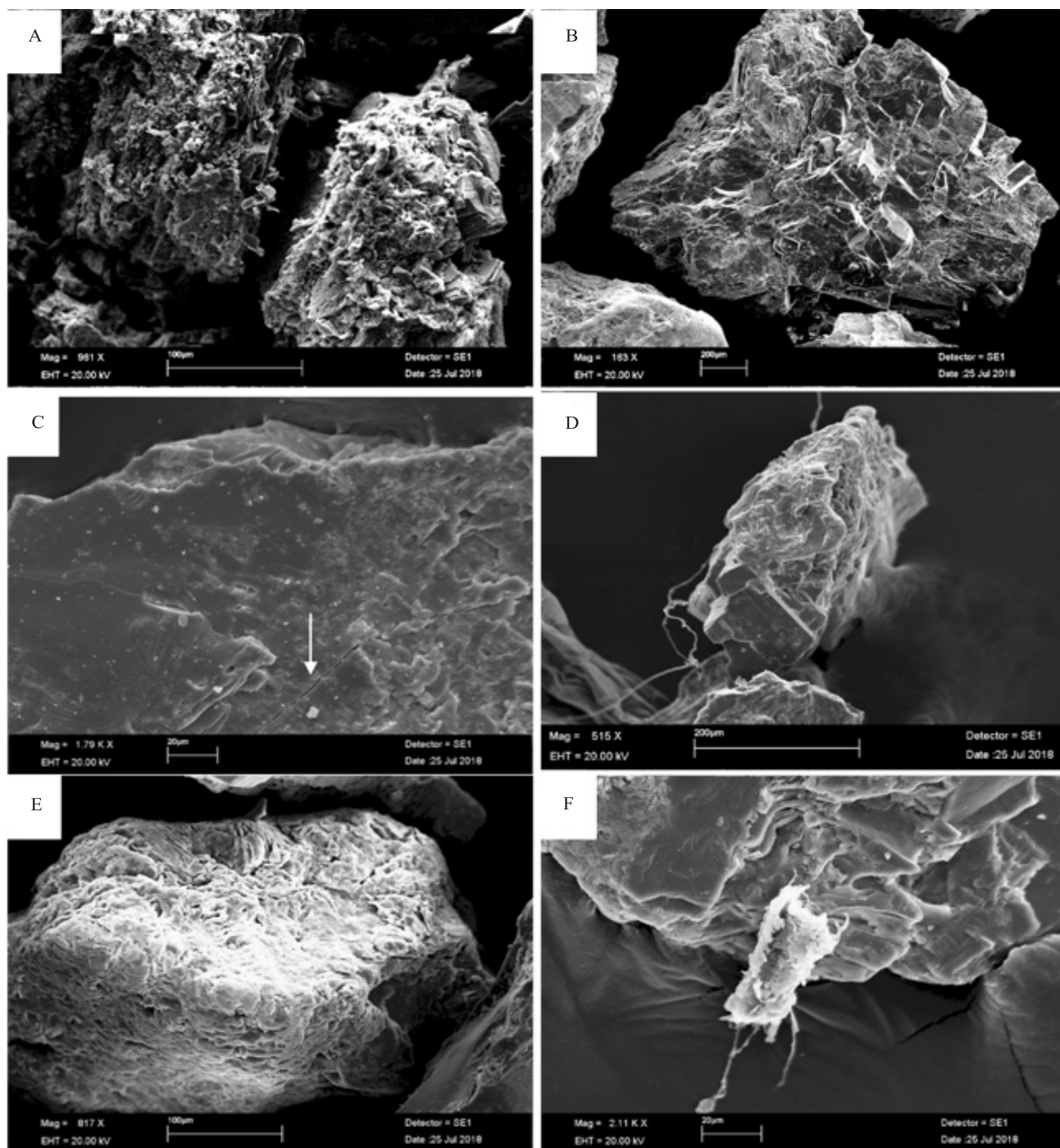


Figure 2. Scanning electron microscopy images of remineralizer (RM) grains, showing: A and B, fine and coarse sand fraction of the grains of the RM used as a control (RM-control), respectively; C, etched pits and a crack probably caused by mechanical stress during comminution (arrow) in the coarse sand fraction of the RM after being buried for 154 days in soil cultivated with corn (*Zea mays*); D, cleavage surfaces (possibly of a feldspar) and biological filament entangled to it in the fine sand fraction in the RM after being buried for 378 days in soil with elephant grass (*Pennisetum purpureum*); E, rounded surfaces, possibly due to preferential edge dissolution in the fine sand fraction in the RM after being buried for 378 days in soil in the woods, contrasting with the coarse sand fraction of the RM-control; and F, biological structure (possibly biofilm) at the edge of the grain, whose corrosion seems more intense around the biological structure in the coarse sand fraction in the RM after being buried for 378 days in the woods.

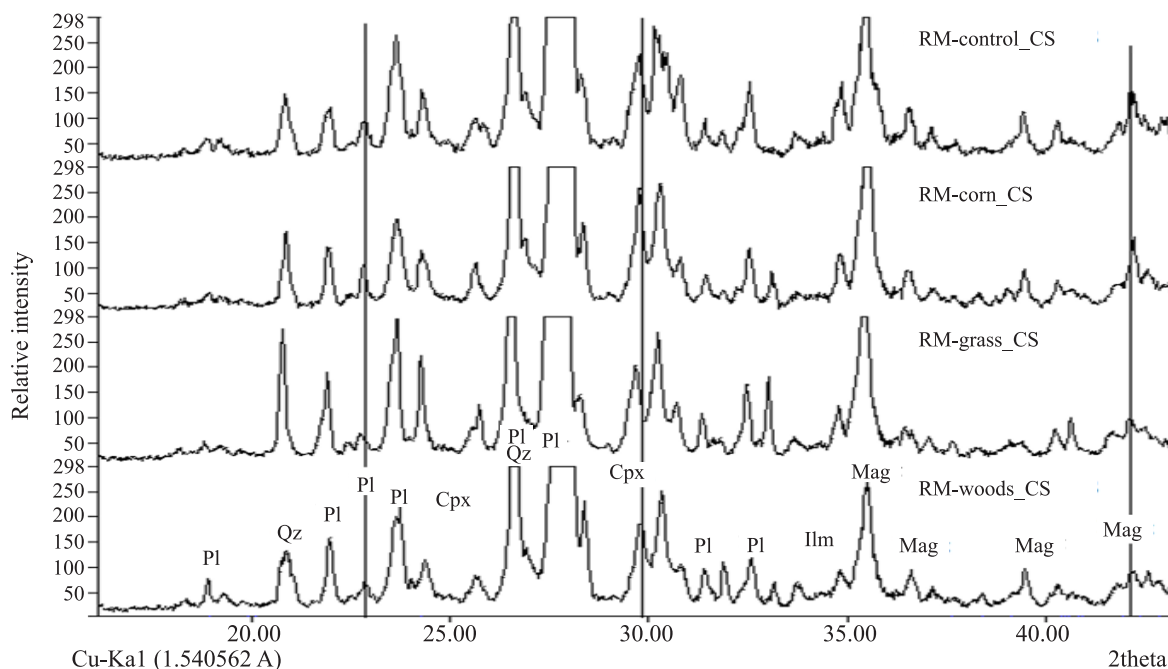


Figure 3. X-ray diffraction scans of the coarse sand fraction (CS) of the remineralizer used as a control (RM-control), after being buried for 154 days in soil cultivated with corn (*Zea mays*) (RM-corn) and for 378 days in soil under elephant grass (*Pennisetum purpureum*) (RM-grass) and woods (RM-woods). Pl, plagioclase; Qz, quartz; Cpx, clinopyroxenes; Ilm, ilmenite; and Mag, magnetite.

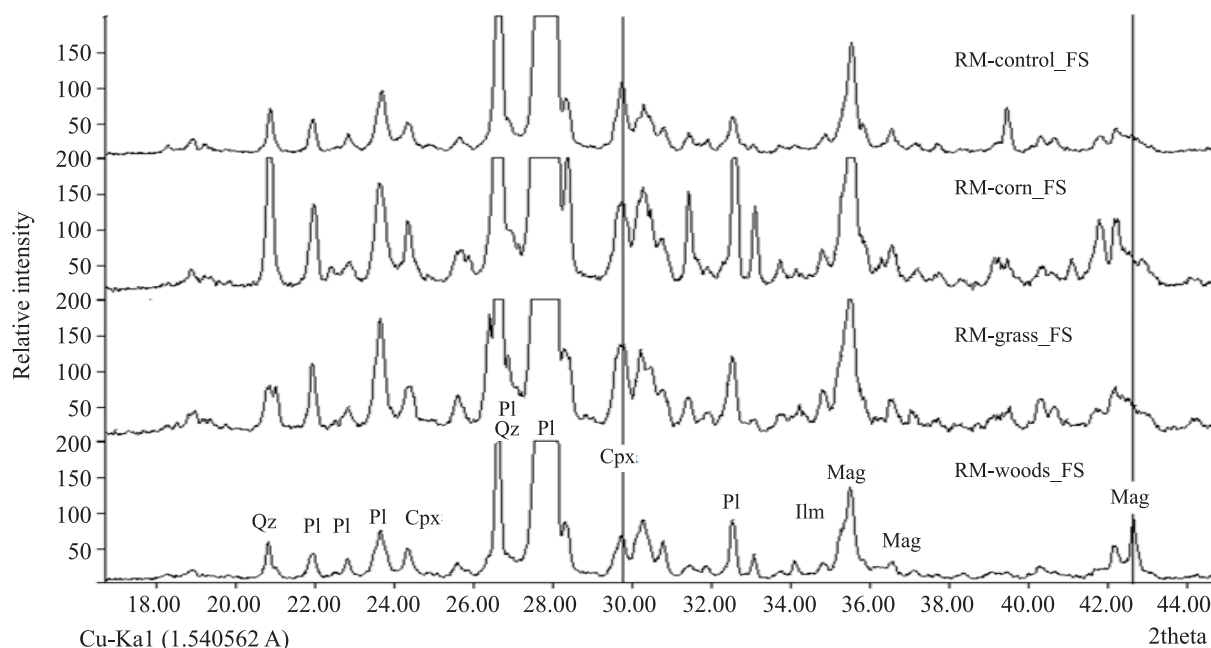


Figure 4. X-ray diffraction scans of the fine sand fraction (FS) of the remineralizer used as a control (RM-control), after being buried for 154 days in soil cultivated with corn (*Zea mays*) (RM-corn) and for 378 days in soil under elephant grass (*Pennisetum purpureum*) (RM-grass) and woods (RM-woods). Qz, quartz; Pl, plagioclase; Cpx, clinopyroxenes; Ilm, ilmenite; and Mag, magnetite.

the most affected by dissolution in the analyzed samples. Besides the decrease observed for the relative intensities, an increase in peak width (full width at half maximum) and asymmetry seemed to have occurred, suggesting the advancement of weathering and the loss of crystallinity (Figures 3, 4, and 5), which is in agreement with the losses in elemental mass balance (Figure 6). Of the found minerals, the most dissolved were Mg and Na, since pyroxenes and plagioclase feldspars were the source of Mg and Na, respectively, and the elemental mass balance showed that the loss of Mg and Na was the greatest in all land uses, which roughly agrees with the changes observed in the XRD scan. It is interesting, though, that all land uses had the same pattern and magnitude of gains and losses of elements.

The amount of iron determined in the dithionite-citrate-bicarbonate and oxalate ammonium acid solutions (Fe_d and Fe_o , respectively) that was extracted from the RMs in the bags was from 9.5 to 13.3 and

from 15.9 to 26.1 times greater, respectively, than that in the RM-control (Table 2). Even if some soil particles may have entered the bag, the amount of Fe_d and Fe_o , respectively, was roughly 2 to 3 and about 40 times greater in the RM bags (that is, in RM-corn, RM-grass, and RM-woods) than in the surrounding soil. This suggests contamination should not have been a major process to increase Fe_d and Fe_o in the bags. Interestingly, Krahl et al. (2020) found precipitates they supposed were amorphous phases on the surface of the studied grains due to the rapid oxidation of Fe(II). Despite the great increase observed for Fe_d and Fe_o , their values were mostly erratic along the timeline. For RM-grass and RM-woods, the greatest Fe_o value was verified in the first unburied bag at 86 days, suggesting that the Fe release was fast and occurred in the first three months. In fact, the incongruent dissolution of silicates results in a great mass of chemical elements released at the beginning of dissolution, followed by a smaller, roughly constant rate of release (Wild

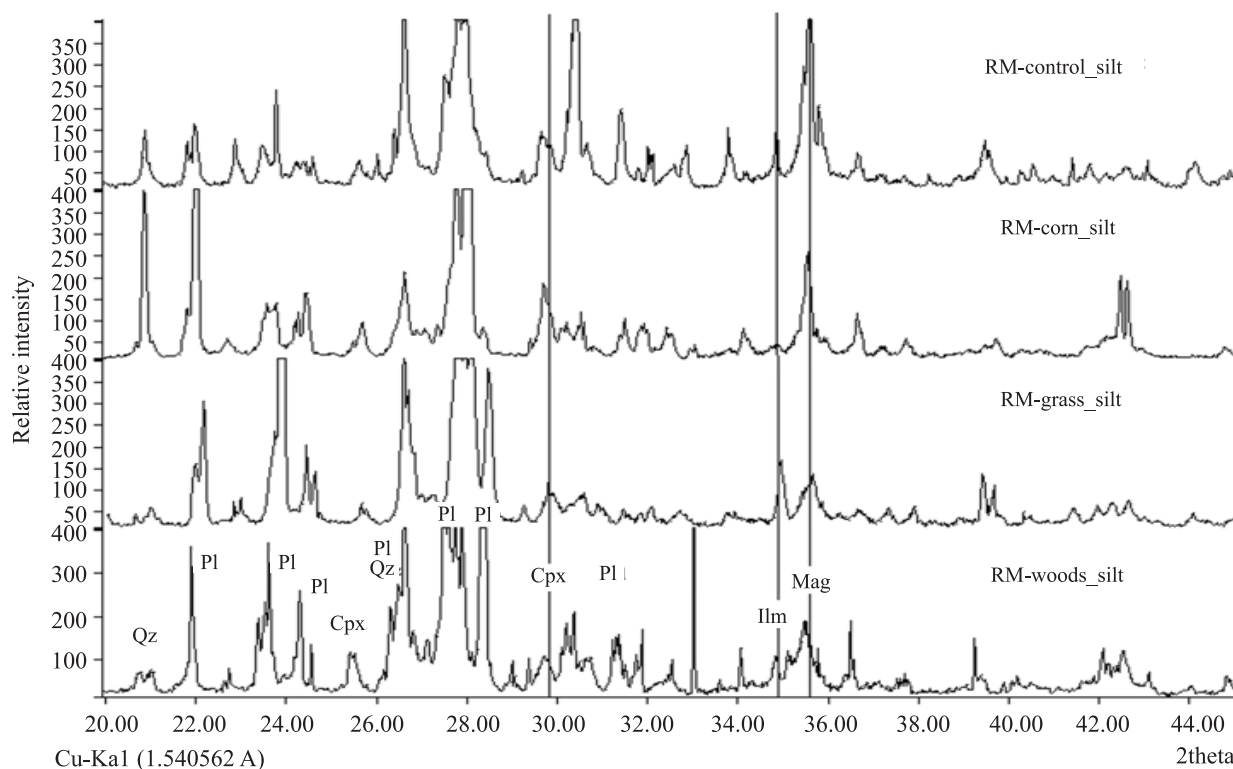


Figure 5. X-ray diffraction scans of the silt fraction of the remineralizer used as a control (RM-control), after being buried for 154 days in soil cultivated with corn (*Zea mays*) (RM-corn) and for 378 days in soil under elephant grass (*Pennisetum purpureum*) (RM-grass) and woods (RM-woods). Qz, quartz; Pl, plagioclase; Cpx, clinopyroxenes; Ilm, ilmenite; and Mag, magnetite.

et al., 2016). It was surprising, though, that, in open system conditions, the dissolution peak occurred in less than three months. The sources of Fe in the RM were the Fe-Mg silicates, mainly pyroxenes, which dissolve incongruently, and primary Fe-oxides, such as magnetite and ilmenite, which dissolve congruently (Crundwell, 2015).

The values of Al determined in the dithionite-citrate-bicarbonate solution (Al_d) were also erratic, varying from 1.9 to 2.8 times the content in the RM-control, with no apparent relationship with Fe_d . This could be attributed to the fact that the source of Al_d is mainly the Al in isomorphic substitution in the atomic structure of reducible metal oxides, such as Fe and Mn oxides; the total Fe_2O_3 and MnO in the RM-control was 14.4 and 0.24%, respectively. The most impressive increase in the ratio between the RM-bags and RM-control was found for Al determined in oxalate ammonium acid solution (Al_o), which was 120 to 175 times greater, indicating an extensive transformation in the Al forms. However, the elemental mass balance for Al_2O_3 was about zero (Figure 6). Together, the elemental mass balance and the Al_d and Al_o RM-bag/RM-control ratios suggest that, despite the loss of Al_2O_3 being in the same order of the overall mass loss of the RM, the Al atoms had a massive transfer from

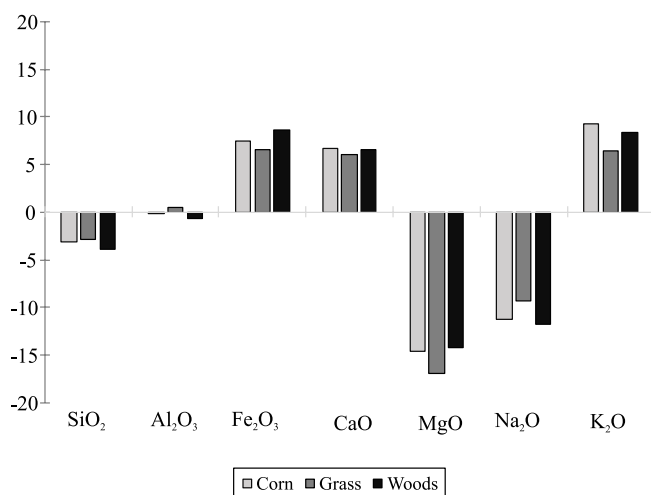


Figure 6. Elemental mass balance based on the total chemical analysis of the remineralizer (RM) samples unburied after 154 days in soil cultivated with corn (*Zea mays*) and after 378 days in soils under elephant grass (*Pennisetum purpureum*) and woods, in comparison with the pristine RM (control).

crystalline and lithogenic minerals to amorphous ones. This could be attributed to the fact that the elemental mass balance accounts only for the mass of elements that leaves the “volume of control” of the system, i.e., the volume of the bags. Therefore, the obtained result is indicative of the loss of elements, as observed for MgO and Na_2O , or of their residual concentration, as for Fe_2O_3 and CaO , but does not inform about their phase transformations in situ – from the crystalline to the amorphous phase, for example. The large increase in Al_o is certainly related to plagioclase weathering, the main and abundant source of Al in the RM, with 11.90% total Al_2O_3 in the RM-control. Plagioclase was also the source of Na and Ca, with 3.06% total Na_2O

Table 2. Iron and aluminum contents extracted with dithionite citrate bicarbonate (Fe_d and Al_d) and ammonium oxalate (Fe_o and Al_o) solutions that were found in the remineralizers both in pristine conditions (RM-control) and after being buried in soil under different land uses⁽¹⁾ and for different periods (number of days).

Days ⁽²⁾	Fe_d	Fe_o	Al_d	Al_o	Fe_o/Fe_d	Al_o/Al_d
----- (g kg ⁻¹) -----						
RM-control	3.51	1.04	1.59	0.02	0.3	0.01
RM-corn						
59	38.7	20.4	3.5	2.9	0.5	0.8
86	41.7	21.7	3.1	3.0	0.5	1.0
119	46.7	20.0	4.3	2.8	0.4	0.7
154	46.1	22.5	3.2	3.2	0.5	1.0
RM-grass						
86	40.5	22.0	3.7	3.2	0.5	0.9
182	33.5	16.6	4.4	2.4	0.5	0.5
274	38.5	20.5	4.0	3.0	0.5	0.8
378	38.4	18.3	4.2	2.6	0.5	0.6
RM-woods						
86	33.2	27.2	4.1	3.5	0.8	0.9
182	35.3	25.4	3.3	3.1	0.7	0.9
274	33.9	22.2	3.1	2.9	0.7	0.9
378	41.0	22.6	3.8	3.2	0.6	0.9

⁽¹⁾RM-corn, corn (*Zea mays*) crop; RM-grass, elephant grass (*Pennisetum purpureum*); and RM-woods, forest fragment.

⁽²⁾Days counted from the burial of the bags in January 30, 2014.

and 6.94% total CaO in the RM-control, respectively. The loss of Na contrasts with the residual increase in Ca can be explained both by the greater mobility of Na (Hudson, 1995) and the albitic (Na-rich) composition of the borders of the plagioclase grains that should weather before their more anorthitic (Ca-rich) core that should weather later. In addition to these processes, the mineralization of carbon or mineral carbonation – which causes the carbon in atmospheric CO₂ to react with alkaline earth metals (usually Ca) and precipitate CaCO₃ (Moosdorf et al., 2014; Kantola et al., 2017; Taylor et al., 2017; Beerling et al., 2018) – may have occurred inside the bags, since it was observed at a much lower RM concentration in the soil (Manning, 2008; Manning et al., 2013; Washbourne et al., 2015). If this process happened inside the bags, some amount of Ca would accumulate as CaCO₃.

In summary, the results of the elemental mass balance calculated in the present study with a very simple approach agreed roughly with those of the XRD scans. The great loss in MgO and Na₂O fits well with the expectation that Fe-Mg silicates (mainly pyroxenes) and plagioclases should weather first. Potassium was enriched into the bags because it should be present in the K-feldspars, which are more resistant to weathering than the plagioclases (Ca-feldspars) (Bakker et al., 2019). Fe₂O₃ accumulated residually, but, as shown by the results for DCB and AAO, has gone through a great transfer from the lithogenic to the pedogenic and amorphous forms. Aluminum went through a similar transformation from primary minerals to amorphous ones, which was up to 175 times greater for Al_o in the RM-bags than in the RM-control (Table 2), possibly explaining why its loss was comparatively greater than that of Fe₂O₃ (Figure 6). Silicon, the most abundant element in the RM (52.10% SiO₂ in the RM-control) should also have gone through extensive transformations since Si is a major element in the composition of silicates, pyroxenes, and plagioclases that have undergone extensive weathering (Stefánsson, 2001); however, its loss was not significant in the mass balance because its mobility is intermediary (Hudson, 1995) and it forms amorphous silica layers on the mineral's surface (Daval et al., 2011, 2018; Hellmann et al., 2013).

These findings are interesting because they serve as a reference (including some order of magnitude) to infer mechanisms of diabase dissolution and to

elaborate hypotheses to test the role of RMs applied to the soil beyond the regular release of plant nutrients and potentially toxic elements. Further research could be carried out on the potential to capture atmospheric carbon, the protection of organic matter by the formation of organic-mineral complexes between organic substances and recently precipitated amorphous metal oxides, the impact of recently precipitated amorphous metals in the “fixation” of phosphate applied to agricultural soils, and the role of soil microbiomes and the rhizosphere in the dissolution rate of RMs, among others.

Conclusions

1. Plagioclases and pyroxenes are the most weathered minerals found in the diabase remineralizer (RM) buried in bags into the soil.

2. The three land uses evaluated show the same pattern of gain and losses of elements.

3. The ratios iron determined in oxalate ammonium acid solution (Fe_o) in the RM-bags/Fe_o in the RM-control and aluminum determined in oxalate ammonium acid solution (Al_o) in the RM-bags/Al_o in the RM-control express a massive transfer of these elements from the crystalline and lithogenic to the pedogenic and amorphous phase, with values from 16 to 26 and 120 to 175, respectively, but a small mobility of aluminum.

Acknowledgments

To Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes), for financing, in part, this study (Finance Code 001), through a grant to the first author; to Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), for financial support (process number 406600/2013-9) and grants (process numbers 305725/2012-2 and 304660/2016-7); and to the Godoy family, owners of the Paineira Branca farm, for the partnership in this research.

References

- ALVARES, C.A.; STAPE, J.L.; SENTELHAS, P.C.; GONÇALVES, J.L. de M.; PAROVEK, G. Köppen's climate classification map for Brazil. *Meteorologische Zeitschrift*, v.22, p.711-728, 2013. DOI: <https://doi.org/10.1127/0941-2948/2013/0507>.

- ANDA, M.; SHAMSHUDDIN, J.; FAUZIAH, C.I. Improving chemical properties of a highly weathered soil using finely ground basalt rocks. **Catena**, v.124, p.147-161, 2015. <https://doi.org/10.1016/j.catena.2014.09.012>.
- BAKKER, E.; LANSON, B.; FINDLING, N.; WANDER, M.M.; HUBERT, F. Mineralogical differences in a temperate cultivated soil arising from different agronomic processes and plant K-uptake. **Geoderma**, v.347, p.210-219, 2019. <https://doi.org/10.1016/J.GEODERMA.2019.04.010>.
- BEERLING, D.J.; LEAKE, J.R.; LONG, S.P.; SCHOLES, J.D.; TON, J.; NELSON, P.N.; BIRD, M.; KANTZAS, E.; TAYLOR, L.L.; SARKAR, B.; KELLAND, M.; DELUCIA, E.; KANTOLA, I.; MÜLLER, C.; RAU, G.H.; HANSEN, J. Farming with crops and rocks to address global climate, food and soil security. **Nature Plants**, v.4, p.138-147, 2018. <https://doi.org/10.1038/s41477-018-0108-y>.
- BENEDETTI, M.F.; MENARD, O.; NOACK, Y.; CARVALHO, A.; NAHON, D. Water-rock interactions in tropical catchments: field rates of weathering and biomass impact. **Chemical Geology**, v.118, p.203-220, 1994. DOI: [https://doi.org/10.1016/0009-2541\(94\)90177-5](https://doi.org/10.1016/0009-2541(94)90177-5).
- CRUNDWELL, F.K. The mechanism of dissolution of the feldspars: Part I. Dissolution at conditions far from equilibrium. **Hydrometallurgy**, v.151, p.151-162, 2015. DOI: <https://doi.org/10.1016/j.hydromet.2014.10.006>.
- DAVAL, D.; CALVARUSO, C.; GUYOT, F.; TURPAULT, M.-P. Time-dependent feldspar dissolution rates resulting from surface passivation: experimental evidence and geochemical implications. **Earth and Planetary Science Letters**, v.498, p.226-236, 2018. DOI: <https://doi.org/10.1016/j.epsl.2018.06.035>.
- DAVAL, D.; SISSMANN, O.; MENGUY, N.; SALDI, G.D.; GUYOT, F.; MARTINEZ, I.; CORVISIER, J.; GARCIA, B.; MACHOUK, I.; KNAUSS, K.G.; HELLMANN, R. Influence of amorphous silica layer formation on the dissolution rate of olivine at 90°C and elevated pCO₂. **Chemical Geology**, v.284, p.193-209, 2011. <https://doi.org/10.1016/j.chemgeo.2011.02.021>.
- FARIA, C.A. **Evolução magmática do Sill de Limeira: petrografia e geoquímica**. 2008. 106p. Dissertação (Mestrado) – Universidade de São Paulo, São Paulo.
- GANOR, J.; LU, P.; ZHENG, Z.; ZHU, C. Bridging the gap between laboratory measurements and field estimations of silicate weathering using simple calculations. **Environmental Geology**, v.53, p.599-610, 2007. DOI: <https://doi.org/10.1007/s00254-007-0675-0>.
- GARRELS, R.M.; CHRIST, C.L. **Solutions, minerals and equilibria**. New York: Harper & Row, 1965.
- GILL, R. **Rochas e processos ígneos: um guia prático**. Porto Alegre: Bookman, 2014. 427p.
- HARLEY, A.D.; GILKES, R.J. Factors influencing the release of plant nutrient elements from silicate rock powders: a geochemical overview. **Nutrient Cycling in Agroecosystems**, v.56, p.11-36, 2000. DOI: <https://doi.org/10.1023/A:1009859309453>.
- HEINDEL, R.C.; LYONS, W.B.; WELCH, S.A.; SPICKARD, A.M.; VIRGINIA, R.A. Biogeochemical weathering of soil apatite grains in the McMurdo Dry Valleys, Antarctica. **Geoderma**, v.320, p.136-145, 2018. DOI: <https://doi.org/10.1016/j.geoderma.2018.01.027>.
- HELLMANN, R.; DAVAL, D.; WIRTH, R. Formation of amorphous silica surface layers by dissolution-reprecipitation during chemical weathering: implications for CO₂ uptake. **Procedia Earth and Planetary Science**, v.7, p.346-349, 2013. DOI: <https://doi.org/10.1016/j.proeps.2013.03.154>.
- HUDSON, B.D. Reassessment of Polynov's ion mobility series. **Soil Science Society of America Journal**, v.59, p.1101-1103, 1995. DOI: <https://doi.org/10.2136/sssaj1995.03615995005900040022x>.
- KANTOLA, I.B.; MASTERS, M.D.; BEERLING, D.J.; LONG, S.P.; DELUCIA, E.H. Potential of global croplands and bioenergy crops for climate change mitigation through deployment for enhanced weathering. **Biology Letters**, v.13, 20160714, 2017. DOI: <https://doi.org/10.1098/rsbl.2016.0714>.
- KRAHL, L.L.; PAZ, S.P.A. da; ANGELICA, R.S.; VALADARES, L.F.; SOUSA-SILVA, J.C.; MARCHI, G.; MARTINS, É. de S. Successive off take of elements by maize grown in pure basalt powder. **African Journal of Agricultural Research**, v.15, p.229-239, 2020. DOI: <https://doi.org/10.5897/AJAR2019.14546>.
- LEONARDOS, O.H.; THEODORO, S.H.; ASSAD, M.L. Remineralization for sustainable agriculture: a tropical perspective from a Brazilian viewpoint. **Nutrient Cycling in Agroecosystems**, v.56, p.3-9, 2000. DOI: <https://doi.org/10.1023/A:1009855409700>.
- MANNING, D.A.C. Biological enhancement of soil carbonate precipitation: passive removal of atmospheric CO₂. **Mineralogical Magazine**, v.72, p.639-649, 2008. DOI: <https://doi.org/10.1180/minmag.2008.072.2.639>.
- MANNING, D.A.C. Mineral sources of potassium for plant nutrition. A review. **Agronomy for Sustainable Development**, v.30, p.281-294, 2010. DOI: <https://doi.org/10.1051/agro/2009023>.
- MANNING, D.A.C.; RENFORTH, P.; LOPEZ-CAPEL, E.; ROBERTSON, S.; GHAZIREH, N. Carbonate precipitation in artificial soils produced from basaltic quarry fines and composts: an opportunity for passive carbon sequestration. **International Journal of Greenhouse Gas Control**, v.17, p.309-317, 2013. DOI: <https://doi.org/10.1016/j.ijggc.2013.05.012>.
- MCKEAGUE, J.A. **Manual on soil sampling and methods of analysis**. 2nd ed. Ottawa: Canadian Society of Soil Science, 1978. 212p.
- MEHRA, O.P.; JACKSON, M.L. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. **Clays and Clay Minerals**, v.7, p.317-327, 1958. DOI: <https://doi.org/10.1016/B978-0-08-009235-5.50026-7>.
- MOORE, D.M.; REYNOLDS, R.C. **X-ray diffraction and the identification and analysis of clay minerals**. Oxford: Oxford University Press, 1997.
- MOOSDORF, N.; RENFORTH, P.; HARTMANN, J. Carbon dioxide efficiency of terrestrial enhanced weathering. **Environmental Science & Technology**, v.48, p.4809-4816, 2014. DOI: <https://doi.org/10.1021/es4052022>.
- PALANDRI, J.L.; KHARAKA, Y.K. **A compilation of rate parameters of water-mineral interaction kinetics for**

- application to geochemical modeling.** Menlo Park: U.S. Geological Survey, 2004. Open File Report 2004-1068. DOI: <https://doi.org/10.3133/ofr20041068>.
- RAIJ, B. VAN; ANDRADE, J.C. de; CANTARELLA, H.; QUAGGIO, J.A. (Ed.). **Análise química para avaliação da fertilidade de solos tropicais.** Campinas: IAC, 2001. 285p.
- RAMOS, C.G.; QUEROL, X.; OLIVEIRA, M.L.S.; PIRES, K.; KAUTZMANN, R.M.; OLIVEIRA, L.F.S. A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer. **Science of the Total Environment**, v.512-513, p.371-380, 2015. DOI: <https://doi.org/10.1016/j.scitotenv.2014.12.070>.
- SANTOS, H.G. dos; JACOMINE, P.K.T.; ANJOS, L.H.C. dos; OLIVEIRA, V.Á. de; LUMBRERAS, J.F.; COELHO, M.R.; ALMEIDA, J.A. de; ARAÚJO FILHO, J.C. de; OLIVEIRA, J.B. de; CUNHA, T.J.F. **Sistema brasileiro de classificação de solos.** 5.ed. rev. e ampl. Brasília: Embrapa, 2018a. 356p.
- SANTOS, J.C.B. dos; LE PERA, E.; SOUZA JÚNIOR, V.S. de; OLIVEIRA, C.S. de; JUILLERET, J.; CORRÊA, M.M.; AZEVEDO, A.C. de. Porosity and genesis of clay in gneiss saprolites: the relevance of saprolithology to whole regolith pedology. **Geoderma**, v.319, p.1-13, 2018b. DOI: <https://doi.org/10.1016/j.geoderma.2017.12.031>.
- SILVA, R.C. da; CURY, M.E.; IEDA, J.J.C.; SERMARINI, R.A.; AZEVEDO, A.C. de; Chemical attributes of a remineralized Oxisol. **Ciência Rural**, v.47, e20160982, 2017. DOI: <https://doi.org/10.1590/0103-8478cr20160982>.
- SOIL SURVEY STAFF. **Keys to soil taxonomy.** 12th ed. Washington: USDA, 2014. 360p.
- STEFÁNSSON, A. Dissolution of primary minerals of basalt in natural waters: I. Calculation of mineral solubilities from 0°C to 350°C. **Chemical Geology**, v.172, p.225-250, 2001. DOI: [https://doi.org/10.1016/S0009-2541\(00\)00263-1](https://doi.org/10.1016/S0009-2541(00)00263-1).
- TAYLOR, L.L.; BEERLING, D.J.; QUEGAN, S.; BANWART, S.A. Simulating carbon capture by enhanced weathering with croplands: an overview of key processes highlighting areas of future model development. **Biology Letters**, v.13, 20160868, 2017. DOI: <https://doi.org/10.1098/rsbl.2016.0868>.
- VAN STRAATEN, P. Farming with rocks and minerals: challenges and opportunities. **Anais da Academia Brasileira de Ciências**, v.78, p.731-747, 2006. DOI: <https://doi.org/10.1590/S0001-37652006000400009>.
- WASHBOURNE, C.-L.; LOPEZ-CAPEL, E.; RENFORTH, P.; ASCOUGH, P.L.; MANNING, D.A.C. Rapid removal of atmospheric CO₂ by urban soils. **Environmental Science & Technology**, v.49, p.5434-5440, 2015. DOI: <https://doi.org/10.1021/es505476d>.
- WHITE, A.F.; BRANTLEY, S.L. The effect of time on the weathering of silicate minerals: why do weathering rates differ in the laboratory and field? **Chemical Geology**, v.202, p.479-506, 2003. DOI: <https://doi.org/10.1016/j.chemgeo.2003.03.001>.
- WHITE, G.N.; FELDMAN, S.B.; ZELAZNY, L.W. Rates of nutrient release by mineral weathering. In: LUCIER, A.A.; HAINES, S.G. (Ed.). **Mechanisms of forest response to acidic deposition.** New York: Springer, 1990. p.108-162. DOI: https://doi.org/10.1007/978-1-4612-3364-0_4.
- WILD, B.; DAVAL, D.; GUYOT, F.; KNAUSS, K.G.; POLLET-VILLARD, M.; IMFELD, G. pH-dependent control of feldspar dissolution rate by altered surface layers. **Chemical Geology**, v.442, p.148-159, 2016. DOI: <https://doi.org/10.1016/j.chemgeo.2016.08.035>.
- YOKOYAMA, T.; MATSUKURA, Y. Field and laboratory experiments on weathering rates of granodiorite: separation of chemical and physical processes. **Geology**, v.34, p.809-812, 2006. DOI: <https://doi.org/10.1130/G22625.1>.