THESE

Pour l'obtention du Grade de

DOCTEUR DE L'UNIVERSITE DE POITIERS

Faculté des Sciences Fondamentales et Appliquées
(Diplôme National - Arrêté du 25 mai 2016)

Ecole Doctorale : Sciences pour l'environnement – Gay Lussac

Secteur de Recherche : Terre solide et enveloppes superficielles

Présentée par :

Vanessa Thoma BERTOLAZI

****

EVOLUTIONS MINERALOGIQUES DES SOLS DU SUD DU BRESIL : PROCESSUS D'ALTERATION PEDOGENETIQUE ET IMPACT ANTHROPIQUE

****

Directeurs de Thèse en cotutelle :
Dr. Laurent CANER – Université de Poitiers
Dr. Alberto Vasconcellos Inda – Université Fédérale du Rio Grande do Sul - Brésil

****

Soutenue le 24 février 2017

devant la Commission d'Examen

****

JURY

Rapporteur	**Jérôme Poulenard**	Professeur, Université Savoie Mont-Blanc
Rapporteur	**Antonio Azevedo**	Professeur, Université de São Paulo, Brésil
Examinateur	**Emmanuel Joussein**	Maître de Conférences, Université de Limoges
Examinateur	**André S. Mexias**	Professeur, Université Fédérale du Rio Grande do Sul, Porto Alegre, Brésil
Directeur	**Laurent Caner**	Maître de Conférences, Université de Poitiers
Directeur	**Alberto Vasconcellos Inda**	Professeur, Université Fédérale du Rio Grande do Sul, Porto Alegre, Brésil

UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
FACULDADE DE AGRONOMIA
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA DO SOLO
&
UNIVERSIDADE DE POITIERS

(CO-TUTELA)

ALTERAÇÃO MINERALÓGICA EM SOLOS DO SUL DO BRASIL: EVOLUÇÃO PEDOGÊNICA E IMPACTO ANTRÓPICO

Vanessa Thoma Bertolazi
(Tese de Doutorado)

UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
FACULDADE DE AGRONOMIA
PROGRAMA DE PÓS-GRADUAÇÃO EM CIÊNCIA DO SOLO
&
UNIVERSIDADE DE POITIERS

(CO-TUTELA)

ALTERAÇÃO MINERALÓGICA EM SOLOS DO SUL DO BRASIL: EVOLUÇÃO PEDOGÊNICA E IMPACTO ANTRÓPICO

VANESSA THOMA BERTOLAZI
Engenheira Agrônoma (UFSM)
Mestre em Ciência do Solo (UFSM)

Tese apresentada como
um dos requisitos à obtenção do
Grau de Doutor em Ciência do Solo

Porto Alegre (RS) Brasil
Fevereiro de 2017

CIP - Catalogação na Publicação

Bertolazi, Vanessa Thoma
ALTERAÇÃO MINERALÓGICA EM SOLOS DO SUL DO BRASIL: EVOLUÇÃO PEDOGÊNICA E IMPACTO ANTRÓPICO / Vanessa Thoma Bertolazi. -- 2017.
122 f.

Orientador: Alberto Vasconcellos Inda.
Coorientador: Laurent Caner.

Tese (Doutorado) -- Universidade Federal do Rio Grande do Sul, Faculdade de Agronomia, Programa de Pós-Graduação em Ciência do Solo, Porto Alegre, BR-RS, 2017.

1. Argilominerais de solo. 2. Balanço geoquímico. 3. Intemperismo . 4. Alteração mineralógica. 5. Integração lavoura-pecuária. I. Inda, Alberto Vasconcellos, orient. II. Caner, Laurent, coorient. III. Título.

Elaborada pelo Sistema de Geração Automática de Ficha Catalográfica da UFRGS com os dados fornecidos pelo(a) autor(a).

VANESSA THOMA BERTOLAZI
Engenheira Agrônoma (UFSM)
Mestre em Ciência do Solo (UFSM)

TESE
Submetida como parte dos requisitos
para a obtenção do Grau de
DOUTORA EM CIÊNCIA DO SOLO

Programa de Pós-Graduação em Ciência do Solo
Faculdade de Agronomia
Universidade Federal do Rio Grande do Sul
&
Universidade de Poitiers
Porto Alegre (RS), Brasil

Aprovada em ___ / ___ / ___ .
Homologada em ___ / ___ / ___ .

BANCA EXAMINADORA:

Prof. Jérome Poulenard
Universidade de Savoie Mont-Blanc

Prof. Antonio Azevedo
ESALQ

Prof. Emmanuel Joussein
Universidade de Limoges

Prof. André S. Mexias
UFRGS

Prof. Alberto Vasconcellos Inda Junior
Orientador no Brasil – UFRGS

Prof. Laurent Caner
Orientador na França – Universidade de Poitiers

É com o coração que se vê
corretamente; o essencial é
invisível aos olhos.

Antoine de Saint-Exupéry

A todos os ***meus professores***
que desde a infância
me serviram de inspiração e apoio,
dedico este trabalho.

AGRADECIMENTOS

A Deus pelas oportunidades que a mim confiou.

À Faculdade de Agronomia da UFRGS.

À CAPES, pelo suporte financeiro para a realização deste trabalho.

Ao PPG Ciência do Solo da UFRGS, pela oportunidade de realização do curso, infraestrutura oferecida e conhecimento transmitido.

Ao professor Alberto Inda pela orientação, troca de conhecimentos e amizade.

Ao professor Laurent Caner pelo acolhimento, orientação e parceria durante o período na França.

A Universidade de Poitiers pela oportunidade de realização do doutorado em cotutela

A todos os professores do Departamento de Solos, do PPG Ciência do Solo e do Departamento de Geociências da UFRGS.

Aos funcionários do Departamento de Solos, em especial, ao Jader, pela dedicação e amizade junto aos alunos.

Aos professores e funcionários da Universidade de Poitiers.

As minhas colegas do PPG, Jessica Souza, Naihana Schefer, Amanda Martins e Estéfane Chaves que com sua amizade e parceria tornaram meus dias em Porto Alegre mais felizes.

A todos os colegas de PPG e do grupo de pesquisa em Mineralogia do solo.

Aos colegas e amigos da Universidade de Poitiers pela amizade e troca de aprendizadoscientíficos e culturais.

Aos meus irmãos, Carla e Leonardo, pelo carinho, incentivo e amizade.

Aos meus pais, Wera e Antonio Carlos, pelo amor incondicional, incentivo e apoio em todos os momentos.

ALTERAÇÃO MINERALÓGICA EM SOLOS DO SUL DO BRASIL: EVOLUÇÃO PEDOGÊNICA E IMPACTO ANTRÓPICO[1]

Autora: Vanessa Thoma Bertolazi

Orientador no Brasil: Prof. Alberto Vasconcellos Inda

Orientador na França: Laurent Caner

Local e data da defesa de tese: Porto Alegre, 24 de Fevereiro de 2017.

RESUMO

O sul do Brasil é uma região com uma agricultura muito intensa e com grande pressão de uso do solo, consideravelmente mais intenso do que na região da Amazônia. Assim, é necessário desenvolver estudos que relacionem o desenvolvimento do solo com seu respectivo material de origem, detalhando as transformações na zona de transição solo-rocha e suas implicações para as atividades ambientais e humanas. Neste contexto, este trabalho tem como objetivo: (i) caracterizar os aspectos mineralógicos, pedoquimicos e geoquimicos dos perfis de alteração desenvolvidos na ausência ou mínima ação humana; (ii) caracterizar qualitativa e semi-quantitativamente os minerais primários e os minerais pedogênicos em solos inseridos em regiões ecossistêmicas importantes do Rio Grande do Sul; e (iii) avaliar o impacto de diferentes intensidades de pastejo na mineralogia de um Latossolo, sob sistema de produção integrada soja-bovinos de corte no sul do Brasil.Este estudo foi realizado em solos do Rio Grande do Sul, onde o clima subtropical (temperatura média anual ~ 17°C, precipitação anual média de 1800mm/ano) favorece o acúmulo de matéria orgânica ea ocorrência de argilominerais 2:1.Os índices de intemperismo (Weathering Intensity Scale - WIS e Chemical Index of Alteration - CIA), considerando a composição mineralógica dos perfis de alteração, indicaram a seguinte sequência crescente do grau de intemperismo: esmectita < caulinita - esmectita < caulinita. O estudo mostrou diferenças importantes nos solos, mesmo entre aqueles formados a partir do mesmo material de origem, devido às diferenças climáticas e de relevo. Por fim, após 12 anos sob um sistema integrado de produção de soja-bovinos de corte, as áreas não pastejadas apresentaram menor intensidade para os argilominerais 2:1. Por outro lado, as áreas sob pastejo intensivo e pastejo moderado apresentaram comportamento semelhante, devido à maior aluminização da entrecamada dos argilominerais 2:1. A maior aluminização sob pastejo intensivo e moderado pode ser um dreno de alumínio na fase sólida do solo, tornando-o menos disponível para as plantas e diminuindo sua fitotoxicidade.

Palavras-chave: Mineralogia do solo; índices de intemperismo; argilominerais, aluminização.

---

[1] Tese de Doutorado em cotutela. Programa de Pós-Graduação em Ciência do Solo – Universidade Federal do Rio Grande do Sul, Porto Alegre, Brasil. Escola Doutoral em Ciências Ambientais Gay Lussac – Universidade de Poitiers, França. (112p.). Janeiro, 2017.

EVOLUTIONS MINERALOGIQUES DES SOLS DU SUD DU BRESIL : PROCESSUS D'ALTERATION PEDOGENETIQUE ET IMPACT ANTHROPIQUE[2]

Auteure: Vanessa Thoma Bertolazi

Directeur thèse au Brésil : Prof. Alberto Vasconcellos Inda

Directeur thèse en France: Laurent Caner

Lieu et date de la soutenance: Porto Alegre, le 24 février 2017

RÉSUMÉ

Le Sud du Brésil est une région où l'agriculture est très intensive et la pression sur les sols est beaucoup plus importante que dans la région amazonienne. Ainsi, il est nécessaire de développer des études qui relient le développement du sol avec son matériau source respectif, en détaillant les transformations dans la zone de transition sol-roche et ses implications pour les activités environnementales et humaines. Dans ce contexte, ce travail vise à: (i) caractériser les aspects minéralogique, pédochimique et géochimiquedes profils d'altération développés en l'absence d'action humaine ou avec une intervention minimale; (ii) caractériser qualitativement et semi-quantitativement les minéraux primaires et les minéraux pedogenic dans les sols insérés dans les régions importantes de l'écosystème du Rio Grande do Sul; et (iii) évaluer l'impact des différentes intensités de pâturage sur la minéralogie d'un Oxisol sous système intégré de production soja-élevage dans le sud du Brésil. Cette étude concerce des sols du Rio Grande do Sul dont le climat subtropical (températures moyennes annuelles ~17°C, précipitations moyennes annuelles ~1800 mm/an) favorise l'accumulation de matiére organique ainsi que la formation de minéraux argileux 2:1. Les indices d'altération (Weathering Intensity Scale - WIS et Chemical Index of Alteration - CIA) établis à partir de la composition chimique des profils d'altération permettent de classer les profils selon leur degré d'altération qui correspond également à des compositions minéralogiques différentes (smectite, smectite + kaolinite, kaolinite). L'étude a montré que des sols formés à partir de la même roche ont des différences importantes liées aux différences climatiques et de relief. Finalement, après 12 ans de culture des sols avec un système intégré culture-élevage, les surfaces non pâturées présentent une proportions moins important de minéraux 2:1. D'autre part, les surfaces sous pâturage intensif et pâturage modéré présentent un comportement similaire attribué à une aluminisation plus élevée de la couche interfoliaire de minéraux 2:1. L'aluminisation plus élevée sous gestion intensive et modérée peut fixer une partie de l'aluminium dans la phase solide du sol, ce qui pourrait le rendre moins disponible pour les plantes et diminuer sa phytotoxicité.

Mots-clés: Minéralogie du sol; indices d'altération; minéraux argileux; aluminisation.

---

[2] Thèse de Doctorat en CotutelleProgramme de Pos Graduation en Science du Sol – Université Fédérale du Rio Grande do Sul, Porto Alegre, Brésil.École Doctorale Science pour l'Environnement Gay Lussac – Université de Poitiers, France. (112 p.). Janvier, 2017.

MINERALOGICAL ALTERATION IN THE SOIL OF THE SOUTH OF BRAZIL: PEDOGENETIC EVOLUTION AND ANTHROPIC IMPACT[3]

Author: Vanessa Thoma Bertolazi

Adviser in Brazil: Prof. Alberto Vasconcellos Inda

Adviser in France: Laurent Caner

Place and date of the defense: Porto Alegre, February 24th 2017

ABSTRACT

The Southern Brazil is a region with a very intensive agriculture and the pressure on soil use is considerably more intense than in the Amazonian region. Thus, it is necessary to develop studies that relate the soil development with its respective source material, detailing the transformations in the soil-rock transition zone and its implications for the environmental and human activities. In this context, this work aims to: (i) characterize the mineralogical and pedochemical alterations and geochemical evolution the profiles of the alteration developed in the absence, or the minimal human action; (ii) characterize both qualitatively and semi-quantitatively the primary and pedogenic minerals present in soils of important ecosystems in Rio Grande do Sul; And (iii) evaluate the effect of grazing intensities on the mineralogy of an Oxisol, in an integrated soybean-cattle beef production system of southern Brazil. This study concerns soils of Rio Grande do Sul, where the subtropical climate (mean annual temperature ~17°C, mean annual precipitation 1800mm/yr) favored the accumulation of organic matter and occurrence of 2:1 clay minerals. The indexes of weathering (Weathering Intensity Scale - WIS and Chemical Index of Alteration - CIA), considering the mineralogical composition of the alteration profiles, indicated the following increasing sequence of the degree of weathering: smectite composition <kaolinite-smectite composition <kaolinite composition. The study showed that the soils have important differences, even between those formed from the same material of origin, due to climatic differences and relief. Lastly, after 12 years under an integrated soybean–beef cattle production system, the ungrazed areas presented lower intensity of 2:1 minerals. On the other hand, areas under intensive grazing and moderate grazing presented similar behaviour due to the higher aluminization of the interlayer of 2:1 minerals. The higher aluminization under intensive and moderate grazing managements may be a drain on aluminum in the soil solid phase, making it less available to plants and decreasing its phytotoxicity.

Keywords: Soil mineralogy; indexes of weathering; clay minerals; aluminization.

---

[3] Doctoral thesis in co-supervision. Graduate program in soil science – Federal University of Rio Grande do Sul, Porto Alegre, Brazil. Graduate school environmental science Gay Lussac – University of Poitiers, France. (112 p.). January, 2017.

RESUMO EXPANDIDO

Introdução

O Rio Grande do Sul, estado mais meridional do Brasil, é formado por quatro grandes províncias geomorfológicas (Planalto, Escudo Sul-rio-grandense, Depressão central e Planície costeira), as quais têm origens geológicas distintas (Brasil, 1986; CPRM, 2006). Em duas dessas províncias predominam rochas ígneas ou magmáticas, o Escudo Sul-rio-grandense e o Planalto. O Escudo se localiza na parte centro-sul do estado, apresentando as rochas mais antigas, com idades que variam do período Cambriano (~542 Ma) até provavelmente o Arqueano (mais de 2500 Ma). Além de muito antigo, o Escudo compreende uma geologia muito complexa, formada por vários tipos de rochas magmáticas plutônicas, principalmente de composição granítica, associadas a cinturões de rochas metamórficas, distribuídas em relevos ondulados.

Essa diversidade de paisagens e litologias, associada a diferenças climáticas expressivas, resultaram em uma ampla variabilidade pedológica no Rio Grande do Sul (Brasil, 1973; Streck et al, 2008). Em geral esses solos apresentam baixa fertilidade natural, expressa por uma baixa saturação por bases, forte acidez e elevada saturação por alumínio. Os solos do Planalto, originados na maioria de basaltos, apresentam expressiva variabilidade devido à diversidade climática.

Nesta província observa-se um gradiente de altitude decrescente no sentido leste (~ 900 m - Taquara) a oeste (~ 60 m – São Borja), o que induz a um forte gradiente orográfico leste-oeste do clima (temperatura e precipitação). Em altitude o clima é temperado com precipitação média anual em torno de 2000 mm ano^{-1} e uma temperatura média anual de 14,4 ^{o}C (Maluf, 2000). Com a diminuição da altitude o clima varia de superúmido a subtropical subúmido, com precipitação média anual de ~1300 mm ano^{-1} e temperatura média anual 20 ^{o}C (Maluf, 2000).

Tais condições dão origem a solos que variam, no sentido leste-oeste, de altamente intemperizados (baixa CTC, ácidos, baixa saturação por bases, alta saturação por Al) como os Latossolos e Nitossolos com mineralogia caulinítica e oxídica, para solos pouco intemperizados (alta CTC, pH próximo a neutralidade, alta saturação por bases) como Neossolos, Chernossolos e Vertissolos com mineralogia esmectítica.

A superfície cultivada no Rio Grande do Sul é de cerca de 6 milhões de hectares. A agricultura (cereais, soja, pastagens) e a pecuária (bovinos, suínos, aves) são muito intensas comparadas a outros estados brasileiros. Essa agricultura intensiva exerce uma pressão importante sobre os solos (exportação de nutriente, redução de matéria orgânica, compactação, erosão, etc...), a qual depende dos diferentes usos e manejos do solo. O comportamento físico e químico do solo é fortemente influenciado por sua composição mineralógica (Kämpf e Curi, 2003).

As ações previstas no presente estudo de doutorado serão divididas em dois eixos principais. O primeiro eixo (**estudo 1**) se baseia em estudo dos processos de alteração em basalto e gnaisse em diferentes regiões climáticas do RS, a fim de identificar os mecanismos de intemperização das rochas e a mineralogia das argilas associadas aos processos e fatores que controlam a formação dos solos. O segundo eixo (**estudo 2**) busca separar o efeito da agricultura intensivaem relação à evolução pedogenética, e as possíveis mudanças na mineralogia das argilas e nas propriedades físico-químicas do solo.

Neste contexto, este trabalho de tese tem como objetivos (i) caracterizar as alterações mineralógicas, pedoquímicas e a evolução geoquímica em perfis de alteração localizados em ausência ou mínima ação antrópica no Sul do Brasil (estudo 1); (ii) caracterizar qualitativa e semi-quantitativamente os minerais primários e os minerais pedogênicos em solos inseridos em regiões ecossistêmicas importantes do Rio Grande do Sul (estudo 1); e (iii) avaliar o impacto de diferentes intensidades de pastejo na mineralogia de um Latossolo, sob sistema de produção integrada soja-bovinos de corte no sul do Brasil (estudo 2).

Material e Métodos

Os locais selecionados para descrição e coleta dos 3 perfis de alteração (rocha sã – saprolito – horizontes pedogenéticos) para o **estudo 1** estão localizados nos municípios de São Borja (Basalto - 28°57’30’’S, 55°43’60’’W); Taquara (Basalto - 29°44’30’’S, 50°51’40’’W) e Eldorado do Sul (Gnaisse - 30°06’11’’S, 51°40’33’’W), no estado do Rio Grande do Sul, Brasil.

O **estudo 2** está inserido em uma área experimental em um sistema integrado de produção agropecuária (SIPA) com experimento de longa duração com diferentes intensidades de pastejo, localizada no município de São Miguel das Missões (28°57'23"S, 54° 21'22"W). O sistema de cultivo utilizado na área baseia-se na cultura da soja (*Glycine max*) no verão e espécies forrageiras de inverno (aveia-preta) em adição ao azevém (ressemeadura natural). Os tratamentos correspondem às diferentes intensidades de pastejo durante o inverno: pastagem intensiva (PI) com retorno dos animais às parcelas quando a pastagem atinge 10 cm de altura, pastagem moderada (PM) com retorno dos animais às parcelas quando a pastagem atinge 30 cm de altura, e se sem pastagem (SP). Para avaliar as propriedades químicas e a mineralogia dos solos, as amostras foram coletadas nas seguintes camadas 0-5; 5-10; 10-20 e 20-40 cm, em novembro de 2013.

O carbono orgânico total (COT) foi determinado por combustão seca, em analisador de carbono orgânico total SHIMADZU. O cálcio, magnésio e alumínio trocáveis foram extraídos com solução de KCl 1 $molL^{-1}$ e quantificados através de absorção atômica (Ca, Mg) e por titulação para Al. O potássio e o sódio foram extraídos com acetato de amônio à 1 $molL^{-1}$ e quantificado por fotometria de chama. Os teores de H + Al trocáveis foram determinados por extração com solução de acetato de cálcio 0,5 $molL^{-1}$ tamponada a pH 7,0 e determinados por titulação, conforme descrito por Embrapa (1997). A partir destes dados foram calculados: capacidade de troca de cátions ($CTC_{pH\ 7,0}$), soma de bases (S), saturação por alumínio (Al%) e saturação por bases (V%).

As análises químicas totais foram realizadas em amostras de rocha, saprolito e solo, finamente moídas. Após ataque triácido ($HF\text{-}HNO_3\text{-}HClO_4$) para a abertura das amostras, os elementos foram determinados por Espectroscopia de Emissão Atômica com Plasma de Acoplamento Indutivo (ICP), no Bureau Veritas – Mineral Laboratories (Canadá). A composição química das amostras foi utilizada para calcular os índices de intensidade de alteração, como o Weathering Intensity Scale - WIS (Meunier et al, 2013) e o Chemical Index of Altération - CIA (Nesbitt et Young, 1982).

O WIS quantifica a perda de sílica no processo de alteração utilizando o parâmetro Δ4Si (diferença entre a composição 4Si da amostra alterada e da rocha não alterada) e o acúmulo relativo de ferro e alumínio com a relação molar R^{3+} / (R^{3+} R^{2+}+ M^{+} - ; $R^{3+} = Al^{3+} + Fe^{3+}$; $R^{2+} = Fe^{2+} + Mg^{2+}$; $M^{+} = Na^{+} + K^{+} + 2xCa^{2+}$) (Meunier et al, 2013). O CIA quantifica o acúmulo de alumínio durante o processo de alteração ($CIA = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$) proposto por Nesbitt et Young (1982).

A composição granulométrica foi determinada após dispersão das amostras de fração terra fina seca ao ar (TFSA) com NaOH 1 $molL^{-1}$ (pH < 9) e agitação mecânica. A fração areia foi separada por tamisagem úmida (peneira malha 0,053 mm). A fração argila foi determinada pelo método da pipeta (Embrapa, 1997). A fração argila (<2 µm) foi obtida por sedimentação, obedecendo à lei de Stokes.

O fracionamento da argila foi realizado com objetivo de obter uma melhor visualização das mudanças mineralógicas em virtude da ação antrópica (estudo 2), sobretudo sobre os argilominerais 2:1 hidroxi-entrecamada. Este fracionamento foi efetuado por centrifugação (Heraeus Biofuge stratos) com velocidades e tempo de rotações diferentes, para obter cada fração em função das especificações do rotor. A fração argila foi dispersa. A fração inferior a 0,05 µm foi obtida com uma velocidade de rotação de 1400 rpm durante 15 minutos; a fração inserida entre 0,05 e 0,1 µm com centrifugação a 8500 rpm por 10 minutos; e o material residual é formado por partículas entre 0,1 e 2 µm. Cada ciclo de centrifugação foi realizado até o esgotamento (sobrenadante incolor) para extração completa das partículas. Após o fracionamento, as amostras foram liofilizadas para uma melhor recuperação do material e para evitar perdas.

A determinação da área superficial específica (ASE) foi realizada por diferença de peso (obtido em balanças analíticas) entre amostras secas em atmosfera a 0 % e após adsorção de água em atmosfera a 20 % de umidade relativa conforme Quirk (1955).

O Fe referente aos óxidos de ferro pedogênicos (Fed) foram extraídos com ditionito-citrato-bicarbonato de sódio a 80°C (Mehra e Jackson, 1960). O Fe referente às formas de óxidos de ferro de baixa cristalinidade (Feo) foram extraídos com solução de oxalato de amônio 0,2 $molL^{-1}$ a pH 3, no escuro (Schwertmann, 1964).

Para as amostras relativas ao estudo de impacto antrópico (estudo 2), a fração argila (< 2 µm) foi desferrificada (tratada com DCB) antes do estudo mineralógico por difração de raio-X (DRX) e do fracionamento inframicrométrico.

Após a recuperação das frações, as amostras foram saturadas com cálcio e potássio para realizar a DRX em argilas homogêneas. A saturação foi realizada por contato com solução (3-5 saturações) de Ca ($CaCl_2$ 0,5 $molL^{-1}$) e K (KCl 1 $molL^{-1}$). Depois de saturadas, as amostras foram lavadas para remoção do excesso de sais. Lâminas orientadas foram preparadas pela deposição de uma fina camada da suspensão de argila em lâminas de vidro, as quais foram secas à temperatura ambiente (seca ao ar – 25°C). As lâminas saturadas com Ca passaram também por solvatação com vapor de etileno-glicol (EG), a 50 °C, no interior de um dessecador, durante 16 horas. As lâminas saturadas com K foram analisadas após tratamentos térmicos a 110, 330 e 550 °C. Os difratogramas das lâminas orientadas foram registrados em um difratômetro Bruker D8 Advance (Cu Kα).

Estudo 1: Alteração mineralógica e formação de solos em rochas ígneas no sul do Brasil

Resultados

Propriedades gerais do solo

Os teores de C orgânico para os solos desenvolvidos de basalto foram altos (> 30 g kg^{-1}) em superfície e decresceram com em profundidade. Os valores de pH em água indicaram reações moderadamente ácida (5,9) a moderadamente alcalina (7,8) no solo de São Borja (Vertic Hapludolls – VH), e moderadamente ácida (5,9) a praticamente neutra (6,7) no solo de Taquara (Typic Hapludolls – TH) (Embrapa, 2006). A capacidade de troca de cátions é alta (CTC ≥ 15 $cmol_c$ kg^{-1}), com valores mais elevados no solo VH. A saturação por bases foi superior a 70% em todos os horizontes, com predomínio dos cátions Ca^{2+} e Mg^{2+}, enquanto a saturação por Al^{3+} foi praticamente nula. Os altos teores de Ca^{2+} na CTC reforçam a constatação de campo da ocorrência de concreções carbonáticas no solo VH.

Para o perfil formado a partir de gnaisse (Rhodic Paleudult - RP) em Eldorado do Sul, os teores de C orgânico foram menores (< 12 g kg^{-1}) e diminuíram em profundidade. A reação do solo foi fortemente ácida (4,3 a 5,3) ao longo de todos os horizontes. Os valores da CTC variaram de baixo a médio, sendo inferiores a 8,1 $cmol_c$ kg^{-1}. A dessaturação do solo se expressou na baixa soma de bases (≤ 2,2 $cmol_c$ kg^{-1}) e saturação por bases (V ≤ 40%). O Al trocável foi alto (1,2 ≤ Al ≤3,7 $cmol_c$ kg^{-1}), bem como a saturação por Al (35 ≤ m ≤ 69%). Esses resultados caracterizam quimicamente o solo RP como intensamente lixiviado e em avançado grau de intemperização.

Mineralogia dos perfis de alteração

Os minerais que foram identificados nas rochas, saprolitos e solos foram piroxênios, feldspatos potássios, plagioclásios e quartzo, e minerais secundários como argilominerais 2:1, caulinita e óxidos de ferro. A DRX da fração TFSA dos materiais saprólito e solo alterado dos basaltos diferiram fundamentalmente pela presença de reflexões intensas de argilominerais 2:1 no perfil São Borja, inclusive nos horizontes A e B, e pela ausência de caulinita; comparativamente ao perfil Taquara, onde as reflexões de argilominerais 2:1 diminuem de intensidade em direção a superfície do solo e ocorrem reflexões indicando a presença de caulinita. A DRX da fração TFSA dos materiais saprólito e solo alterados de gnaisse foi muito semelhante ao longo do perfil de alteração, sendo composta, predominantemente, por quartzo e caulinita.

Os DRXs da fração < 2 µm do solo de São Borja apresentaram predominância de argilominerais 2:1 em todos os horizontes, com pequenos reflexos de quartzo nos horizontes A e B. Os argilominerais 2:1 presentes nesse solo pertencem ao grupo das esmectitas em função da expansão verificada nos DRXs de espaçamentos d ~ 15 Å para espaçamentos d ~ 17 Å após solvatação com etilenoglicol. A presença do quartzo em horizontes superficiais tem sua origem associada ao Arenito Botucatu intertrápico aos derrames basálticos no sul do Brasil.

A fração < 2 µm do perfil Taquara apresentou reflexões intensas relativas à ocorrência de esmectita e caulinita. Foram ainda observadas reflexões com muito baixa intensidade relativas ao quartzo no horizonte A e de feldspatos no saprolito na profundidade de 3 a 3,5 m. Diferentemente do verificado no perfil São Borja, nos DRXs do perfil Taquara as intensidades das reflexões de esmectita foram marcantes na camada saprolítica e no horizonte C, e diminuíram nos horizontes A e B. Por outro lado, as reflexões relativas a ocorrência da caulinita apresentaram aumento de intensidade em direção aos horizontes mais superficiais (horizontes A e B), sugerindo que a formação de caulinita nesse perfil ocorre às expensas da dissolução-neoformação/transformação das esmectitas.

Para o perfil Rhodic Paleudult (RP) as reflexões de DRX da fração < 2 µm apresentaram maior intensidade na ocorrência de caulinita e quartzo. Em adição, embora não tenha sido constatada nas frações areia e silte desse solo, reflexões em espaçamento d ~ 10 Å identificaram a presença de mica (mica/ilita) na fração argila, as quais diminuem em direção a superfície do solo. A composição essencialmente caulinítica da fração argila do solo RP, desenvolvido de gnaisse, confere ao mesmo o grau de alteração mais intenso entre os três perfis de alteração avaliados nesse estudo.

Índices de alteração

Nos perfis de alteração desenvolvidos de rochas basálticas, os valores dos três índices de intemperismo analisados (Δ4Si; $R^{3+}/(R^{3+}+R^{2+}+M^{+})$; CIA) aumentaram desde a rocha até a superfície do solo, indicando um avanço do grau de intemperismo ao longo do perfil. Considerando que os valores dos índices foram semelhantes nos dois basaltos, os maiores valores dos índices verificados no perfil Taquara indicaram um grau de intemperismo mais avançado em relação ao perfil São Borja. No perfil formado a partir de gnaisse, exceto no saprolito Cr2, onde os valores de $R^{3+}/(R^{3+}+R^{2+}+M^{+})$ e CIA foram 0,72 e 72,6, respectivamente; os demais valores foram expressivamente elevados (superiores a 0,92 e 93,3, respectivamente), caracterizando um grau de intemperização desse perfil mais avançado em comparação aos perfis desenvolvidos de basalto. Esses resultados suportam os resultados obtidos nas análises por DRX.

Os valores dos índices de alteração dos horizontes superficiais dos perfis São Borja e Taquara são diferentes. Os valores mais baixos de 4Si, Δ4Si et R^{3+} / (R^{3+}+ R^{2+}+ M^{+}) para o perfil São Borja podem estar ligados a uma mineralogia dominada por esmectitas que implicam em perdas mais baixas de Si, Ca e Mg.

No diagrama ternário M^{+} - 4Si - R^{2+} os valores para o perfil Eldorado do Sul estão próximos do pólo 4Si devido a perdas importantes de cátions alcalinos e alcalino terrosos. Esses valores estão em acordo com uma mineralogia predominantemente caulinitica desse solo. Ressalta-se também que os teores de cátions alcalinos e alcalino terrosos são mais baixos no gnaisse do que nos basaltos.

Considerações finais

Os basaltos dos perfis de alteração São Borja (Vertic Hapludolls) e Taquara (Typic Hapludolls) apresentam os mesmos minerais, feldspatos potássicos, piroxênios, plagioclásios e traços de óxidos. O basalto do perfil São Borja apresenta minerais maiores e melhor preservados, ao passo que o basalto do perfil Taquara apresenta feições de amígdalas com presença de celadonita em seu interior. Os minerais dominantes nesses perfis de alteração são esmectitas no perfil São Borja; caulinita, esmectita e esmectita com hidróxi-Al^{3+}no perfil Taquara, e caulinita e quartzo no perfil Eldorado do Sul.

O conjunto de análises realizadas indicou a seguinte sequência intempérica para os três perfis de alteração: São Borja < Taquara < Eldorado do Sul. No perfil São Borja, as esmectitas são neogênicas, formadas a partir da dissolução dos plagioclásios e feldspatos alcalinos. No perfil Taquara, a sequência de alteração observada é: plagioclásios e feldspatos alcalinos →Esmectita→HIS→Caulinita. No perfil Eldorado do Sul, a caulinita é formada por transformação de minerais primários (micas, plagioclásios e feldspatos potássios) e reprecipitação. Nos três perfis os oxihidróxidos de ferro são formados por alteração dos minerais ferromagnesianos (piroxênios nos basaltos e biotita no gnaisse).

Estudo 2: Impacto de um sistema integrado soja-bovinos de corte sobre a mineralogia de um Latossolo no sul do Brasil

Resultados

Propriedades gerais do solo

Os atributos químicos do solo apresentaram estratificação dos valores ao longo do perfil do solo. A única exceção foi para o pH, onde valores semelhantes foram observados em todas as camadas de solo avaliadas. O tratamento com pastejo intenso (PI) apresentou maior pH em H_2O em comparação com o pastejo moderado (PM) e sem pastejo (SP). As concentrações de COT na camada de 0-5 cm apresentaram diferenças significativas entre as diferentes intensidades de pastejo, com concentrações mais baixas no PI e PM, em comparação com o SP.

Nenhuma diferença significativa na disponibilidade de elementos nutritivos (P disponível, Ca trocável, CTC) e no estado de acidez do solo (Al trocável) foi observada entre as intensidades de pastejo. As concentrações de Mg trocável apresentaram uma relação positiva com a taxa de lotação animal, com valores mais altos e mais baixos respectivamente observados sob PI e SP. Finalmente, os tratamentos pastejados (PI e PM) mostraram baixa disponibilidade de K independentemente da camada de solo em comparação com o SP.

Mineralogia da argila e sub-frações

Os argilominerais identificados na fração < 2 µm de SP e PI foram a caulinita (7.14 e 3.57Å) e argilominerais 2:1 (14.2 e 4.74 Å). Os argilominerais 2:1 não apresentaram deslocamento do pico na sequência de solvatação com etileno glicol, indicando ausência de expansão das camadas. Este mineral pode então ser identificado como vermiculita com hidroxi-entrecamadas. As frações mais finas são praticamente desprovidas de argilominerais 2:1 e contêm ainda caulinita mal cristalizada, conforme indicado pela largura dos picos em 7.14 e 3.57 Å para todos os tratamentos e camadas. De maneira oposta, a fração mais grosseira (0.1-2 µm) apresenta picos bem definidos e intensos para caulinita e argilominerais 2:1. A fração intermediária (0,05-0,1 µm) apresenta picos de caulinita com largura maior do que na fração mais grosseira e ainda picos mal definidos para os argilominerais 2:1.

Do mesmo modo como para o SP, o tratamento PI apresentou um aumento da intensidade e uma diminuição da largura dos picos com aumento do tamanho de partícula. A assembléia mineral é semelhante à observada para o tratamento SP.

Para a amostra PI - 0-5 cm, o pico em 14.25 Å desloca-se a 14.30 Å após a solvatação com EG e o pico em 4.76 Å (e em aproximadamente 2.84 Å) na fração 0.1-2 µm apresentam diferenças após solvatação com EG, indicando a presença de pequena quantidade de camadas expansivas.

Para a amostra de superfície (0-5 cm) o colapso dos picos após saturação com K e o aquecimento a 350 e 550°C é menos significativo para SP especialmente para a fração 0.1-2 µm. O pico em 14.25 Å (Ca 25°C) apresenta uma divisão resultando em dois picos, em 11.48 Å e 10.48 Å (PI 0-5 cm). Este comportamento indica que os argilominerais 2:1 correspondem a vermiculita (colapso completo para 10 Å) e vermiculita com hidroxi-alumínio entrecamada, VHE (colapso parcial). O pico em 10 Å é mais definido do que para o SP indicando um menor grau de aluminização dos minerais hidróxi-entrecamada (HE).

Para a camada de 20-40 cm verifica-se a mesma tendência, no entanto, um menor colapso após a saturação com K e aquecimento, o que indica maior quantidade de VHE do que na superfície ou um grau mais elevado de aluminização com HE. Para a fração do tratamento PI na camada de 20-40 cm o pico em 14.27 Å desloca-se para 14.31 Å após a solvatação com EG e o pico em 4,76 Å (e em aproximadamente 2.84 Å) apresenta ligeira diferença após a solvatação EG, indicando uma quantidade muito pequena de camadas de expansão.

As análises de DRX revelaram a presença de argilominerais 2:1HE nas duas parcelas estudadas, independente da profundidade. Esses minerais HE se formam em razão de uma forte aluminização do solo. A presença de um pastejo intensivo tem uma tendência a favorecer a formação de VHE causando diminuição da CTC do solo.

Considerações finais

Semelhante mineralogia da fração argila do solo foi observada nos diferentes tratamentos, com a predominância de caulinita e minerais 2:1HE. No entanto, após 12 anos sob um sistema de produção integrada de soja-bovinos de corte, as áreas sem pastejo apresentaram menor intensidade para minerais 2:1. Áreas sob pastejo intensivo e moderado apresentaram comportamento semelhante com maior aluminização dos minerais 2:1 entrecamada. A maior aluminização sob manejo de pastejo intenso e moderado pode servir como um dreno de alumínio na fase sólida do solo, tornando-o menos disponível para as plantas e diminuindo sua fitotoxicidade.

A certificação do efeito da intensidade de pastejo na mineralogia do solo só pode ser verificada com o estudo detalhado da fração argila, o que necessariamente inclui o seu fracionamento. Assim, é altamente recomendável realizar o fracionamento da argila, especialmente quando estudando minerais 2:1 entrecamada.

As variações mineralógicas observadas estão ligadas à evolução dos principais fatores (acidez, disponibilidade de Al, teor de MO) relacionados à formação dos argilominerais 2:1HE. Em virtude da presença e ação do pastejo e da pedofauna, a matéria orgânica do PI se acumula menos, condição que favorece a formação de VHE no solo. Pois que, haverá menor complexação de Al pela MO e assim, favorecer a incorporação desse nos argilominerais 2:1, formando HE’s as despensas dos argilominerais expansivos. A maior disponibilidade de K nas áreas pastejadas, associada à presença de dejeto animal, tem também importante influência na formação dos minerais entrecamada, ao mesmo tempo em que o K pode concorrer com o Al para ocupar espaço nas entrecamadas dos minerais 2:1HE.

RÉSUMÉ ÉTENDU

Introduction

Le Rio Grande do Sul (RS), l'Etat le plus méridional du Brésil, est formé par quatre grandes provinces géomorphologiques (Escudo Sul-rio-grandense, Depressão Central, Planalto et Planicie costeira), qui ont des origines géologiques distinctes (Brésil, 1986; CPRM, 2006). Dans les provinces de l'Escudo Sul-rio-grandense et du Planalto les roches ignées ou magmatiques prédominent. L'Escudo Sul-rio-grandensese situe dans la partie centre-sud de l'état et présente les roches les plus anciennes datées de la période cambrienne (~ 542 Ma) jusqu'à probablement la période archéenne (plus de 2500 Ma). Du fait de son ancienneté, ce bouclier comprend une géologie très complexe formée par des roches magmatiques plutoniques, de composition principalement granitique, associées à des ceintures de roches métamorphiques distribuées en reliefs ondulés.

Cette diversité de paysages et de lithologies associées aux différences climatiques importantes induisent une grandevariabilité de la pédogenèse et des types de sols dans le Rio Grande do Sul (Brésil, 1973; Streck et al, 2008). En général, les sols du RS ont une faible fertilité naturelle, exprimée par une forte acidité, une faible CEC (capacité d'échange cationique) et une faible saturation enbases et des teneurs élevées en aluminium échangéable. Les sols du Planalto, principalement développés sur basalte, présentent une grande variabilité en raison de la diversité climatique liée à la topographie.

Dans cette province on observe un gradient d'altitude en espalier décroissant de l'ouest (~900 m - Taquara) vers l'est (~60 m - São Borja) qui induit un fort gradient orographique ouest - est du climat (T, P). En altitude le climat est tempéré avec des précipitations moyennes annuelles de l'ordre de 2000 mm an^{-1} et une température moyenne annuelle de 14,4°C (Malouf, 2000). Avec la diminution de l'altitude le climat varie de super-humide à subtropical sub-humide avec des précipitations moyennes annuelles de ~1300 mm an^{-1} et une température moyenne annuelle de 20°C (Malouf, 2000).

Les sols du RS sont globalement fortement altérés du fait du climat subtropical de cette région mais detelles conditions donnent lieu à une répartition spatiale selon une séquence est – ouest :

- sols très altérés (forte acidité, faible CEC et taux de saturation en bases, saturation élevée par Al) comme les Oxisols et les Alfisols riches en kaolinite, oxy-hydroxydes de feret avec présence de minéraux 2:1 HI (hydroxy-interfoliare) à l’ouest ;

- sols plus faiblement altérés et/ou développés (pH proche de la neutralité, CEC et taux de saturation en bases élevés) comme les Entisols, Mollisols et Vertisols avec une minéralogie dominée par les smectites.

La superficie cultivée au Rio Grande do Sul est d’environ 6 millions d'hectares. L’agriculture (céréales, soja, pâturage) et l’élevage (bovin, porcin, volailles) sont très intensifs comparé aux autres états brésiliens. Cette agriculture intensive exerce une pression importante sur les sols (exportation des nutriments, réduction de la teneur en matière organique, compaction, érosion, etc...), qui dépend des différentes utilisations et des modes de gestion des sols. Le comportement physique et chimique du sol est fortement influencé par leur composition minéralogique (Kämpf et Curi, 2003).

Les actions prévues dans la présente étude de doctorat seront divisées en deux axes principaux. Le premier axe (**étude 1**) porte sur l’étude des processus d’altération sur basalte et sur gneiss dans différentes régions climatiques du RS afin de préciser l’intensité de l’altération, de la minéralogie des argiles associée à ces processus et les facteurs qui contrôlent la formation des sols. Le deuxième axe (**étude 2**) questionne l'effet des activités humaines (principalement agriculture intensive) sur l’évolution pédogénétique et notamment les changements possibles de la minéralogie des argiles et des propriétés physico-chimiques.

Dans ce contexte, ce travail de thèse a comme objectifs :(i) caractériser les aspects minéralogique, pédochimique et géochimique des profils d'altération développés en l'absence d'action humaine ou avec une intervention minimale (étude 1); (ii) caractériser qualitativement et semi-quantitativement les minéraux primaires et les minéraux pedogenic dans les sols insérés dans les régions importantes de l'écosystème du Rio Grande do Sul (étude 1) ; et (iii) évaluer l'impact des différentes intensités de pâturage sur la minéralogie d’un Oxisol sous système intégré de production soja-élevage dans le sud du Brésil (étude 2).

Matériels et méthodes

Les emplacements choisis pour la description et la collecte des trois profils d'altérations (roche saine - saprolite - horizons pédogénétiques) de **l’étude 1** sont situés dans les municipalités de São Borja (basalte - 28°57’30’’S, 55°43’60’’W); de

Taquara (basalte – 29°44’30’’S, 50°51’40’’W) et d’Eldorado do Sul (gneiss – 30°06’11’’S, 51°40’33’’W), dans l'état du Rio Grande do Sul, Brésil.

L’étude 2 a été menée sur un essai de long terme de suivi des propriétés des sols et de la production agricole mis en place en 2001 et situé à São Miguel das Missões dans le Rio Grande do Sul, Brésil (28 ° 57'23 "S, 54 ° 21'22"W). Les rotations de cultures correspondent au soja en été et à un mélange avoine noire + ray-grass Italien en hiver. Les parcelles de l’aire expérimentale sont soumises à différentes intensités de pâturage pendant l’hiver: le pâturage intensif (PI) avec un retour des animaux sur les parcelles dès que l’herbe atteint 10 cm de hauteur, pâturage modéré (PM) avec un retour des animaux sur les parcelles dès que l’herbe atteint 30 cm de hauteur, et sans pâturage (SP). Pour évaluer les propriétés chimiques et la minéralogie des sols, des échantillons ont été prélevés aux profondeurs 0-5 cm, 5-10 cm, 10-20 cm, 20-40 cm, en novembre 2013.

Le carbone organique total a été déterminé par combustion sèche avec un Analyseur Shimadzu Carbone Organique Total (COT). Le calcium, le magnésium et l’aluminium échangeables sont extraits avec une solution de KCl 1 mol L^{-1} et quantifiés par absorption atomique (Ca, Mg) et par titration pour Al. Le potassium et le sodium sont extraits avec de l'acétate d'ammonium à 1 mol L^{-1} et quantifiés par photométrie de flamme. Les teneurs en H + Al échangeables sont déterminées par extraction avec une solution d'acétate de calcium 0,5 mol L^{-1} tamponnée à pH 7,0 et déterminées par titration selon les procédures décrites par l'EMBRAPA (1997). Ces données sont utilisées pour calculer : la capacité d'échange cationique (CECpH 7,0), la somme des bases (SB), la saturation en aluminium (% Al) et le taux de saturation en bases (%V).

Les analyses chimiques totales ont été effectuées sur des échantillons de roche, de saprolite et de sol, finement broyés. Les éléments ont été déterminées par spectroscopie d'émission atomique avec plasma à couplage inductif (ICP) après dissolution en milieu acide (HF-HNO_3-$HClO_4$) au Laboratoire de Minéralogie du Bureau Veritas au Canada.La composition chimique a été utilisée pour calculer des indices d'intensité d’altération comme le Weathering Intensity Scale –WIS (Meunier et al, 2013) et le Chemical Index of Altération – CIA (Nesbitt et Young, 1982).Le WIS quantifie la perte en silice au cours de l’altération en utilisant le paramètre Δ4Si (différence entre la composition 4Si de l’échantillon altéré et de la roche non altérée) et l’accumulation relative de fer et d’aluminium avec le ratio molaire R^{3+} /

(R^{3+} R^{2+}+ M^{+} - ; $R^{3+} = Al^{3+} + Fe^{3+}$; $R^{2+} = Fe^{2+} + Mg^{2+}$;$M^{+} = Na^{+} + K^{+} + 2xCa^{2+}$) (Meunier et al, 2013). Le CIA quantifie l’accumulation d’aluminium au cours de l’altération ($CIA = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$) proposé par Nesbitt et Young (1982).

La composition granulométrique est déterminée après dispersion des échantillons séchés à l’air dans de l’eau distillée avec quelques gouttes de NaOH $1molL^{-1}$ ($pH < 9$) et agitation mécanique. La fraction sableuse est séparée par tamisage à l’aide d’un tamis 0,053mm. La fraction argileuse(<2µm) a été séparée de la fraction limoneuse par sédimentation suivant la loi de Stokes, et la fraction limoneuse est déterminée par la méthode de la pipette. La fraction argileuse (<2µm) est obtenue par sédimentation, obéissant à la loi de Stokes.

Le fractionnement des argiles a été réalisé dans le but d’obtenir une meilleure visualisation des modifications minéralogiques engendrées par l’action anthropique (étude 2), notamment sur les minéraux 2:1 hydroxy-alumineux (hydroxy aluminium entre les feuillets). Ce fractionnement est effectué par centrifugation (Heraeus Biofuge stratos) avec des vitesses et un temps de rotation différents pour obtenir chaque fraction et fonction des spécificités du rotor. La fraction argileuse est alors dispersée. La fraction inférieure à 0,05µm est obtenue avec une vitesse de rotation de 14000tr/min pendant 15min ; la fraction comprise entre 0,05 et 0,1µm est obtenue pour une vitesse de 8500tr/min pendant 10min; et le matériel résiduel est compris entre 0,1 et 2µm. Chaque cycle de centrifugation est réalisé jusqu’à épuisement (surnageant clair) pour extraire la totalité des particules. Après fractionnement, les échantillons ont été lyophilisés pour une meilleure récupération du matériel et pour éviter des pertes.

La détermination de la surface spécifique du sol est réalisée par mesure de différence de masse (obtenue à l’aide d’une balance) entre des échantillons secs (humidité relative de 0%) et après absorption d’eau à une humidité relative de 20% (Quirk, 1955).

Le fer correspondant aux oxy-hydroxydes de fer (Fe_d) totaux (bien cristallisés + mal cristallisés) estextrait à l’aide du réactif Citrate-Bicarbonate-Dithionite (CDB) de sodium à 80°(Mehra & Jackson, 1960). Le réactif CDB agit par l'effet réducteur du dithionite et le pouvoir complexant du citrate.

Le fer des oxydes de fer de faible cristallinité (Fe_o) a été extrait à l'aide d'une solution d'oxalate d'ammonium 0,2molL^{-1} à pH 3 et à température ambiante à dans l'obscurité pendant 4 h.

Pour les échantillons relatifs à l'étude de l'impact anthropique (étude 2) la fraction argileuse (<2 µm) a été déferrifiée (traitement CBD) avant l'étude minéralogique par diffraction des rayons X (DRX) et le fractionnement infra-micrométrique.

Après récupération, les fractions argileuses ont été saturées avec du calcium et du potassium pour réaliser la DRX sur des argiles homogeniques. La saturation a été réalisée par la mise en contact de l'échantillon avec une solution de KCl 1 molL^{-1} ou avec une solution de $CaCl_2$ 0,5molL^{-1} cinq fois avec un cycle de centrifugation entre chaque nouvelle mise en contact. L'excès de $CaCl_2$ et KCl a été éliminé par des lavages en centrifugeuse ou par dialyse. Des lames orientées ont été réalisées avec la même masse de fraction et séchées à l'air libre. Les lames avec dépôt saturé Ca ont été saturées à l'éthylène glycol (EG) en phase gazeuse. Les lames avec dépôt saturé K ont été chauffées à 150°C, 350°C et 550°C. Les diffractogrammes des préparations orientées ont été enregistrés avec un diffractomètre Bruker D8 Advance (Cu Kα).

Etude 1 : Altération minéralogique et formation de sols sur les roches ignées au sud du Brésil

Résultats

Propriétés générales du sol

Les teneurs en C organique des sols développés sur basalte sont élevées (> 30 g kg^{-1}) en surface et diminuent avec la profondeur. Les valeurs de pH indiquent des conditions modérément acides (5,9) à légèrement alcaline (7,8) dans le sol de São Borja (Vertic Hapludolls – VH) et modérément acide (5,9) à neutre (6,7) dans le sol de Taquara (Typic Hapludolls – TH) (EMBRAPA 2006). La capacité d'échange cationique est élevée (CEC ≥ 15 cmolc kg^{-1}), avec des valeurs plus élevées dans le sol VH. La saturation en bases est supérieure à 70% pour tous les horizons, avec une prédominance des cations Ca^{2+} et Mg^{2+}, alors que la saturation en Al^{3+} est pratiquement nulle. La forte proportion de Ca^{2+} dans la valeur de CEC est cohérente avec l'observation sur le terrain de concrétions carbonatées dans le sol VH.

Pour le profil formé à partir de gneiss (Rhodic Paleudult - RP) à Eldorado do Sul, les teneurs en C organique étaient plus faibles (<12 g kg^{-1}) avec une diminution en profondeur. Le sol est fortement acide avec des pH allant de 4,3 à 5,3 pourtous les horizons. La CEC allait de faible à moyenne avec des valeurs inférieures à 8,1 cmolc kg^{-1}. La désaturation du sol est exprimée par une faible somme des bases (≤ 2,2 cmolc kg^{-1}) et saturation en base (V ≤ 40%). L'Al échangeable (1,2 ≤ Al ≤3,7 cmolc kg^{-1}) et la saturation Al (35 ≤ m ≤ 69%) est à l'inverse élevée. Ces résultats chimiques caractérisent le sol RP comme intensément appauvri et avec un degré avancé d'altération.

Minéralogie des profils d'altération

Les minéraux identifiés dans les roches, les saprolites et les sols sont les pyroxènes, les feldspaths potassiques, les plagioclases et le quartz et des minéraux secondaires argileux 2:1, la kaolinite et les oxydes de fer. Les DRX de poudre de saprolite et de sol diffèrent principalement par la présence de réflexions intenses de minéraux 2:1 et l'absence de kaolinite dans les horizons A et B du sol de São Borja, par rapport au profil Taquara pour lequel l'intensité des réflexions des minéraux 2:1 diminue vers la surface du sol, alors que les réflexions de la kaolinite sont plus intenses. La DRX de poudre de saprolite et de sol sur gneiss indique une minéralogie très similaire dans tout le profil d'altération, constituée principalement de quartz et de kaolinite.

La DRX de la fraction<2 µm du sol de São Borja montre une prédominance de minéraux 2:1 dans tous les horizons, avec des réflexions de quartz peu intenses pour les horizons A et B. Les minéraux 2:1 présents dans ce sol appartienent au groupe de smectite en raison du déplacement du pic à d~15 Å AD à d~17 Å après solvatation avec l'éthylène glycol. La présence de quartz dans les horizons de surface est très probablement liée à la présence de bancs de grès de la formation Arenito Botucatu entre les coulées basaltiques.

La fraction < 2 µm du profil Taquara montre des réflexions intenses correspondant à la smectite et la kaolinite. Des réflexions du quartz de très faible intensité sont observées dans l'horizon A. Des feldspaths sont identifiés dans la saprolite à une profondeur de 3 à 3,5 m. A l'inverse du profil de São Borja, dans le profil Taquara les intensités des réflexions de smectite sont marquées dans la saprolite et l'horizon C et diminuent dans les horizons A et B. D'autre part, l’intensité des réflexions de la kaolinite augmentent dans les horizons superficiels (horizons A et B), ce qui suggère que la formation de kaolinite dans ce profil se produit au détriment de la smectite (dissolution – recristallisation).

Pour le profil Rhodic Paleudult (RP) les réflexions DRX de la fraction < 2µm les plus intenses correspondent à la kaolinite et au quartz. En outre, les réflexions à d ~ 10 Å indiquent la présence de mica (mica/illite) dont la proportion diminue vers la surface du sol. La composition essentiellement kaolinitique de la fraction d'argile du RP indique un degré d’altération plus important pour ce profil parmi les trois profils d’altération évalués dans cette étude.

Indices d’altération

Pour les profils d'altération développés à partir de roches basaltiques, les valeurs des trois indices analysés (Δ4Si; R^{3+} / (R^{3+}+ R^{2+}+ M^{+}); CIA) augmentent de la roche à la surface du sol, ce qui indique une progression du degré d'altération au long du profil. Considérant les valeurs des paramètres 4Si, R^{3+}+ R^{2+}+ M^{+} similaires dans les deux basaltes non altérées ; les valeurs plus élevées pour Δ4Si et R^{3+} / (R^{3+}+ R^{2+}+ M^{+}) trouvées pour le profil Taquara indiquent un degré d'altération plus avancé que pour le profil São Borja. Pour le profil formé à partir de gneiss les valeurs de R^{3+} / (R^{3+}+ R^{2+}+ M^{+}) et le CIA sont supérieures à 0,92 et 93,3 indiquant un degré d'altération de ce profil plus avancée que ceux développés sur basalte. Seul le saprolite Cr2 possède des valeurs plus faibles avec un CIA de 72.6 et un R^{3+} / (R^{3+}+ R^{2+}+ M^{+}) de 0,72. Ces résultats confirment les résultats obtenus à partir des analyses DRX. Les valeurs des indices d’altération des horizons de surface des profils São Borja et Taquara sont différents. Les valeurs plus faibles de 4Si, Δ4Si et R^{3+} / (R^{3+}+ R^{2+}+ M^{+}) pour le profil São Borja peuvent être liée à une minéralogie dominée par les smectites qui impliquent des pertes plus faibles en Si, Ca et Mg.

Dans le diagramme ternaire M^{+} - 4Si – R^{2+} les valeurs du profil d’Eldorado do Sul sont proches du pôle 4Si en raison de pertes importantes des cations alcalins et alcalino-terreux. Ces valeurs sont en accord avec une prédominance de la kaolinite dans la minéralogie du sol. Il faut également noter que les teneurs en alcalins et alcalino-terreux sont plus faibles dans le gneiss que dans les basaltes.

Considérations finales

Les basaltes des profils de São Borja (Vertic Hapludolls) et de Taquara (Typic Hapludolls) ont une minéralogie proche composée de feldspaths, pyroxènes, plagioclases et quelques oxydes. Le profil São Borja présente les minéraux mieux conservé, tandis que le basalte profil Taquara présente des vésicules contenant de la céladonite. Les minéraux dominants de ces profils d'altération sont la smectite pourle profil São Borja; la kaolinite, la smectite et les smectites et/ou vermiculites avec hydroxy-Al^{3+}interfoliaire pour le profil Taquara, et la kaolinite et le quartz pour le profil d'Eldorado do Sul.

L'ensemble des analyses indique la séquence d'altération suivante pour les trois profils : São Borja <Taquara <Eldorado do Sul. Pour le profil São Borja, les smectites sont néoformées à partir de la dissolution des plagioclases et des feldspaths alcalins. Pour le profil Taquara la séquence d'altération suivante est proposée : plagioclases et feldspaths alcalins → smectite → HIS → kaolinite. Pour le profil Eldorado do Sul la kaolinite est néoformée par dissolution des minéraux primaires (micas, plagioclases et feldspaths potassiques) et reprécipitation. Dans les trois profils les oxy-hydroxydes de fer sont formés par l'altération des minéraux ferromagnésiens (ex. pyroxènes pour le basalte et biotite pour le gneiss)

Etude 2 : Impact d'un système intégré de production agricole de soja-élevage sur la minéralogie Oxisol dans le sud du Brésil

Résultats

Propriétés générales du sol

Les propriétés chimiques du sol présentent une stratification des valeurs le long du profil du sol. La seule exception concerne le pH, qui montre des valeurs similaires dans tous les horizons. Le traitement avec le pâturage intensif (IG) a présente un pH H_2O plus élevé que le pâturage modéré (MG) et l'absence de pâturage (NG). Les concentrations de COT de la couche 0-5 cm présentent des différences significatives entre les différentes intensités de pâturage avec des concentrations plus faibles observées pour IG et MG par rapport à NG.

Aucune différence significative de la disponibilité des éléments nutritifs (P disponible, calcium échangeables, CEC) et de l'état d'acidité du sol (Al échangeable) n'a été observée entre les intensités de pâturage. Les concentrations en Mg échangeable présentent une relation positive avec le taux de charge des animaux, les valeurs les plus élevées et les plus faibles étant respectivement observées pour IG et NG. Enfin, les traitements de pâturage (IG et MG) ont montré une disponibilité de K plus faible quelle que soit la couche de sol, par rapport à NG.

Minéralogie de la fraction argileuse et fractionnement infra-micrométrique

Les minéraux argileux identifiés dans la fraction <2 µm de NG et IG sont des kaolinites (7.14 et 3.57Å) et des minéraux argileux 2:1 (14.2 et 4.74 Å), qui ne se déplacent presque pas après la solvatation avec de l'éthylèneglycol révélant l’absence de feuillets gonflants. Ce minéral peut être identifié comme de la vermiculite avec l’aluminium hydroxylé interfoliaire. Les fractions les plus fines sont presque dépourvues de minéraux argileux 2:1 et contiennent de la kaolinite mal cristallisée comme indiqué par la largeur des pics à 7,14 et 3,57 Å pour tous les traitements et profondeurs. En revanche, la fraction plus grossière (0,1-2 µm) présente des pics bien définis et intenses de kaolinite et de minéraux argileux 2:1. La fraction intermédiaire (0,05-0,1 µm) présente des pics de kaolinite plus larges que dans la fraction plus grossière et des pics mal définis de minéraux argileux 2:1.

Comme pour le NG, IG présente une augmentation de l'intensité et une diminution de la largeur des pics à mesure que la taille des particules augmente. L'assemblage de minéraux argileux est semblable à celui observé pour la gestion des NG.

Pour l'échantillon IG 0-5 cm le pic à 14,25 Å se déplace à 14,30 Å après EG et le pic à 4,76 Å (et à environ 2,84 Å) de la fraction 0,1 à 2 µm présente des différences après solvatation EG, indiquant la présence d'une faible quantité de feuillets gonflants.

Pour l'échantillon de surface (0-5 cm), la fermeture des feuillets après saturation K et chauffage à 350 et 550°C est moins importante que pour le NG et en particulier pour la fraction 0,1-2 µm. Le pic à 14,25 Å (Ca AD) a une fermeture et une séparation en deux pics à 11,48 Å et 10,48 Å (IG 0-5 cm). Ce comportement indique que les minéraux argileux 2:1 correspondent à de la vermiculite (fermeture complète à 10 Å) et à de la vermiculite hydroxy-alumineuse ou HIV (fermeture partielle). Le pic obtenu à 10 Å pour IG est plus défini que pour NG indiquant un degré inférieur d’aluminisation des HIM.

La couche 20-40 cm présente la même tendance, cependant, avec une fermeture plus faible des feuillets après saturation K et chauffage indiquant une plus grande quantité de HIV qu'en surface ou un degré d'aluminisation plus élevé des HIM. Pour la fraction 0,1-2 µm du traitement IG à la profondeur 20-40 cm, le pic à 14,27 Å déplace à 14,31 Å après solvatation EG et le pic à 4,76 Å (et à environ 2,84 Å) présente de légères différences après la solvatation EG, indiquant la présence d'une très faible quantité de feuillets expansibles.

Les analyses au DRX ont révélé la présence de HIV dans les deux parcelles étudiées, quelle que soit la profondeur. Les HIV se forment en raison d'une forte aluminisation du sol. La présence d'un pâturage intensif a tendance à favoriser la formation de HIV ce qui entraîne une diminution de la CEC du sol.

Considérations finales

Une minéralogie similaire a été observée pour la fraction d'argile du sol des différents traitements, principalement kaolinite et minéraux 2:1HI. Cependant, après 12 ans dans le cadre d'un système de production intégrée soja-élévage, les zones non pâturées présentées plus faible intensité de minéraux 2:1. Les échantillons des zones sous pâturage intensif et pâturage modéré présentent un comportement similaire en raison de l'aluminisation supérieure de la couche interfoliaire desminéraux 2:1. L'aluminisation supérieure sous les pâturages intensifs et modérés peut être un drain pour l'aluminium dans la phase solide du sol, ce qui pourrait le rendre moins disponible pour les plantes et diminuer de sa phytotoxicité.

L'impact de l'intensité du pâturage sur la minéralogie du sol ne peut être vérifié que par une étude détaillée de la fraction argileuse. Il est fortement recommandé d'effectuer le fractionnement de la fraction argileuse en fractions inframicométriques pour étudier particulier les minéraux 2:1 avec de l'aluminium interfoliaire.

Les variations minéralogiques observées sont liées à l'évolution des principaux facteurs (acidité, disponibilité d'Al, teneur de MO) impliqués dans la formation de minéraux 2:1HI. Donc grâce à la présence et l'action du pâturage ainsi que de la pédofaune, la matière organique de IG s'accumule moins du fait d'une exportation plus élevée. Ainsi, une plus large quantité de matière organique aura tendance à entraîner la dissolution de l'Al des minéraux et ainsi à favoriser l'incorporation de celui-ci dans les minéraux argileux de type 2:1 pour former les

HIMs au dépend des minéraux argileux gonflants. La plus grande disponibilité de K dans les zones pâturées, associé aux déchets animaux, a aussi une influence importante sur la formation de ces minéraux avec de l’aluminium interfoliaire. Dans ces condition il peut y avoir une compétition entre K et Al comme cations interfoliaires des minéraux 2 :1.

SUMARY

LIST OF TABLES

LIST OF FIGURES

LIST OF ANNEXES

1. APRESENTAÇÃO GERAL

O presente trabalho de doutorado faz parte de um Programa COFECUB/CAPES Te 761/12 intitulado “Evolução mineralógica de solos do sul do Brasil: caracterização dos processos de alteração e do impacto antrópico”, estabelecido entre a Universidade Federal de Santa Maria (Brasil) e a Universidade de Poitiers (França), no qual colaboram ainda a Universidade Federal do Rio Grande do Sul (Brasil) e a Universidade de Passo Fundo (Brasil).

A condução desta tese foi realizada em modalidade de co-tutela entre a Universidade Federal do Rio Grande do Sul e a Universidade de Poitiers (França), com permanência de 18 meses na França na equipe E2 HydrASA do laboratório l’UMR IC2MP da Universidade de Poitiers.

O tema de investigação principal do programa busca evidenciar, através de indicadores mineralógicos e físico-químicos, o impacto de ações antrópicas nos solos.

2. PRESENTATION GENERAL

Ce projet fait partie du programme CAPES/COFECUB Te 761/12 intitulé « Evolution minéralogique des sols du sud du Brésil: caractérisation des processus d'altération et de l'impact anthropique » établi entre l'Université Fédérale de Santa Maria (Brésil) et l'Université de Poitiers (France), avec la collaboration de l'Université Fédérale de Rio Grande do Sul (Brésil) et l'Université de Passo Fundo (Brésil).

La conduite de cette thèse a été réalisée en cotutelle entre l'Université et Fédérale do Rio Grande do Sul (Brésil) et de l'Université de Poitiers (France), avec un séjour de 18 mois (mai 2014 – novembre 2015) en France dans l'équipe E2 HydrASA de l'UMR IC2MP de l'Université de Poitiers.

L'axe du programme de recherche vise à démontrer, par des indicateurs minéralogiques et physico-chimiques, l'impact des actions humaines sur les sols.

3. GENERAL INTRODUCTION

Everywhere where human societies settled in a stable way, clay was an important element of artistic expression as well as an economy's support. So in trade since the Phoenicians, ceramics were used to transport grain, wine, and oil. The Chinese had a relevant contribution in this area, because they were very advanced in elaboration of ceramics from very remote times, with a record of 3,300 to 2050 BP.

Over the years, this development reached the Mediterranean Basin with Marco Polo, which arived China between 1274 and 1291, encountering a high quality interest clay. It was the kaolin, which had the origin of its name associated to the village of Kao Ling (China), from where pegmatite clay was extracted (Meunier et al., 2016).

Although his microscopic size, clays have fundamental importance even in studies on the origin of life, since they are markers of the presence of water, an essential condition for human development. However, to better identify and understand the characteristics of the different types of clay, it is necessary to have techniques adapted to small particles analysis, such as electron microscopy, spectroscopy, X-ray diffractometry, chemical microanalysis and others.

The clays have great adaptability to almost all conditions of the earth's crust from the presence of water, resulting in an appreciable diversity of species. With this, clays are widely used in the pharmaceutical and petrochemical industries, as well as in different research areas such as geology, engineering, chemistry and soil science.

Within soil science, clays are essential constituents in soil formation, together with silt and sand fractions, representing an important part in the determination of the productive potential of the soil, through the cation exchange capacity (CEC), the adsorption properties and the specific surface area (SSA). The soil is an open system, alive and subject to permanent changes and because of this, clays present in soils are also exposed to these changes, caused by changes in the soil system, by his different uses and also by the anthropic impact.

Actually, the function and importance of clays in considered "critical zone", which is the zone between atmosphere and the lithosphere, in other woerd, the soil, is a central element in this transition zone where important biogeochemical reactions occur. According to Chorover et al. (2007), reactions that occur at the boundary between the solid, liquid and gaseous phases of several components in weathering systems are critical in sustaining the quality of water and soil on Earth. The removal of pollutants, the sustainable supply of clean water and the support to productive ecosystems are all interconnected and associated with the diversity and reactivity of natural interfaces formed by the interaction of biota and water with lithogenic materials in the critical zone.

In this sense, the clays act intensely in the critical zone. Due to their high specific surface area (10-800 m^2 g^{-1}), these phases can dominate the interface solid-water, even when in small amount. Their high surface charge and their reactive functional groups make clays effective sequestering agents for several metals and contaminants.

Recently, some lines of research discuss a kind of symbiosis in which plant helps the clay to develop hersef, restoring its water and nutrients reserves. This new approach is instigating and deserves to be well developed among the different professionals and researchers involved in this issue, because it’s relies on the exploration of fine particles that advances in X-ray diffraction and electron microscopy tecniques alow us to understand. Therefore, is interesting to know soils and the role of clays in this interface.

The structure of the 2:1 clay minerals gives a good example of this, since his 2:1 structure allows the consumption of a large part of the elements Si, Al, Fe, Mg and K released by dissolution of the primary minerals of the rocks and/or other sources (plant and animal waste). The storage is never definitive because these elements can return into solution if local conditions (microsystems) become aggressive for some clayey species (Meunier et al., 2016).

The occupation of the interlayer space of the 2:1 clay minerals by Al represents a situation of great scientific and practical interest in the soil science and agricultural science, since the aluminum in solution is extremely toxic to the plants and occurs when the pH of the soil is less than 5,3. However, captived in a non-exchangeable way in the crystalline structure of a clay, it is neutralized and leaves the nutritional circuit. The same is true for other metals whose toxicity may also affect humans. The purifying role of expansible clays is particularly interesting for the environment, public health and food production.

4. HYPOTHESES

The physical-chemical properties of the soils, which condition their productivity, are directly related to the clay-mineral constituents evaluated from the geochemical evolution of the soil profiles;

The intensification of agriculture, through cultivation systems, has an impact on clay-minerals in the soil.

5. GENERAL OBJECTIVES

(i) Characterize the mineralogical and pedochemical alterations and geochemical evolution of alteration profiles located in environments with no history of anthropic actions in southern Brazil;

(ii) Characterize both qualitatively and semi-quantitatively the primary and pedogenic minerals present in soils of important ecosystems in Rio Grande do Sul;

(iii) Evaluate the effect of grazing intensities on the mineralogy of an Oxisol, in an integrated soybean-cattle beef production system of southern Brazil.

6. CHAPTER I – BIBLIOGRAFIC REVIEW

6.1. Importance of minerals and rocks

More than 70% of the crust is formed by oxygen and silicon. As a result, the silicates are the predominant mineral group, constituting more than 90% of the crust volume. Of the more than four thousand known minerals, approximately ten are considered rock-forming minerals, because they are essential constituents of the most abundant rocks in the terrestrial crust. This is due to the fact that the crust is almost composed by only ten chemical elements (Figure 1).

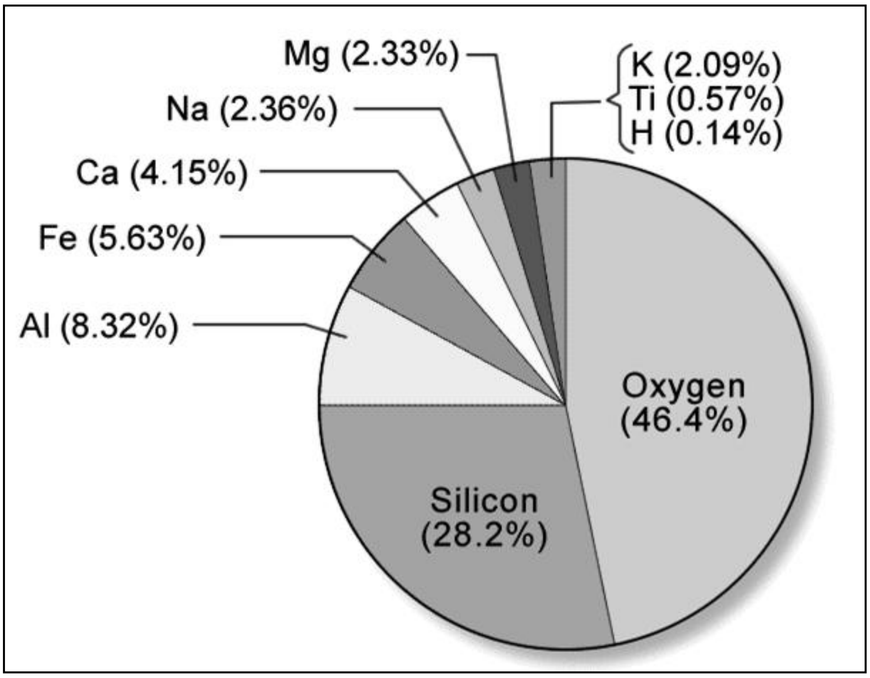


Figure 1.Most abundant chemical elements in the terrestrial crust (Adapted from Andrade et al., 2009).

The minerals are formed by different types of natural processes that mainly involve: the crystallization from magmas or from saturated aqueous solutions, solid state reactions between minerals, and the degradation of pre-existent minerals due to the reaction with fluids. The magmatic crystallization is the product from the cooling of magmas (liquids of normally silica composition). Such crystallization is not homogeneous, and minerals stable at higher temperatures crystallize first. As the temperature decreases, other minerals crystallize according to the crystallization sequence, referenced as the Bowen's series (Szabo et al., 2009) (Figure 2).

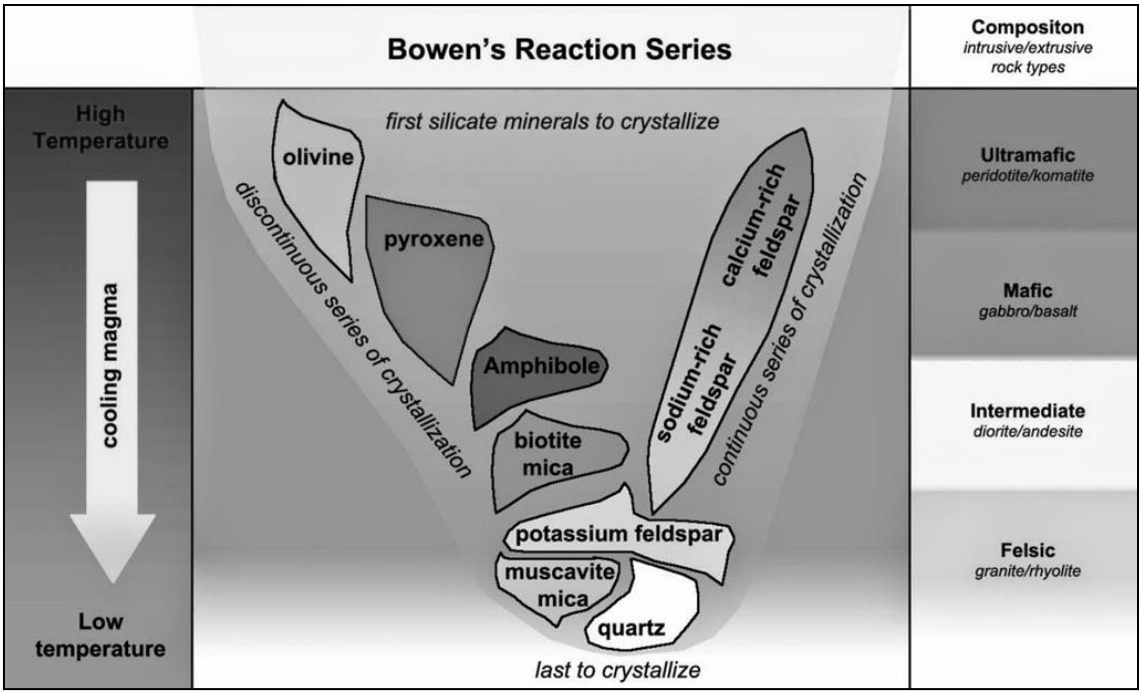


Figure 2.Bowen's reaction series (Adapted from Szabo et al., 2009).

The heterogeneity of rocks is of fundamental importance for the planet evolution, because it is expressed not only in the interior zoning, but also in the difference that exists between the continental and the oceanic terrestrial crust. The continental crust is formed essentially by aluminous silicates (global composition similar to granite), with thickness of 25 to 50 km. The oceanic crust presents thickness of 5 to 10 km and is composed essentially by basalt, formed by magnesium silicates and being denser than the continental crust due to its higher iron contents. The collision between plates is always accompanied by a deformation of the rocks present in the shock area, which results in the formation of new plutonic and volcanic rocks.

The rocks are grouped according to their origin, in igneous or magmatic, sedimentary and metamorphic types. The igneous rocks constitute approximately 80% of the lithosphere volume and result from the crystallization of minerals from the cooling of the magma between 1200 and 400°C. There are two main types of igneous rocks: extrusive or volcanic and intrusive or plutonic. The extrusive igneous rocks are originated by extrusion of magma to the terrestrial crust surface, through volcanoes or cracks in the crust. Intrusive igneous rocks are produced by the crystallization of magmas that did not reach the surface of terrestrial crust. Generally, these rocks undergo a slower cooling as compared to the extrusive igneous rocks that are chemically equivalent, also presenting a higher content in volatile constituents.

Finally, in the study of rocks chemical composition, one of the most important parameters is the silica content (weight percentage of SiO_2). The igneous rock may be acidic (silica content above 66%), intermediate (silica content between 52 and 62%), basic (silica content between 45 and 52%) and ultrabasic (silica content lower than 45%) (Szabo et al., 2009) (Figure 2). Among them, the granite, classified as acidic, and the basalt, classified as basic, are the two types of igneous rocks more representative of terrestrial crust, being highlighted due to its abundance.

6.2. Geology of Rio Grande do Sul

The origins of the current geomorphological configuration of Rio Grande do Sul State (RS) are related to more than one an approach and separation cycleof continental mass (craton) through the movement of continental plates. The distribution of geomorphological provinces begins to be explained from the Pre-Cambrian period between 450-650 million years ago, when the ancient masses of the planet were aggregated as Pangea.

The geological evolution from the beginnings of the planet Earth until the Carboniferous period is recorded in the rocks of the current province of **Escudo Sul-rio-grandense.** From this period the process of subsidence begins in the region where RS is currently partforming a wide topographic depression, which is filled by sediments, giving rise the sedimentary Paraná basin. In the current province of **Depressão Periférica** is possible to observe part of these sediments. Other part of these sediments is covered by volcanic rocks of the current province of **Planalto** do RS (Figure 3).

The sinking of the sedimentary basin increased slowly as the deposited sedimentary layer mass pressure was intensified, which continued for about 140 million years, reaching a considerable thickness of sedimentary rocks up to 1 km in RS. The movement of tectonic plates separation triggered a volcanism with numerous fissures, with lavas from basaltic to dacitic origin, and many magma extrusions occurred in an interval less than ten million years. The volcanic rocks covered an area of approximately 1.3 million km^2, denominated as the province of **Planalto do RS**.

The continuity of volcanism caused this crevice to widen and allow the entrance of seawater, originating the Atlantic Ocean and the continents of South America and Africa, in a process that persists until this moment through the expansion of the plates. Approximately 65 million year ago, in the beginning of the Cenozoic period, shortly after the fissures volcanism and the separation between South America and Africa, the shoreline was cropped and formed by basaltic, granitic and metamorphic rocks of the **Escudo Sul-rio-grandense**. Thus, the coast is the geologically younger region of the RS, originated from successive sea level oscillations which began after the end of the Tertiary period and in the Quaternary period, establishing the current province of the **Planície Costeira**.

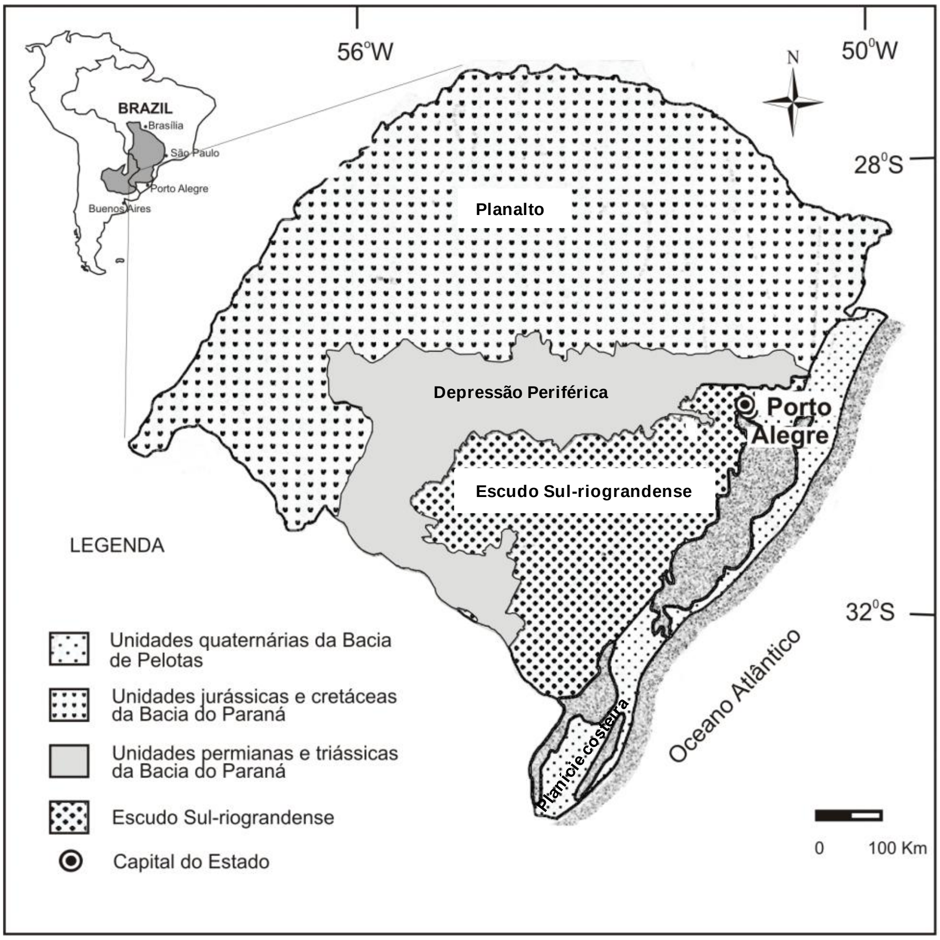


Figure 3. Location map of Paraná Basin in South America and simplified geology of Rio Grande do Sul(Adapted from Souza and Marques-Toigo, 2005). (50 anos geologia pg. 223).

6.2.1. Escudo Sul-rio-grandense

The Escudo Sul-rio-grandense (ESRG) represents the basement of RS, located in the center-south region, being the result of the orogeny that promoted the union of Neoproterozoic lands, giving rise to the Western Gondwana Paleocontinent. The ESRG has about 65,000 km^2 of area in RS (Chemale Jr., 2000) and is delimited to the North, West and Southwest by the Paraná Basin, and to the East by the Pelotas Basin, also known as Província Costeira of the Rio Grande do Sul. The ESRG's rocks are distributed in undulate to strong undulate relief, from an altitude lower than 100 to 500 m. The ESRG is also called a crystalline basement, because it forms the base that supports other geological formations, and because of the high degree of consolidation of its rocks.

The ESRG is predominantly formed by igneous and metamorphic rocks, such as granite, gneisses, shales and mafic and ultramafic volcanic rocks.

Developed from granite and gneisses, in reliefs varying from soft to strong undulate, occur soil types from the classes Argissolos Vermelhos/Vermelho-Amarelos (Red and Red-Yellow Ultisols), Cambissolos (Inceptisols) and Luvissolos Háplicos (Alfisols) and Neossolos Litólicos/Regolíticos (Entisols). Also occur soil types of higher chemical fertility, developed from shales, as Neossolos Regolíticos (Entisols) and Luvissolos Crômicos (Alfisols), and from andesits, as the Chernossolos Ebânicos (Molisols) (Brasil, 1973; Streck et al, 2008).

6.2.2. Depressão Periférica

The Depressão Periférica province is characterized by low altitude lands located at the foothills of the Planalto province, presenting flattened relief of smooth hills with few outcrops and fluvial plains. This unity is formed by sedimentary rocks of Paraná Basin (sandstones, siltstones and argillites), which originated from the deposition of sediments with varied composition and granulometry, which were gradually compacted and lithified.

The Depressão Periférica belongs to an extensive corridor that links the RS from West to East. Hills of up to 200 m are common in this area and represent the old escarpment line of *Serra Geral*. In this way, this geomorphological province presents a complex succession of different sedimentary rock types, eventually exposed as a function of the removal of overlying rocks. In the Southeast segment of this province, soils rich in smectites and with higher chemical fertility occur, as Planossolos (Ultisols or Alfisols) and Luvissolos Háplicos (Alfisols), Chernossolos Argilúvicos (molisols) and Vertissolos Ebânicos (Vertisols). In the South-North and West-East segments, the Planossolos Háplicos (Ultisols or Alfisols) predominate in the flood plains, associated to the Neossolos Flúvicos (Entisols) and Gleissolos Háplicos (Entisols). In other positions of the landscapes, dominated by hills, the Argissolos (Ultisols) predominate, which transition from Argissolos Bruno-Acinzentados (Ultisols) in the lower altitude to Argissolos Vermelhos (Ultisols) in the higher altitude (Brasil, 1973; Streck et al, 2008).

6.2.3. Planalto

The Planalto province covers the northern half and a portion of Southwest of RS. This province is formed by a succession of levels of volcanic basaltic and rhyolitic rocks from the *Serra Geral*. These rocks are situated in a practically tabular relief, excavated by rivers in several points, forming deep scarps and valleys, mainly in the *Serra Gaúcha* region. The northeast region of the RS, named the *Campos de Cima da Serra* region, is dominated by acidic volcanic rocks and have altitudes of up to 1400 m, gradually falling in a westerly direction to less than 100 m in the *Campanha region*.

The sequence of basaltic spills in this area is identified in the form of baselines in the slope of the valleys. This expressive volcanic manifestation dating from the Cretaceous period (130 to 140 million years) interrupted the sedimentation of the Paraná Basin. Thus, volcanic lava spills covered much of the sediments of the Paraná Basin, exposing only the portion related to Depressão Periférica region.

The first volcanic spills present, in general, basaltic composition with predominance of elements such as Fe, Ca and Mg; whereas the most recent spills present rhyolitic composition, with higher silica contents and lower Fe, Ca and Mg contents. Intermediary rock types of dacitic composition also occur. Thus, the northeast region of RS presents basaltic spills at lower altitudes, forming the bases and slopes of the hills, while the rhyolitic spills are identified in the higher altitudes, usually above 700 m (Streck et al., 2008). In the intervals between the successive lava spills some sandy eolic sediments are observed and constituted intercalated sandstones, denominated Arenito Botucatu.

In the Campos de Cima da Serra region (Annex 1), located in northeast of RS with smooth to strong wavy relief is considered as the coolest and rainy region predominate acidic soils (gibbsitic/kaolinitic-goethitic) developed from rhyolite, as Cambissolos Húmicos (Inceptisols) and Neossolos Regolíticos/Litólicos Húmicos (Entisols). In the East-West segment of Planalto region with basaltic lithology with smooth wavy to wavy relief, predominate the Latossolos (oxisols), which vary between Latossolos Brunos (kaolinitic-goethitic oxisols) and Latossolos Vermelhos (kaolinitic-hematitic oxisols). In the same sense, the Oxisols vary from clayey (East) in the higher altitudes to the sandy

(Center-West) as the altitude decreases, due to the increase of Arenito Botucatu (intercalated sand stone) influence as soil source material. In the Fronteira Oeste and Campanha regions, hotter and less rainy, soils of high chemical fertility occur, as Neossolos Litólicos/Regolíticos Eutróficos (Entisols), generally situated in a smooth wavy relief, with Chernossolos (molisols) and Vertissolos Ebânicos (Vertisols), in flatter areas (Brasil, 1973; Streck et al, 2008).

6.2.4. Planície Costeira

The Planície Costeira province is located at the East of RS, covering the entire coastal strip of the state and some areas of the Porto Alegre metropolitan region. This region is formed by unconsolidated marine and fluvial-lacustrine sedimentary units, belonging to the Pelotas Basin, and is characterized by a very low relief (below 40 m above sea level), extensive wetlands, lakes and lagoons, being highlighted the Laguna dos Patos, the Lagoa Mirim and the Lagoa Mangueira.

The unconsolidated sand, silt and clay sediments were deposited from the end of the Tertiary Period and during the Quaternary Period (less than 2 million years ago). The sedimentation of this material is a characteristic of coastal environment under the influence of advancement and retreat sea level events, possibly related to interglacial and glacial periods, which formed the beach environment, with lagoons and sandy strips, and shallow water marine environment. The sediments of Planície Costeira region compose the emerged portion of a sedimentary basin denominated Pelotas Basin, deposited from the Period Cretaceous. The soils in the Planície Costeira province are distributed in terraces which correspond to different altitudes above sea level. In the superior terraces, occur Argissolos Vermelhos/Vermelho-Amarelos (Ultisols). In intermediate terraces, occur Plintossolos (Plintosols) and Planossolos Háplicos (Alfisols or Ultisols), followed by Planossolos Háplicos/Nátricos and Gleissolos Melânicos (Entisols) on the lower terraces. In flooded areas, near the lakes and canals, are founded Organossolos Háplicos (Histosols), while in areas near the coast are founded Neossolos Quartzarênicos (Entisols) (Brasil, 1973; Streck et al, 2008).

6.3. Climate of Rio Grande do Sul

Of the natural elements, the ones that most influence the formation of a landscape are the climate and the relief, because they interfere and conditionate the other elements and they are also influenced by them. Brazil, a tropical and subtropical country of great territorial extension, presents a geography marked by diversity. According to Ab’Saber (1969), occurs six big natural landscapes in Brazil: the Amazonian Domain; the Caatinga’s Domain; the Cerrado’s Domain; the Mares de Morro’s Domain; the Araucária’s Domain and the Pradaria’s Domain (Pampa Biome) (Figure 4).

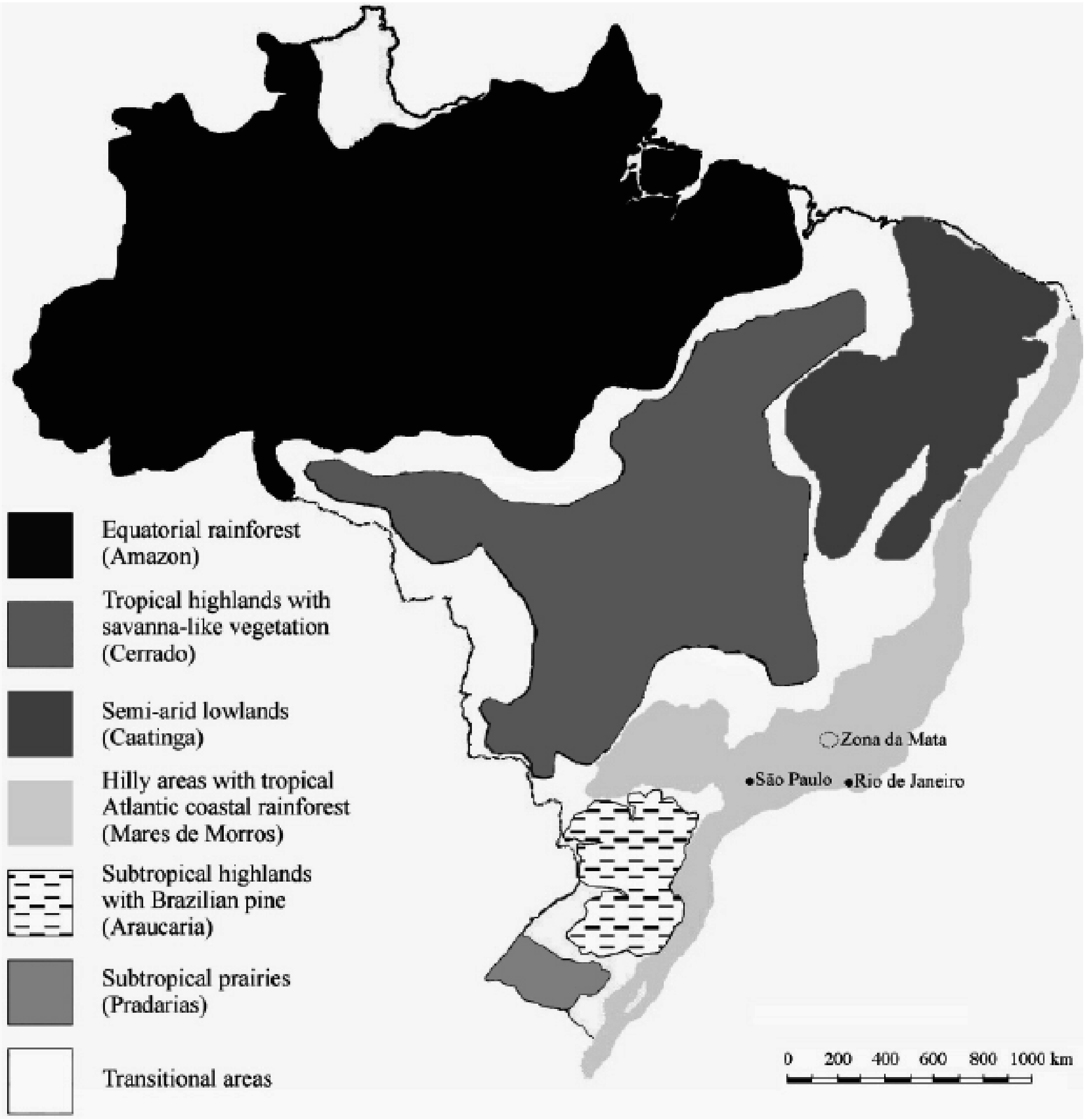


Figure 4. Morphoclimatic domains of Brazil (adapted from Aziz Ab'Saber, 1969).

Situated in the North of Brazil, the Amazonian Domain is the continental biome of greater extension, with 49.29% of Brazilian territory (IBGE, 2004). This domain is characterized by the existence of innumerous rivers and by an abundant annual precipitation (2,500 mm yr^{-1}). In this domain, the occurred soils are basically the Latossolos (Oxisols), Argissolos (Ultisols) and Plintossolos (Plintosols). The Cerrado’s Domain is the second higher Brazilian domain in territorial extension, where predominate the Latossolos (Oxisols), with color varying from red and yellow.

The Brazilian Southern, differently from the Amazonian region and the rest of the country, is inserted in a subtropical environment, with high annual average precipitation and lower temperatures as compared to the other Brazilian regions. In the South region, two important morphoclimatic domains occur: the Pradaria’s Domain and the Araucária’s Domain, particularly characterized as a function of vegetation type. The Pradaria’s Domain, also known as Pampa Biome or Campanha Gaúcha, is situated in low altitudes with smooth wavy relief and covered by herbaceous vegetation of prairie, where there is the predominance of relatively fertile soils, as Chernossolos (Molisols) and Vertissolos (Vertisols) (Streck et al., 2008). On the other hand, the Araucária forest is a vegetal formation characterized by the presence of *Araucaria angustifolia*, with altitudes varying from 500 and 1,300 m in the three Southern states (Silva, 1996). The Araucária forest is an ecosystem of Mata Atlântica, which extends through the States of Paraná, Santa Catarina and Rio Grande do Sul and some parts of the States of São Paulo and Minas Gerais. The soils of such domain (Araucária’s Domain) are composed mainly by Latossolos (Oxisols), Cambissolos (Inseptisols) e Neossolos Litólicos/Regolíticos (Entisols).

The climate factor is a complex conception constituted by a series of climatic variables which can be measured, as temperature, precipitation and evapotranspiration. In this way, the determination of such variables allows the expression of a specific climate condition. Thus, the climate is one of the most important soil formation factors, affecting the leaching, the moisture, the organic matter content and quality and the rates of related processes and reactions. Consequently, climate also has an effect in the depth of soil profiles, as well as in the texture and in the mineralogical composition formed.

Mota (1953) elaborated a study on Rio Grande do Sul’s climate according to the Köppen classification (1936) and concluded that the climate is classified in the fundamental type “Subtropical (or almost Temperate)” of Cf formula, with the Cfa and Cfb variants, being:

Cfa – Humid subtropical climate without drought, where the temperature of the hottest month above 22°C and of the coolest month ranging from 3 to 18°C;

Cfb – Temperate climate, where the hottest month presents a temperature below 22°C.

The average annual temperature of RS is 18°C, varying from 16 to 19.4°C, depending on the region (Figure 5). The higher temperatures are observed in the Pampa, in the Missões and in the Depressão Central regions, while the lower ones occur in the Campos de Araucárias, in the Encosta Superior do Nordeste and in the Planalto Médio regions. The average monthly temperature varies from 9.9 to 13.6°C in the coolest month, normally in July, and 22.3 to 26.1°C in the hottest month, January.

More recently, Maluf (2000) suggested a new climate classification for the RS, where three climate classes are distributed in the different regions: Subtropical (ST), Subtemperate (STE) and Temperate (TE). These classes were delimited considering the average annual temperatures (Ta) and the average monthly temperature of the coolest month (Tf). This ordination also presupposes the insertion of dry season to obtain the local climatic type.

A climate variable of expressive importance for understand the pedogenesis is the difference between average precipitation and average evapotranspiration (temperature result) in the different regions of interest (Figure 5). Even considering the climate gradient in the East-West axis of RS, the 1:1 clay mineral kaolinite appears as the predominant mineral in the soils. However, in the West region, the lower leaching becomes the weathering processes less intense, resulting in the formation of 2:1 clay minerals, as smectite and vermiculite. In the East region, the weathering conditions are more intense, promoting a higher soil desilication and reducing the 2:1 clay mineral content, as compared to the kaolinite, and increasing the iron oxides contents, as hematite and goethite. The occurrence of aluminum oxides, as gibbsite, is restricted to soils located in the Araucária’s Domain (Caner et al., 2014), where the leaching causes an intense desilication, similar to that verified in Central Brazil.

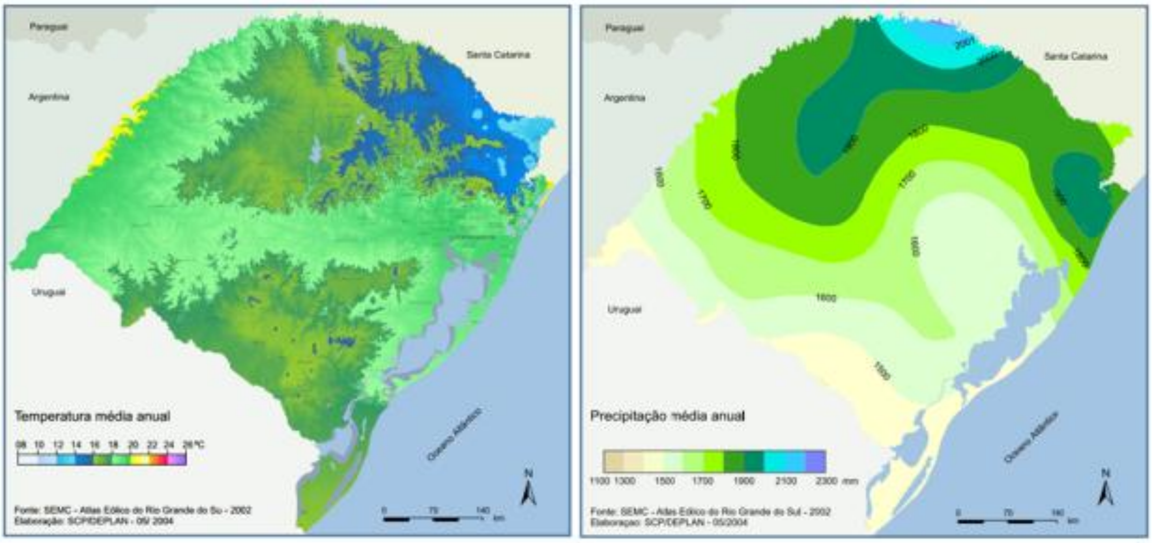


Figure 5. Mean annual temperature (A) and precipitation (B) in the State of Rio Grande do Sul (Source: Atlas Sócio-econômico do Estado do Rio Grande do Sul, Secretaria da Coordenação e Planejamento – 2ª edição 2006).

Mean annual precipitation varies from 1.186 to 2.468 mm/year in RS according to the different physiographic regions (Figure 5). In general, the precipitation increases from the Southwest (Pampa) to the Northeast (Araucária’s Domain). Rainy periods occurs and dry periods with duration, date and frequency well-defined, where normally the rainy months are May, June and September, and the less rainy, November, December and February (Brasil, 1973).

The climate diversity of RS is evidenced in a climate sequence studied by Kämpf and Schwertmann (1983) (Figure 6). In the East-West axis, the altitude varies between 80 m (Pampa and Southern Planalto) and 1400 m (Medium Planalto and Araucária’s Domain) that induce expressive variations in the mean annual precipitation, temperature, solar radiation and evapotranspiration.

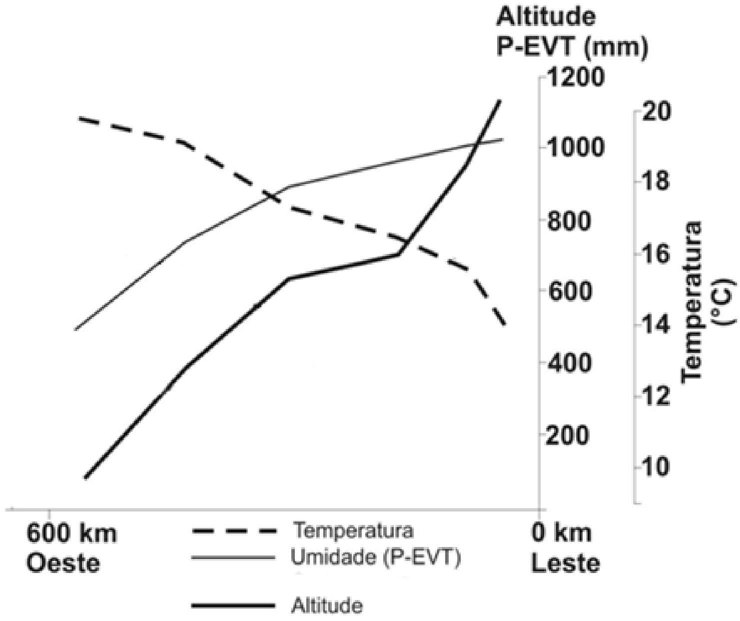


Figure 6. Moisture variation in a climate sequence of the Planalto province in State of Rio Grande do Sul (Adapted from Kämpf and Schwertmann, 1983). P: precipitation; EVT: evapotranspiration.

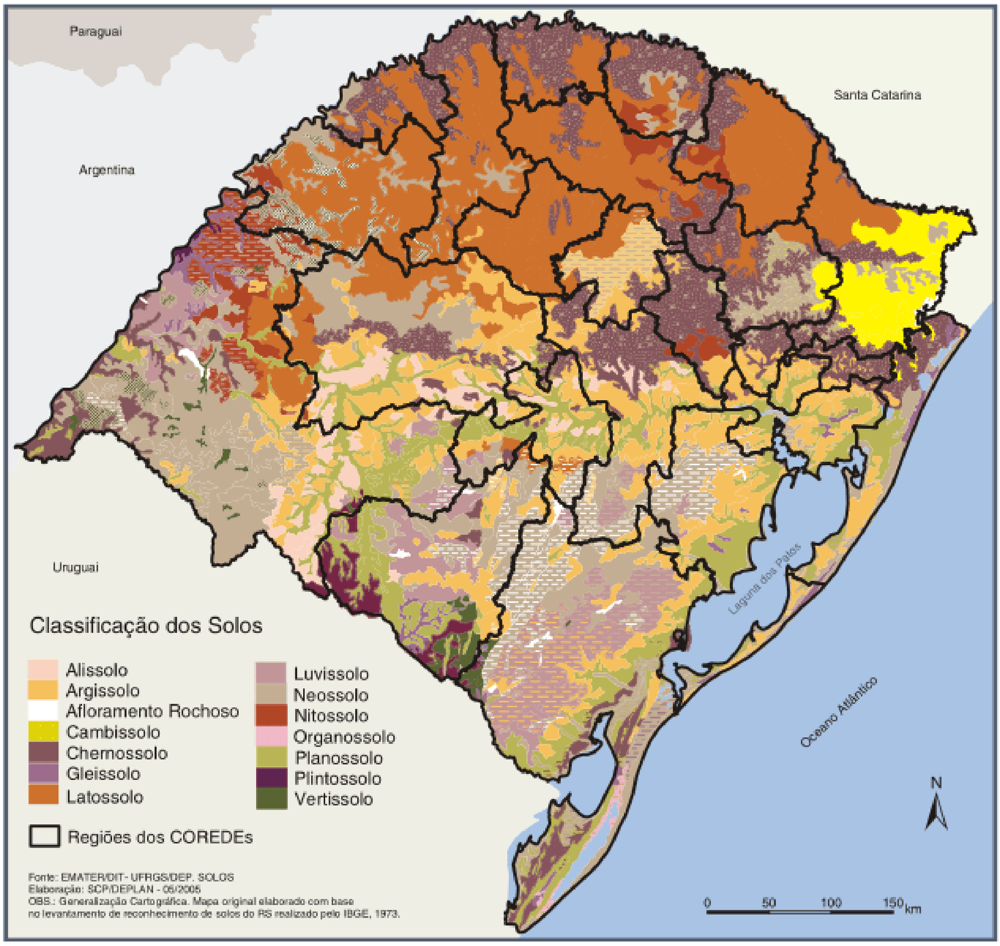
6.4. Great pedogenetic processes of southern Brazil

The pedogenetic processes are combinations among the different soil formation factors (source material, climate, relief, organisms and time). The action of the processes is identified through the morphological, chemical, physical and mineralogical soil attributes.

The thirteen soil orders present in the Brazilian Soil Classification System (SiBCS, acronym in Portuguese) (Embrapa, 2013) results from the joint action of different pedogenetic processes, as for example the processes of ferratilization, eluviation-illuviation and gleization.

The ferralitization process results from a chemical weathering of high intensity in the tropical and subtropical humid regions, which produces the decomposition of primary minerals, mainly by hydrolysis and oxidation reactions. In the ferralitization process, the quick weathering results in deep soils, homogeneous through the profile and with absence of textural gradient. In this process, occurs an intense leaching of basic cations, associated with a desilication that may varies from partial to complete, as a function of the water abundance available for leaching. The released Fe oxidizes and precipitates as iron oxides (goethite, hematite, maghemite). On the other hand, Al can combine with the remaining Si, forming kaolinite; or, in the case of an intensive weathering, can precipitates as aluminum oxide (gibbsite). Although the ferralitization process participates in the formation of various soil orders in the tropical and subtropical regions, the Latossolos (Oxisols) and Nitossolos (Oxisols or Ultisols) are the maximum chemical, physical, mineralogical and morphological expression of its action.

The eluviation-illuviation process consists in the translocation of particles, mainly of fine clay size (<0,2μm), from the soil surface layers to the deeper layers. As a result, the superficial horizons are impoverished in clay and normally sandier, whereas the subsurface horizons present higher clay contents, being more clayey. The soils predominantly formed by the eluviation-illuviation process are characterized by important textural gradients. The main soils that present this feature are the Argissolos (Alfisols) and the Planossolos (Alfisols or Ultisols), may also occurring in Luvissolos (Ultisols) and Plintossolos (Plintosols).



Fonte: EMATER/DIT - UFRGS/DEP. SOLOS
Elaboração: SCP/DEPLAN - 05/2005
OBS.: Generalização Cartográfica. Mapa original elaborado com base no levantamento de reconhecimento de solos do RS realizado pelo IBGE, 1973.

Figure 7. Distribution of soil orders in the State of Rio Grande do Sul (Streck et al, 2008).

The gleization process consists in the manifestation of characteristics that indicate a soil water saturation environment, in which there is absence of oxygen. Thus, the activity of redactors organic compounds and of anaerobic microorganism, that utilize metals as electron acceptors, is favored. In this way, Fe^{3+} and $Mn^{3+,4+}$ are reduced and released. The Fe^{2+} and Mn^{2+} ions migrate in solution, according to the redox gradient, originating poor oxides zones and, therefore, with grayish color. In oxiding places, as pores, interior of aggregate interior, roots and zones with oscillation of the water table, the Fe^{2+} and Mn^{2+} ions oxidize and precipitate, forming oxides as ferrihydrite, goethite, lepidocrocite and hematite. The main soils formed from this process are the Planossolos (Ultisols or Alfisols) and Gleissolos (Entisols).

The importance of these three great pedogenetic processes in Brazil is well-demonstrated through the expressive area (approximately 65%) covered by the soil orders of Latossolos (Oxisols), Argissolos (Ultisols), Planossolos (Ultisols or Alfisols) e Gleissolos (Entisols) (Embrapa, 2006), which have its chemical, physical, mineralogical and morphological characteristics defined by the predominance of one or more than one of these pedogenetic processes. The coverage proportion of these processes in the RS diminished to 50% of the area and its related to the decrease in the area of soils formed by ferralitization (from 32% in Brazil to only 21% in RS) (Figure 7). This fact expresses a lower intensity of weathering processes in Brazilian Southern.

6.4.1. Soil weathering and formation

The weathering is the set of physical (disaggregation) and chemical (decomposition) modifications that rocks suffer when outcrop the terrestrial surface (Toleto et al., 2000). It is characterized as a complex process, in which rocks and minerals are converted in simpler structures, being, therefore, a simplifier process (Formoso, 2006).

The weathering effects are visualized in the form of altered rocks and minerals, and in the formation, commonly imperceptible in short-term, of new minerals and soils. The chemical weathering processes, including those of biological origin, dominate the alterations, which are classified as solid state transformations and mineral dissolution/neoformation (Kämpfet al., 2009).

The factors that control the weathering action on the rocks are the climate, the relief and the biological activity over time, and the altered rock (saprolite or alterite) and the soil are the main products from this weathering. In the soil, the weathering has its continuity with the pedogenesis, through the action of the same chemical processes and the intensification of biological processes. Because weathering is a slow action in nature, the importance of this process tends to be ignored or underestimated by most professionals who work with soils. However, the weathering is part of the daily soil system (Kämpfet al., 2009). As a result, the weathering has far surpassed the frontiers of the external dynamics of terrestrial globe in order to be established as a phenomenon with implications in agriculture, mining and environmental sciences, qualifying itself as an important process nowadays, worthy of further studies in Earth Sciences (Fontes, 2012).

The chemical weathering results from the change in the original formation environment of rocks and minerals. When exposed to the atmosphere, minerals and rocks are submitted to the water, the O_2, the CO_2 and the organic compounds action. The water penetrates through pores, cleavages and cracks of rocks and minerals, dissolving the most soluble constituents and transferring them. The alterations depending on the rock or mineral nature, on the reagents (composition and pH solution) and the conditions that controls the equilibrium (temperature, pressure and leaching).

6.4.2. Reactions involved in the weathering of silicate

The decomposition of primary minerals from rocks results of the separate or joint action of various chemical reactions, of which hydrolysis, oxi-reduction and complexation stand out in tropical and subtropical regions. The most important weather agent is the water, being its effect more intense as it acidifies due to the atmospheric CO_2 dissolution and the presence of humic acids.

The soil pH around 5.5 and 6.0, founded in tropical regions, is an essential factor to control the solubility of various constituents of rocks, especially the aluminum, the iron and other alkaline and alkaline-earth elements. The iron and the aluminum are elements of very low solubility in the pH interval commonly founded in the surface environment and tend to accumulate in the form of oxi-hydroxides. The silica is immobilized in an intermediary form, while the alkaline and earth-alkaline cations are easily leached. The remaining H_4SiO_4 concentration in the system will be determinant in the formation of pedogenic mineral types.

The hydrolysis is a chemical reaction between H^+ and OH^- from water and the ions from mineral, being considered the main reaction of chemical weathering in Brazilian soils (Melfi and Pedro, 1977).The intensity of hydrolysis reaction of a primary mineral and its consequent formation of different secondary minerals may be expressed according to the reactions presented below:

$$2KAlSi_3O_{8s,c,K\text{-}feldspato} + 11H_2O_l = 4H_4SiO_{4aq} + Al_2Si_2O_5(OH)_{4s,c,caolinita} + 2K^+_{aq} + 2OH^-_{aq}$$

In mineral surface, the H^+ ions replace the K^+ ions. The remainder of the mineral is not stable after this substitution, continuing its hydrolytic decomposition.

$$2H(AlSi_3O_8) + 5H^+ + 5OH^- \rightarrow \underset{\text{(kaolinite)}}{2Al_2Si_2O_5(OH)_4} + 4H_2SiO_3$$

Kaolinite formation:

$$4\ NaAlSi_3O_8 + 22\ H_2O + 4\ CO_2 \rightarrow Si_4O_{10}Al_4(OH)_8 + 8\ H_4SiO_4 + 4\ Na^+ + 4\ HCO_3^-$$

Detail of the kaolinite formation:

$$NaAlSi_3O_8 + 4\ H_2O + 4\ H^+ \rightarrow 3\ H_4SiO_4 + Al^{3+} + Na^+$$
$$4\ H_4SiO_4 + 4\ Al^{3+} + 4\ H_2O \rightarrow Si_4O_{10}Al_4(OH)_8 + 12\ H^+$$
$$4\ NaAlSi_3O_8 + 18\ H_2O + 4H^+ \rightarrow Si_4O_{10}Al_4(OH)_8 + 8H_4SiO_4 + 4Na^+$$

The 4 H^+ from the carbonic acid,

$$4\ H_2O + 4CO_2 \rightarrow 4\ H^+ + 4\ HCO_3^-$$
$$4NaAlSi_3O_8 + 22\ H_2O + 4CO_2 \rightarrow Si_4O_{10}Al_4(OH)_8 + 8\ H_4SiO_4 + 4\ Na^+ + 4\ HCO_3^-$$

Gibbsite formation:

$$2Al_2Si_2O_5(OH)_4 + 5H^+ + 5OH^- \rightarrow 2Al(OH)_3 + 2H_4SiO_4$$

(kaolinite) (gibbsite)

Alteration of albite to gibbsite:

$$NaAlSi_3O_8 + 8\ H_2O + CO_2 \rightarrow Al(OH)_3 + 3\ H_4SiO_4 + Na^+ + HCO_3^-$$

Direct formation of gibbsite

$$2{,}3\ NaAlSi_3O_8 + 3H_2O + 2{,}3\ CO_2 \rightarrow Si_{3,7}Al_{0,3}O_{10}Al_2(OH)_2Na_{0,3} + 3{,}2\ H_4SiO_4 + 2\ (Na^+, OH^-)$$

When the hydrolysis is total, the hydrolysis stage is denominated alitization, condition where occurs the relative concentration of Al in the $Al(OH)_3$ form (gibbsite) and of Fe, due to the total silica and basic cations depletion by leaching. In Brazil, the alitization predominates in soils from the equatorial and central regions, hot and humid, where the expressive amount of gibbsite is accompanied by the secondary occurrence of kaolinite. In RS, this intense weathering level is verified only in the Cambissolos (Inseptisols) and Latossolos (Oxisols) of the Araucária's Domain, where occurs the higher amount of water available for the soil leaching.

The monossialitization and bissialitization are stages where the hydrolysis occurrence is partial. In the monossialitization, the cations are totally eliminated and the silica remains at concentrations that allow the precipitation, combined with aluminum, of 1:1 clay minerals, such as kaolinite. There is a domain of this process in humid tropical and subtropical regions. In RS, the monossialitization soil stage becomes evident due to the kaolinite predominance in clay fraction of most soils (Melfi and Pedro, 1977; Schwertmann and Kämpf, 1985; Pedron et al., 2012; Teske et al., 2013).

In the bissialitization, the basic cations and the silica are partially eliminated. In such condition, the silica will combines with aluminum and cations in the formation of both 1:1 (kaolinite) and 2:1 (smectite/vermiculite) minerals. The bissialitization occurs in temperate, steppe and semi-arid regions. In RS, this weathering level is important expressed in the soil orders of Chernossolos (Molisols) and Vertissolos (Vertisols), located in the Campanha and Fronteira Oeste regions.

The complexation occurs when the chemical reactions conducted to the formation of organometallic complexes, which may destabilize the chemical structure of some minerals, increasing the solubility of Fe^{3+} and Al^{3+}, trace elements and heavy metals. Thus, humic compounds and others organic acids accelerate the decomposition of primary and secondary minerals through the formation of complexes. According to Kämpf et al. (2009), the formation of complexes has its importance in pedogenesis because promotes or inhibits the weathering and the formation of new minerals, besides affecting the differentiation of soil horizons.

6.5. Origin and evolution of pedogenic minerals

The silicates are the most abundant mineral group in the terrestrial crust, having the silicon tetrahedron as the fundamental formation unity. They are the main rock-forming minerals, presenting varied types of crystalline structures, as a function of different polymerization modes of silicon tetrahedrons. Among them, the sub-group of phyllosilicates has essential relevance in the mineralogical soil composition, being related to the soil clay minerals. The phyllosilicates are layered minerals with layersbuilt of tetrahedral and octahedral sheets.

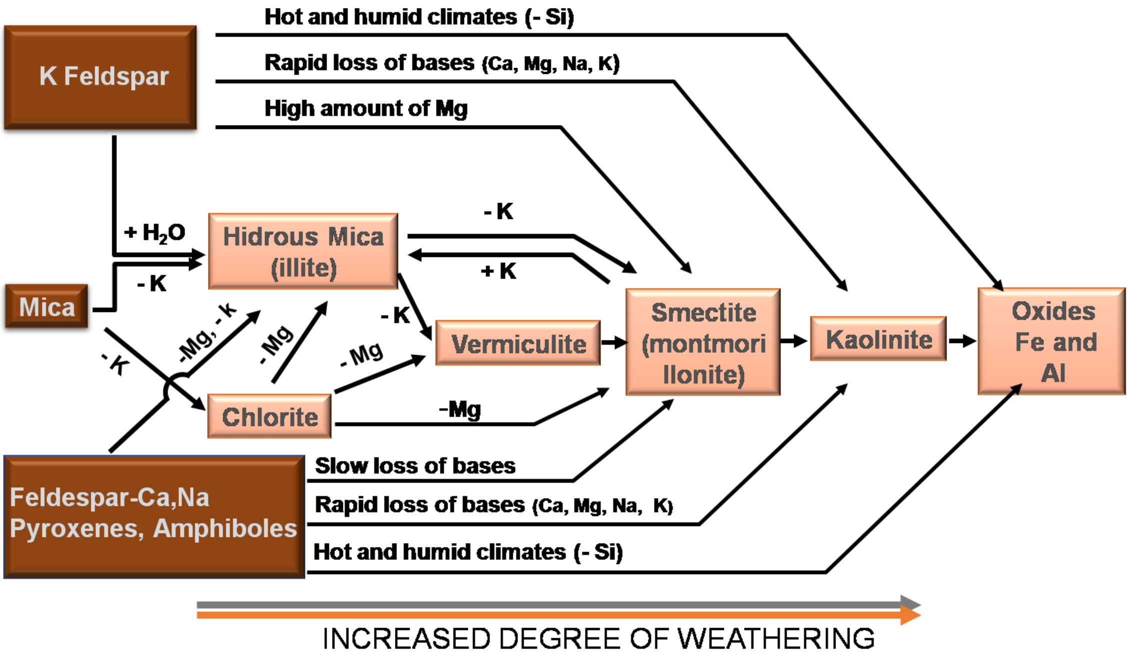


Figure 8. Representative scheme for the transformation of clay minerals.

In the alteration (weathering) of primary minerals in hot and humid climate regions, the losses of base cations and silica are the predominant process with advance of the weathering intensity (Figure 8). The weathering products of feldspars, may be kaolinite or even gibbsite in conditions of well-drainage and intense flux and montmorillonite in semi-arid climate and poorly drained basins under tropical climate. Non-crystalline materials may be intermediary products in these alterations determined by dissolution and neoformation reactions.

In general, the vermiculites do not tend to be the dominant clay minerals in soils, being rare the mention of clay minerals with the standard behavior of vermiculite in Brazilian soils. Normally, they are denominated as aluminous vermiculites, or vermiculite with hydroxy-Al interlayered (HIV). This is because in acid soils and under intense weathering conditions, mica can be directly transformed in HIV, without passing by the intermediary stage of vermiculite (Brasil, 1973; Kämpfet al, 2009). Interstratified minerals mica-vermiculite or mica-HIV are also common in soils with intermediate weathering stage (Kämpf et al, 2009).

With the increase of weathering, desilication rates increase and the dominant secondary minerals are kaolinite and iron oxides. Kaolinite may form directly (Volkoff et al., 1989) or with an intermediary stage of interstratified kaolinite-smectite (Kämpf et al., 1995).

In Chernossolos (Molisols) and NeossolosLitólicos (Entisols) derived from ultrabasic rocks, the interstratification of chlorite-smectite were observed, as the intermediary stage in the transformation of chlorite intosmectite.

In RS, besides the soil variability, the diversity of climate, geology and geomorphology determine distinct mineralogical composition among the soils from the different physiographic regions. Despite the diversity of source materials, the predominant mineralogy in the clay fraction of most soils is kaolinite associated to iron oxides (hematite and goethite) and 2:1 clay minerals with hydroxy-Al^{3+} interlayered, and traces of gibbsite. Higher gibbsite concentrations occur in soils of the Campos de Cima da Serra region (Araucária’s Domain), due to higher intensity of leaching (higher precipitation, lower EP) and/or more acidic (or aluminous) rocks such as rhyodacite. On the other hand, in the Campanha and Fronteira Oeste regions (Pradaria’s Domain), the presence of 2:1 clay minerals must be highlighted, due to the lower rainfall and elevated evapotranspiration in such regions.

6.5.1. Study of the weathering profile: geopedological profile

The weathering profile or geopedological profile is considered in this study as being formed by the fresh/unweathered rock, the saprolite (or weathered rock), which corresponds to the altered portion of the rock that maintains the original rock structure, and by the pedogenetic horizons.

The weathering (or supergene alteration) of rocks, also denominated of active processes near or in the Earth surface, produces the saprolite (in this text, synonym of alterite). Saprolites are constituted by neoformed minerals (secondary or pedogenic) and also by remants of primary minerals constituents of rocks under alteration (Melfi et al., 1999) (Figure 9). For a better comprehension of the weathering profile, the deepest evaluation and knowledge of the weathering processes is imperative, since saprolite develops environmental and technological functions as important as soil.

According to Embrapa (2013), the soil has the atmosphere as the superior limit; being its inferior limit very hard to be defined (Concept of critical zone). This occurs because soil depth can vary with pedological horizons being directly in contact with the fresh rock, or gradually through saprolitic materials or sediments that do not present signals of biological activity influence. Thus, the saprolite/alterite material contrasts with the soil due to the sharp decrease in organic matter and degree of alteration of mineral constituents resulting in properties close to that of the rock (e.g.: porosity, fracturation).

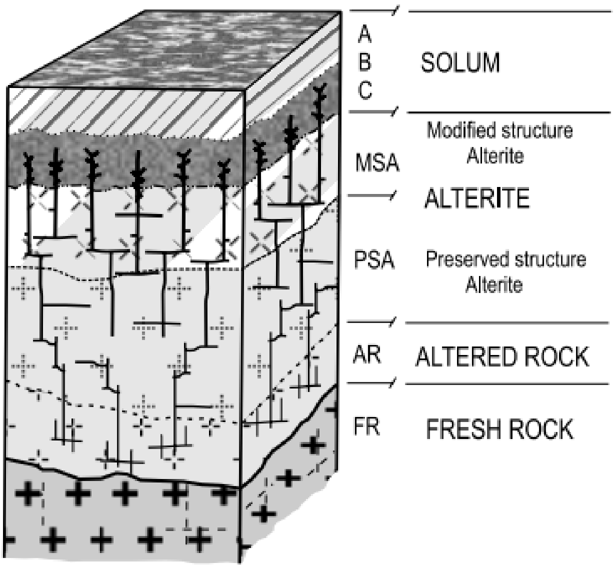


Figure 9. Lateritic profile of a tropical soil (Melfi et al., 1999)

The saprolite, as a soil component, has an important participation in the fundamental environment processes, as filtration of percolation water, retention of fluids and solutes and their possible transformation (Pedron, 2007).

Furthermore, the nutrients and water supply (Witty et al., 2003) to the plants, when the weathering advance occurs near the surface (Bornyasz et al., 2005), as in shallow soils, also represent important functions of saprolite and justify even more its importance as object of study.

Other important information for the agriculture and forest planning are related to the characteristics of porosity and mechanical resistance to penetration in saprolites, which also condition the water infiltration capacity (Sturmer, 2008). Thus, Sternberg et al. (1996) highlight that shallow soils in ecosystems submitted to seasonal dry periods the water retained in the partially weathered rock is of fundamental importance.

The saprolite also influences the geotechnical properties as it frequently reaches tens of meters in hot and humid tropical regions (Pedron, 2007). Thus, in the interpretation of pedological maps for sanitary landfill purposes or as a place for the deposition of industrial or urban waste, it is important to consider the thickness, the constitution and the behavior of the saprolite, especially regarding its sorption properties and hydraulic conductivity, because both influence the dispersion and advance of contaminants in the alteration profile.

6.5.1.1. Measure of the alteration intensity

The study of geochemical balance enables to quantify weathering intensity the losses or gains in relation to the source material, which are important parameters that help in the comprehension of the rock weathering processes and soil formation (Chadwick, et al., 1990; Demattê, et al., 1991).

Through the use of elements of very low mobility as indexes, it is possible to analyze the relationships between the chemical composition, the density and the changes in the soil volume as compared to the source material (unweathered rock).

The geochemical balance is also an important indicator of hydrogeochemical processes of transport that occur during the weathering. The chemical analyses involving rock, saprolite and soil are used to estimate the mobility of elements during the weathering and evaluate the losses by leaching. In this way, such analysis constitutes an important feature for pedogenesis studies, because it is possible to obtain information concerning gains and losses of elements and soil physical changes.

The distribution of chemical elements in soil profile contributes to the comprehension of geochemical, pedochemical, hydrological, biological, climatological and geomorphlogical processes in Earth's surface. Chemical analyses in the soil profile involving the saprolite and the rocks are used to estimate the mobility of chemical elements during the weathering and indirectly infer paleotopography and paleoprocesses (Brimhall et al., 1986).

The calculations are generally based on quantitative estimations of soil constituents related to the quantity of even one element considered immobile (index element). The indexes elements are residually enriched in relation to that more mobile, lost from soluble minerals in the profile leaching zones (Stiles et al., 2003). However, none element in soil should be considered as perfectly immobile, since all elements present a certain mobility, which is conditioned by the weathering environment. In this way, the element of lower mobility is the best to be used as index in the geochemical balance evaluation (Price and Velbel, 2003).

The chemical index of alteration (CIA) is one of the features more accepted for the calculation of weathering intensity (Nesbitt and Young, 1982).This index is based on the removal of bases (Ca^{2+}, Mg^{2+}, Na^+ and K^+) derived from feldspars dissolution and in the relative accumulation of Al^{3+} as weathering product (Nesbitt and Young, 1982). The CIA has been widely used to evaluate the intensity of geochemical alteration in soil and sediments (McLennan, 1993; Scheffler et al., 2003; Rieu et al., 2007), associated with mineralogical data.

Considering that the higher effects of chemical weathering processes are the leaching of most soluble elements, as Ca^{2+} and Na^+, and the relative concentration of residual Al^{3+}, the CIA is based on the molar relationship $Al_2O_3/(Al_2O_3 + Na_2O + CaO)$, where the CaO is associated to the silicates (Nesbitt and Young, 1982). Thus, the CIA was improved using the kinetics and the thermodynamics of dissolution reactions commonly found in weathering processes, and complemented by the chemiographic representation and triangular diagram, including Fe and Mg: Al_2O_3-CaO, Na_2O, K_2O-FeO, MgO (A-CNK-FM) (Nesbitt and Young, 1989). The obtainment of high CIA values indicates an intense alteration, comparable to that occurring in the intertropical areas; while low values reflect limited chemical transformations, typical of temperate and subtropical regions. However, since the A-CN-K or A-CNK-FM systems did not consider the SiO_2 content, this index presents limitations for use and interpretation (Meunier et al., 2013).

From this, some indexes utilize higher oxides, trying to obtain more complete scenarios to the chemical modification during the weathering processes. Meunier et al. (2013) developed a method incorporating SiO_2 in the index calculation and presented a weathering intensity scale (WIS). The WIS describes not only the kaolinitization stage dominated by the Si accumulation,but also the final stage of bauxitization/laterization, characterized by the dessilication stage produced by the general weathering, based on the co-variation between the parameters Δ4Si% and $R^{3+} / (R^{3+}+ R^{2+} + M^{+})$. According to Meunier et al. (2013), independently of the utilized procedure (CIA or WIS), the discrimination of source materials becomes more uncertain as the weathering intensity increases.

In this way, the weathering estimation through geochemical balances allows to understand the functioning and formation processes of the landscape, the elements' mobility, the ground water composition, the soil agricultural potential, the location of mineral deposits and even the occurrence of health problems related to the nutrient and/or toxic elements availability (White and Blum, 1995).

6.5.2. Alteration processes of soil clay minerals

The phyllosilicates are the predominant minerals in soils, being also called as clay minerals when present in the soil clay fraction. These clay minerals influence important soil chemical (cation exchange capacity, pH, sorption), microbiological and physical (texture, structure, consistency) properties (Figure 10), as a function of its small particle size, elevated specific surface area and surface reactivity.

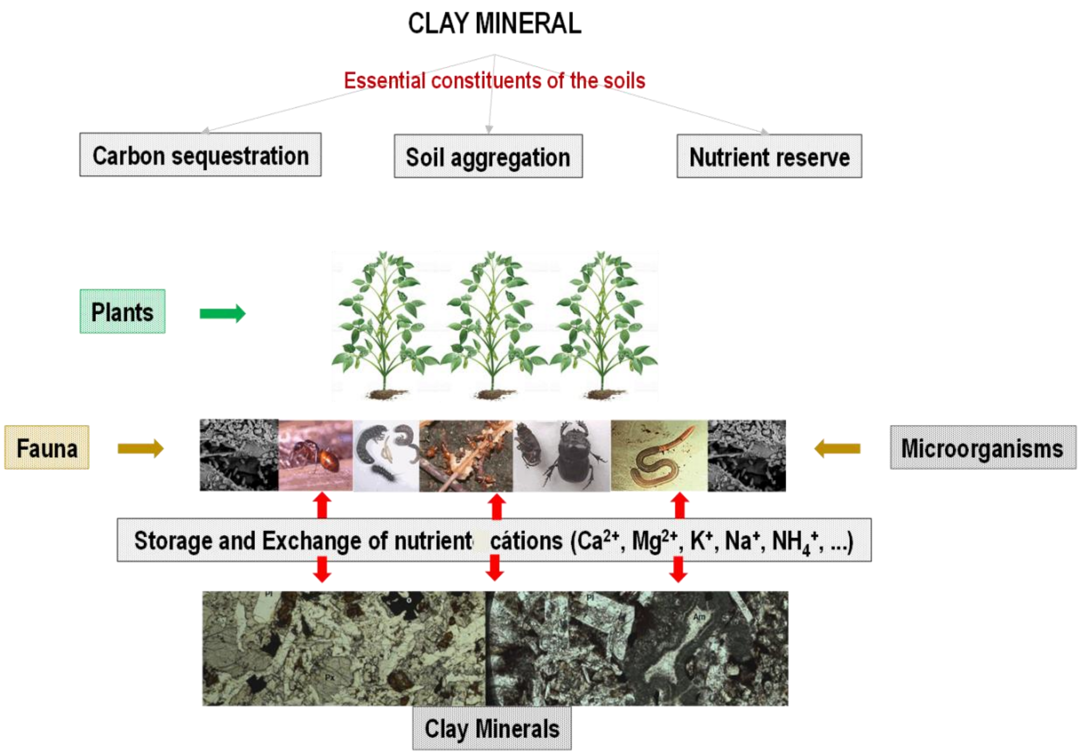


Figure 10. Importance of clay minerals in the soil properties (Adapted from Gobat et al., 2003)

In the phyllosilicate, the clay minerals structure is constituted by tetrahedral sheets adjusted to octahedral sheets, forming layers. The tetrahedral sheets are formed by individual tetrahedrons, which link itself by the sharing of basal oxygen. The octahedral sheets are constituted by individual octahedrons linked laterally by the sharing of octahedral edges.

The distance between a given set of planes is termed d-spacing, which can be determined quite accurately using XRD. The phyllosilicate clay minerals have their respective d-spacing for its identification. The comparison of the variable d-spacings (d001) must be made under standardized conditions (temperature, cation saturation) to enable identification based on differential responses to these conditions. The d-spacing between (001) atomic planes in expansible phyllosilicates varies with temperature, relative humidity, and exchangeable cations in the interlayer region of these minerals (Harris and White, 2008).

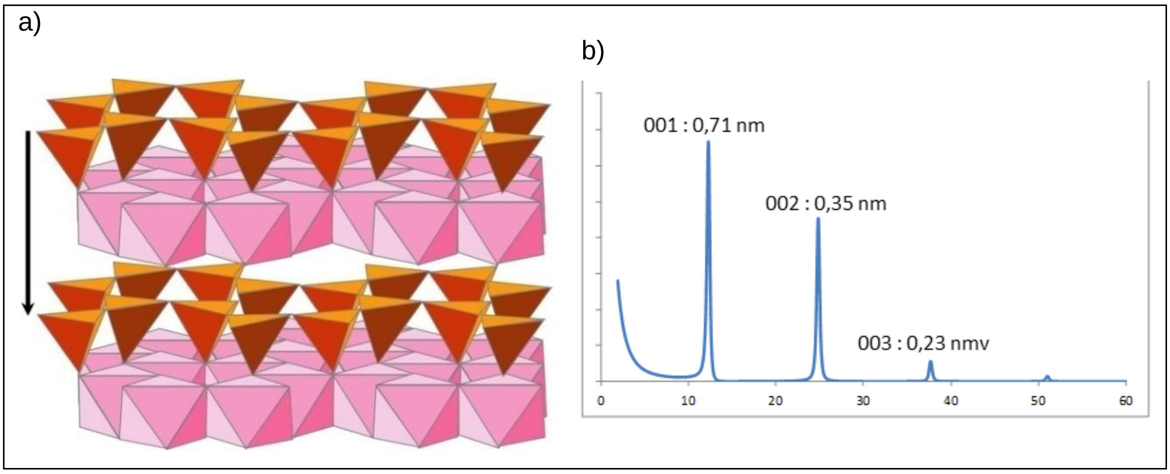


Figure 11. Representation of chemical structure (a) and standard XRD reflection (b) of kaolinite.

In kaolinite, whose ideal structural formula is $Al_2Si_2O_5(OH)_4$, the interlayer space is stable and the basal distance between layers is 0.72 nm (Brown et al., 1978; Dixon, 1989) (Figure 11). The kaolinite is considered a clay with low activity due to its low values of cation exchange capacity (1 to 5 $cmol_c$ kg^{-1}) and of specific surface area (35 m^2g^{-1}). Thus, kaolinitic soils normally present a low nutrient reserve (Kämpf et al., 2012).

Generally, in soils developed under humid and tropical conditions, the kaolinite is the main mineral of clay fraction. The formation of such mineral is favored by conditions of intense chemical weathering and leaching of the mineral dissolution products, mainly the base cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) and silica. The main kaolinite formation process is the dissolution of primary minerals and the reprecipitation of Si^{4+} and Al^{3+} from the soil solution (neoformation). The dessilication process (loss of Si^{4+}) also determines the weathering and the transformation of secondary minerals richer in Si^{4+} (2:1), as those of smectite group, in 1:1 minerals (group to which kaolinite belongs) (Melo and Wypych, 2009).

When compared with the 1:1 phyllosilicates, the 2:1 clay minerals imposed their physical, chemical and morphological typical characteristics in the soil, even when present in a lower proportion.

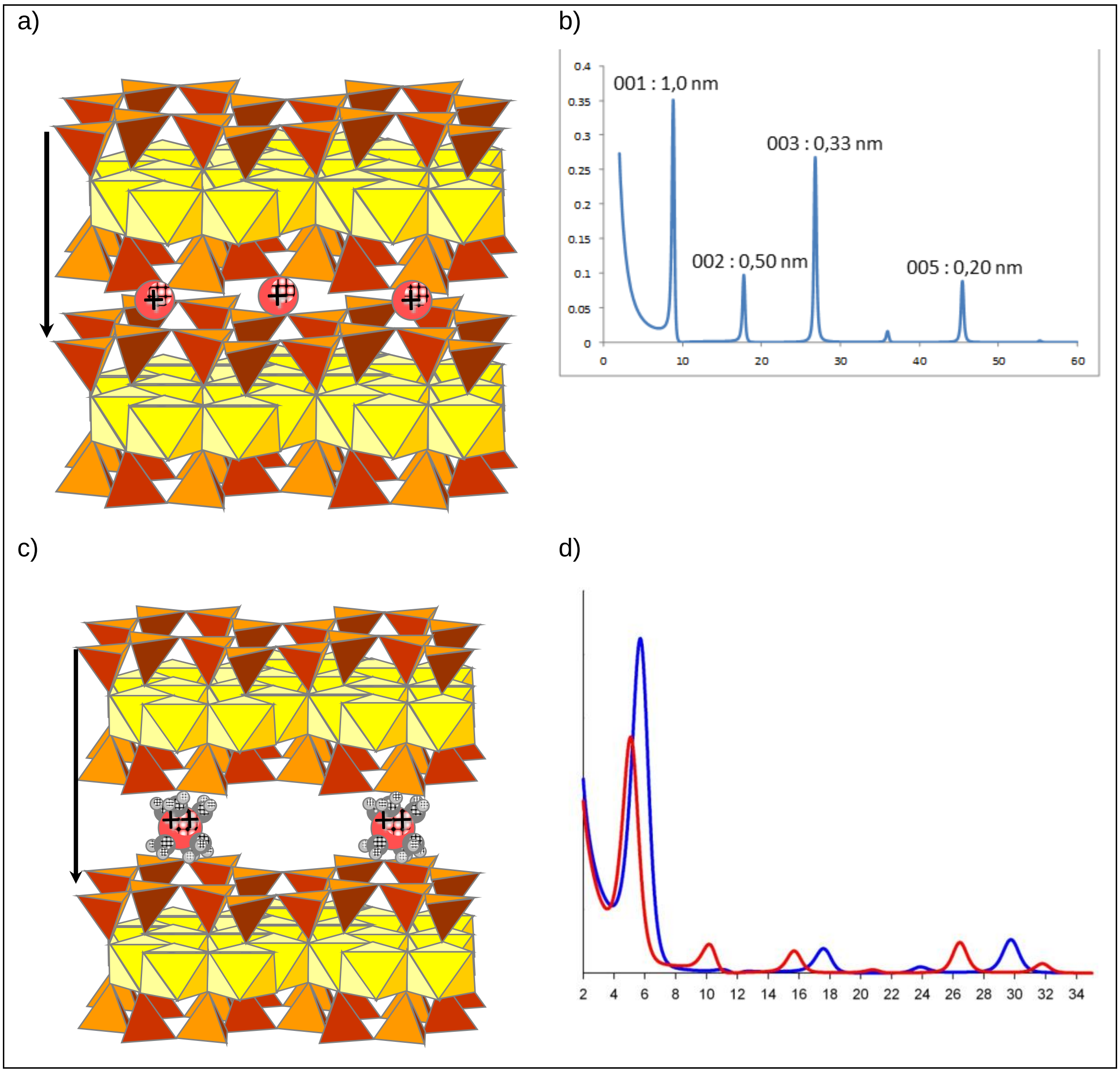


Figure 12. Representation of chemical structure and XRD of illite (a andb) and of smectite (c and d).

The 2:1 clay minerals present variations regarding the specific surface area, the cation exchange capacity and the swelling ability values. The illite (Figures 12a and 12b) belongs to the group of di-octahedral micas, similar to muscovite, but with lower Si^{4+} and water contents and lower amount of K^+ (Kämpf et al., 2012). The smectites has a basal spacing varying between 1.0 and 1.7 nm (Figure 12d), depending on the interlayer cations and molecules and the relative moisture (MacEwan and Wilson, 1980). In turn, they present elevated specific surface area (800 m^2g^{-1}) and cation exchange capacity (50 to 160 $cmol_c\ kg^{-1}$), being highly reactive and denoting good soil chemical fertility.

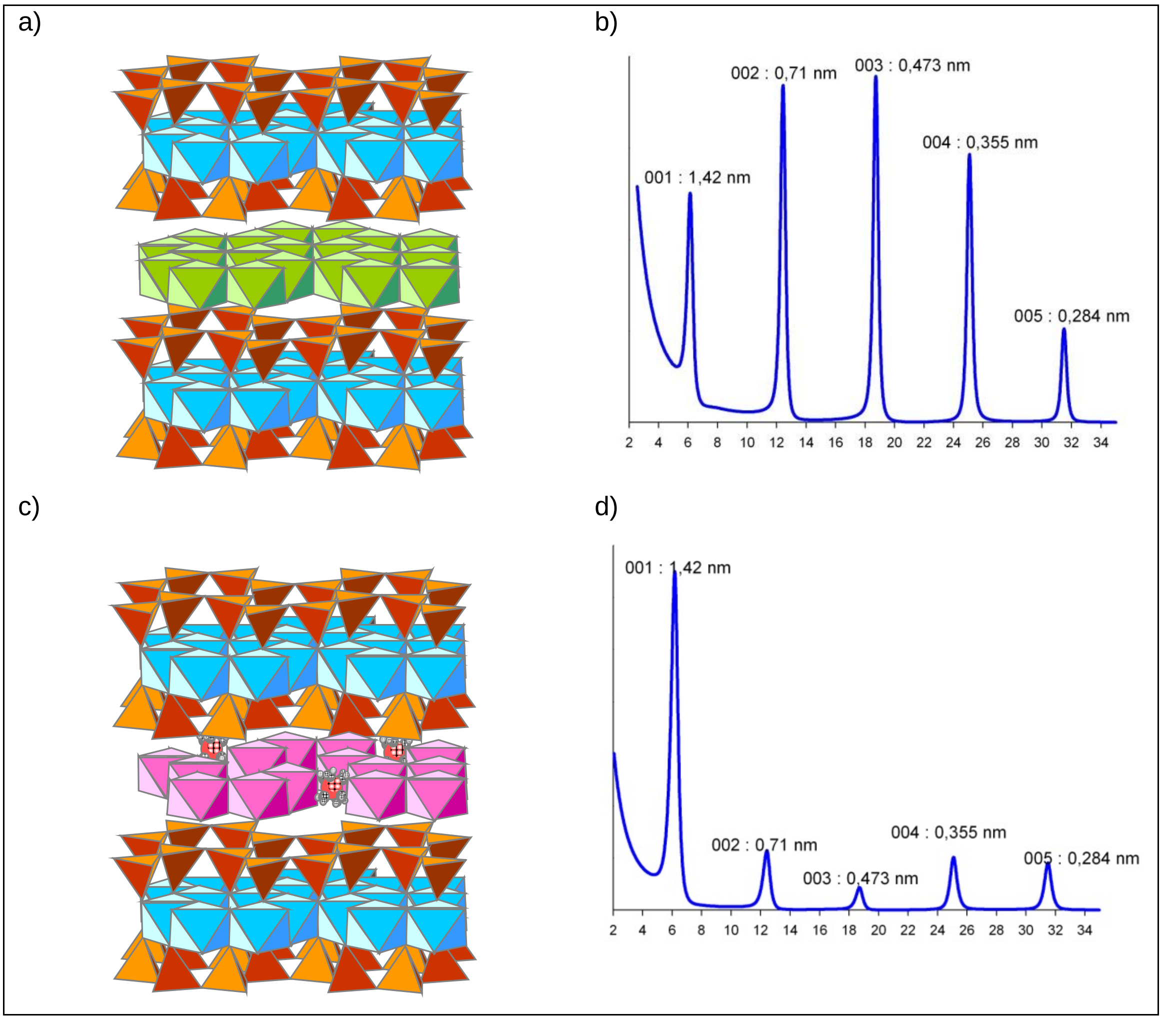


Figure 13. Representation of chemical structure and XRD of chlorite (a and b) and of 2:1 minerals with hydroxy-interlayered (c and d).

The chlorites (Figures 13a and 13b) are primary minerals inherited from the metamorphic or igneous rocks, or even derived from the alteration of ferromagnesian minerals. In soils, the content and the frequency of chlorites are low, and its occurrence is linked to the source material (Kämpf et al., 2012). The low frequency is related to the low stability in the pedoenvironment, or also, due to the difficulty in distinguish when present in low amounts and among the predominance of other clay minerals (kaolinite, vermiculite and smectite) (Barnhisel and Bertcsh, 1989).

The 2:1 phyllosilicates, as vermiculite and smectite, present swelling ability, high specific surface area and, consequently, high cation exchange capacity; thus, playing a fundamental role in soil reactivity (Wilson, 1999; Reid-Soukup and Ulery, 2002; Malla, 2002). In moderate to strong acidic conditions, the 2:1 clay minerals may present intercalation with hydroxy-Al^{3+} interlayers, forming 2:1HI clay minerals (HIV, HIS), with interlayer spacing around 1.42 nm

(Figure 13d). As a consequence, there is a decrease (or loose) of its swelling and of the cation exchange capacity, according to the intercalation level (Figure 13c and 13d) (Barnhisel and Bertsch, 1989; Meunier et al., 2007). However, the stability of 2:1HI clay minerals is greater than vermiculite or smectite free of hydroxy-Al^{3+} interlayers. According to Karathanasis (1988), when the 2:1HI clay minerals reach a high intercalation level by Al^{3+} polymers, they can present a higher stability than kaolinite.

HIV and HIS clay minerals do not have clearly defined specific surface area and cation exchange capacity due to large heterogeneity in chemical composition and structure. However, it is well-known that the fill of interlayer space by hydroxy-Al^{3+} in vermiculites and smectites induces the decrease of soil permanent charge, specific surface area and contraction and swelling ability.

The swelling ability 2:1 minerals are typically found in Vertissolos (Vertisols) in soils associated to arid and semi-arid climate, or poorly drained, as Gleissolos (Entisols) and Planossolos (Alfisols or Ultisols). Soils of estuarine environments, derived from marine/fluvial sediments, as Gleissolos (Entisols) and Organossolos (Histosols) from mangroves, are frequently smectitic. Neossolos Litólicos (Entisols) also can present these minerals, especially when developed from basic and magmatic rocks.

The 2:1HI clay minerals are reported in many soil classes, commonly occurring in acid soils (Kämpf and Klamt, 1978; Almeida et al., 2000; Marques et al., 2002), including Oxisols, but in low content. Soils from subtropical regions, as RS, show a particular occurrence of these minerals, because the alteration process release expressive amounts of Al^{3+} and, since the hydrolysis is partial, there is the formation of 2:1HI minerals. Thus, a portion of released $Al^{3+}$is fixed in the interlayer space and forms HIV and HIS. The 2:1HI clay minerals similar to that studied in the current work are formed by smectite or vermiculite aluminization, and not by degradation of other minerals (mica and chlorite), as observed by Viennet et al. (2015).

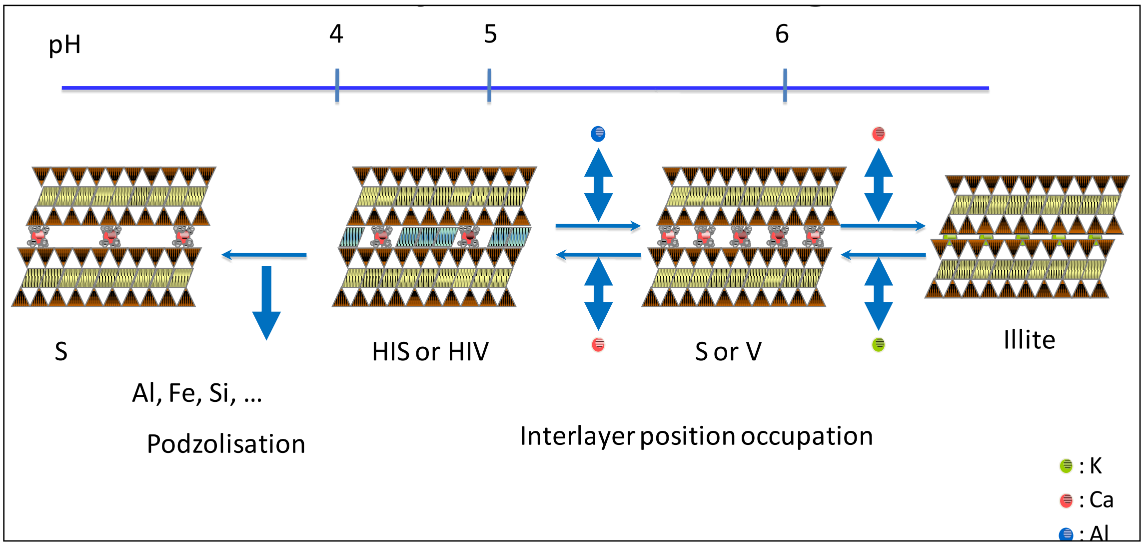


Figure 14. Alteration scheme in 2:1 phyllosilicates.

The changes (transformations) observed in the 2:1 minerals structure are mainly related to the cation exchange in interlayer space, occurring even in a short period of time (Figure 14). In this way, depending on the availability and abundance of elements such as K^+, Ca^{2+} and Al^{3+}, they will be inserted in interlayer space of 2:1 clay minerals structure.

In pedoenvironments with moderate acidity the 2:1 structure will not suffer important changes, what may change is the nature of interlayer material, with the passage of illite to smectite or vermiculite, and then passing to HIV or HIS. In the first case, there is a competition between K^+ and Ca^{2+}, where, in conditions of high K^+ availability, due to the chemical fertilization or the addition of animal manure, will results in an increase of illite formation (in interlayered ilite/smectite) (Bortoluzzi et al., 2012; Mortele et al., 2016). On the other hand, if there is a low K^+ amount, the result will be the formation of illite or smectite (Barré, 2007; Inda et al., 2010; Caner et al., 2014; Mortele et al., 2016). In environments where there is higher Al^{3+} amounts HIV/HIS may form with variable degree of polymerization of aluminium in the interlayer.

In a practical way, the sources of these cations in agriculture are mainly linked to the liming and fertilization practices for Ca^{2+} and K^+, respectively, and to the soil acidity conditions for Al^{3+}. Thus, it is important to highlight that 2:1 clay minerals have a key role in soils, even in low concentrations as observed in soils from RS.

6.5.2.1. Mineralogical modifications in the pedoenvironment

The soil mineralogical modifications occur by transformations in solid state and by dissolution and neoformation reactions. The transformations in solid state furnish the mechanisms for many common alterations of2:1 phyllosilicates, as the transformation of mica into vermiculite or to mixed-layermica-vermiculite, determined by the K^+ loss from interlayers. The transformation of 2:1 phyllosilicates into 1:1 phyllosilicates may imply a stage with an interstratified 2:1-1:1 (e.g. mica-smectite) a stage or occur directly by dissolution and neoformation processes (Churchman, 1990).

Naturally chemical weathering process that occur in the weathering fronts, the saprolite and the soil, and element loss by fluids percolating in the porosity control the elements concentrations of Si^{4+}, Al^{3+} and K^+, and subsequently the formation of clay minerals (1:1 vs 2:1).Changes in the concentration of these elements can alter equilibrium conditions in the soil solution, inducing mineralogical changes. In this sense, 2:1 clay minerals can suffer different polymerization degrees as a function of Al^{3+} or Al(OH)n polymers availability, or even, occupation of interlayer space by K^+, due to the possible addition of these elements in soil. Thus, these modifications make these minerals an important indicator of remote environmental events.

The diverse soil characteristics can be affected by human activity. The study of such impacts will imply soil properties that are considered of agricultural and environmental importance. Soil degradation indicators, as erosion, salinity, pH, fertility indicators and organic carbon stocks are commonly monitored aspects in studies concerning changes in land use, although theycan vary according to the individual, regional and national interests and concerns (Filippiet al., 2016).

The humans can occasion alterations in soils by innumerous actions and, among them, agriculture is highly significant. One objective of agronomy was to increase agricultural production through increase of soil productivity. However, other face increase of soil productivity is to the possible soil chemical properties and mineralogy modifications. The amplitude and intensity of such modifications will possibly depend on time and permanence of these actions.

In the last decades, the interest in the investigation of mineralogical modification induced by anthropic actions (crops, livestock, forest and mining) increased. Azevedo (1993) highlights that the degree of aluminium intercalation in 2:1 HI clay minerals (HIV/HIS) may be influenced by pedoenvironment conditions. Kämpf and Klamt (1978) attribute the relative increase in 2:1HI clay minerals in a Latossolo Bruno (Oxisol) from the Planalto province of RS to the higher stability of the aluminized clay minerals. Karathanasis (1991) suggested the existence of close relationship in the pedological scale of short-term events, as seasonal climatic variations and mineral stability in soils.

On the other hand, Inda et al. (2010) did not evidence significant modifications in the degree of hydroxy-Al^{3+} intercalation into 2:1 clay minerals in a soil under no-till (NT) compared to a soil under conventional tillage (CT), after 26 years of cropping. However, the authors suggested that occurs a decrease in the degree of Al intercalation and atrend with replacement of 2:1HI clay minerals with extensive Al^{3+} intercalation by 2:1HI clay minerals with partial Al^{3+} intercalation.

In a study performed in New Zealand, Officer et al. (2006) observed that, in the place of animal residence or rest, the soil presented only 2:1 clay minerals without hydroxy-Al^{3+} intercalation, being different of adjacent soil. The authors concluded that the pH increase and the action of other factors associated with the manure deposition contribute to neutralize the surface charges of amorphous material from interlayers, facilitating its removal. The transformation of 2:1HI clay minerals under similar conditions were reported by Fink et al. (2014a) in an Argissolo Vermelho (Ultisol) under native pasture withhigh stocking rate. Bortoluzzi et al. (2012) found that grape production during long cropping time (40 years) modified the proportion of soil constituents in a Neossolo (Entisol), in the Serra region of RS. Reductions in clay and organic matter contents were observed, as well as modification in soil clay mineralogy, as the formation of vermiculite from illite. The illite to vermiculite transformation was induced by K^+ loss and adsorption by grape despite the K^+ fertilization.

The RS represents an important portion of food production in Brazil, mainly in grain and bovine meat production. However, aiming to maintain the current production levels, a higher pressure in land use and in the intensification of agricultural activity is necessary, due to the very short or even inexistent time interval between the crop harvest and sowing. In this sense, alternative cropping systems are aimed, that can maintain the high productive indices and allow the alternation between crops and livestock.

6.5.3. Soil response to Integrated Crop-Livestock Systems

The Integrated Crop-Livestock Systems (ICLS) are known and recommended because pretend to optimize the cropping area, where the crop and livestock receive the same management and result in increased benefits for farmer. In this system, while crops and livestock are succeeded, the soil becomes the central compartment of the occurring processes (Carvalho et al., 2010). Thus, the soil chemical, physical and biological alteration is progressive maintained over time and occurs in the positive way of the process. According to Anghinoni et al. (2011), the combined ICLS utilization with the NT technique may contributes to increase the soil organic matter contents and, consequently, improve its fertility and nutrient stocks.

Some studies aiming to evaluate the ICLS effect in different soil characteristics and/or properties are being performed in RS, mainly regarding the chemical aspects and its consequences for the crops and for the soil, as well as that related to physical (Conte et al., 2011) and microbiological aspects (Chavez et al., 2011). Thus, De Oliveira et al. (2011) observed important variations in K^+ balance and concentration in soil, in relation to the season occupied by animals and crops, finding a decreasing gradient from the surface. The authors also verified higher K^+ contents after pasture than after soybean cropping, and the K^+ levels after the first one reach values two times higher in the same area than after the soybean cycle. Such finding highlights the influence of animal presence in the soil K^+ redistribution.

In turn, Martins et al. (2014) observed that after nine years of ICLS utilization, grazed areas were less acidic as compared to non-grazed areas, presenting a higher base saturation and lower aluminum saturation, evidencing that the soil acidification was lower in grazed areas, in the 0-40 cm layer. Accordingto Souza et al. (2009) and Assmann et al. (2014), moderate grazing intensities (20 and 40 cm of pasture sward height) in integrated systems with grasses-soybean under NT, promoted increase in soil total organic C, particulate organic C, total N and N from particulate organic matter stocks, similar to what was verified in non-grazed areas. The referred grazing intensities also represents a good equilibrium between CMI (carbon management index) and the average daily gain of animals, with a higher economic return between CMI and live weight gain per unit of area in the pasture sward height of 20 cm (Da Silva et al., 2014).

The ICLS have been widely studied also in the Brazilian Cerrado region, second largest biome of the country (Marchão et al., 2007; Loss et al., 2012; Batista et al., 2013), where can be observed its potential for the soil agricultural use in a sustainable way, as compared to the conventional production systems utilized in such region.

6.5.3.1. Soil clay minerals in the ICLS

In the ICLS there is the absence of soil tillage which contributes to increase soil moisture and organic matter accumulation, mainly in the surface layer. The permanent protection of soil surface, either by uninterrupted cultivation with annual crops or pastures or by the addition of crop residues limit temperature and humidity variation of topsoil. These pedoenvironmental changes can modify the existent natural equilibrium, determining a new dynamic in soil surface layer, where considerable mineralogical alterations may occur (Azevedo et al., 1996; Officer et al., 2006; Inda et al., 2010; Fink et al., 2014b).

The concentration of 2:1 and 1:1 phyllosilicates and oxides, and their chemical and structural characteristics, vary according to the source material, weathering intensity, soil solution composition and drainage conditions (Motta and Kämpf, 1992; Schaefer et al., 2008) and may be also affected by the soil management system (Silva Neto et al., 2008).

In this sense, long-term ICLS experiments may cause mineralogical modifications that will influence the chemical and physical behavior of soil. This occurs because, for example, ICLS increases soil moisture and organic matter content, which are related to the main dissolution reactions of iron oxides in the pedogenic environment (reduction and complexation) (Schwertmann, 1991; Inda Junior and Kämpf, 2005). In the same way, such changes can also contribute to the 2:1 clay minerals alteration, because they are sensitive to acidity variations, organic matter that govern Al^{3+} availability content and cycles of wetting and drying (Rich,1968).

According to Churchman (1980), in acid systems with the presence of organic complexing acids, the mafic and pedogenic chlorites are dissolved, while the in the absence of them, the same are transformed into vermiculites. Malcolm et al. (1969) reported that organic complexing compounds removed the hydroxy-Al^{3+} interlayered sheets of interstratified 2:1-2:2 clay minerals, forming smectite. The organic complexing acids also can influence the hydrolysis reaction and the Al^{3+} precipitation (Kwonge and Huang, 1979), as well as the type and the crystallization of Al^{3+} (Kodama and Schnitzer, 1980; Huang and Violante, 1986) and iron oxides (Schwertmann et al., 1986).

6.6. Final considerations

In Rio Grande do Sul is possible to observe and to describe the 13 soil orders recognized by SiBCS (Embrapa, 2013), a result of the expressive geological, geomorphological and climatic diversity that occurs in this State. This heterogeneity of soils imply potentials and limitations for the soil use in most diverse activities (Streck et al., 2008).

However, in the academic field of Earth Sciences, is possible to observe large deficiencies in pedological, geological, hydrological and environmental areas, all converging and acting directly in soil. Thus, it is necessary to develop studies that relate the soil development with its respective source material, detailing the transformations in the soil-rock transition zone and its implications for the environmental and human activities.

In the same way, due to the accelerated soil degradation degree, the evaluation of the effects of human alteration is an increasing interest, aiming to a better comprehension of new dynamics expressed in soil system as a function of the use of new agricultural technologies, as well as more intensified food production systems (with only crops or integrating crops and livestock).

The soils of subtropical regions from Rio Grande do Sul and Santa Catarina, present a low proportion of 2:1 clay minerals, that are absent in the soil from tropical regions of Brazil. However, such minerals, even in low proportions, are key factors for the fertility of the soils of these regions. South Brazil is a region with a very intensive agriculture and the pressure on soil use is considerably more intense than in the Amazonian region. In Amazonian region, the biggest challenge is to limit and to control the deforestation advance. In South Brazil the challenge isto maintain favorable conditions of soil fertility for a sustainable crop production.Thus, the soil degradation (erosion, acidification) is avoided.

In view of the foregoing, it becomes evident that the ICLS can represent a good option for food production, with higher resilience and sustainability, as already observed by Russelle et al. (2007), since such systems can influence thesoil system in a positive manner. However, the knowledge of ICLS impact on soil mineralogy and in the behavior of tropical soils is still scarce.

7. CHAPTER II – MINERALOGICAL ALTERATION AND SOIL FORMATION OF THE IGNEOUS ROCK IN SOUTH BRAZIL

7.1. Abstract

In the southern region of Brazil there is a large part of the soils developed from igneous rocks (basalt and granite) and metamorphic rocks (gneisses) with an intermediate to advanced degree of weathering, low content in exchangeable bases and acids. Studies on the geopedochemical weathering and pedogenic processes offer support for identifying the suitability and use of soils, besides supplying information on the fundamental aspects for their conservation. This study aimed to characterize both qualitatively and semi-quantitatively the primary and pedogenic minerals present in soils of important ecosystems in Rio Grande do Sul. The locations selected for description and collection of the weathering profiles are located in the municipalities of São Borja, Taquara and Eldorado do Sul in the state of Rio Grande do Sul, Brazil. The basalts São Borja (Vertic Hapludolls) and Taquara (Typic Hapludolls) weathering profiles exhibit the same minerals, potassium feldspars, pyroxenes, plagioclases and oxide traces. The weathering indices (Weathering Intensity Scale - WIS andChemical Index of Alteration - CIA) revealed the following sequence of the weathering degree: São Borja < Taquara < Eldorado do Sul. When taking into account the mineralogical composition of the profiles, this sequence can also be written as follows: smectite composition <smectite-kaolinite composition <kaolinite composition. In the western region of RS (São Borja profile), which is in the Pampa biome, the physical properties such as the shrinkage and swelling of soils and the low degree of flocculation of this type of clay represent and important limitation for agricultural use and exposes the fragility of these soils when they are managed inadequately.

Keywords: weathering indices; geopedochemical; soil mineralogy; basalt.

7.2. Introduction

The Brazilian territory consists of an extensive tropical area extending to a subtropical region in the south of the country, which includes the states Rio Grande do Sul (RS), Santa Catarina (SC) and Paraná (PR). In these regions, the mineralogical composition of the soil clay fraction is predominantly formed by different proportions of 1:1 clay minerals (kaolinite), iron oxides (hematite, goethite, maghemite), aluminum oxides (gibbsite), associated with 2:1 clay minerals in lower proportions (smectite and vermiculite), which are commonly polymerized by hydroxy-Al^{3+} interlayers (2:1 HI). However, in specific environments with restricted drainage or low rainfall, soils predominantly composed of 2:1 clay minerals may occur (Kämpf and Curi, 2012).

The chemical weathering of rocks is the most important process altering Earth's surface, thus being a critical process during the geochemical cycle of the elements (Brantley, 2003). The geochemical mass balance methods are important tools for the quantitative determination of the elements transfer on Earth's surface (Clayton, 1979; Bricker et al., 2003). These methods are still considered the most accurate means for defining weathering reactions in natural systems (Bricker et al., 2003).

According to Simonson's pedogenic processes model (Chadwick and Graham, 2000), soil changes in a place by means of four multiple processes in the form of addition, loss, transformation and translocation of materials. These processes interact differently, depending on the depth in relation to the soil surface and on the combination of environmental factors at such location. Thus, the soil profile expresses the balance among these processes and the chemical, physical and mineralogical changes. This model has been applied to studies on pedogenic processes in general (Hoosbeck and Bryant, 1992; Gessler et al., 2000) and to those on mass balance of the soil profile constituents (Chandwick et al., 1990).

The climate variables with the greatest pedogenic significance are temperature, rainfall and potential evaporation (Young, 1976). The water available for leaching is the portion of precipitation that exceeds the water lost by evapotranspiration and the one that fulfills the water retention capacity of the soil (Kämpf and Curi, 2012). A small amount of available water for leaching and weathering determines the chemical characteristics of the soil, such as low extractable acidity, elevated pH, high values for saturation by bases, besides favoring a dominant smectite mineralogical composition and the preservation of primary minerals (e.g. plagioclases) present in the Chernossolos (Molisols) and Vertisolos (Vertisols) of southern Brazil (Brasil, 1973; Carvalho, 1976; Kämpf, 1981; Kämpf et al., 1995). On the other hand, intense leaching directly form kaolinite from primary minerals (feldspars) or induces a change in the mineralogy of clay minerals from smectite to kaolinite and oxide.

In the southern region of Brazil, at Mares de Morro's Domain (Atlantic Forest), Planalto of RS and Escudo Sul-rio-grandense regions, there is a large part of the soils developed from igneous rocks (basalt and granite) and metamorphic rocks (gneisses), with an intermediate to advanced degree of weathering poor in exchangeables bases. The mineralogy of the clay fraction is dominated by kaolinite associated to iron and aluminum oxides and 2:1 HI clay minerals. However, at Pradaria'sDomain (Pampa biome), there are fertile soils developed on basaltic lithology with high levels of base cations and significant amounts of expandable 2:1 clay minerals and calcium carbonate concretions (Cogo, 1972; Almeida, 1996).

In Rio Grande do Sul, thirteen soil classes described in the Brazilian System for Classification of Soils (Embrapa, 2013) have been mapped based on their lithological, climatic and relief diversity (Brasil, 1973; Streck et al., 2008). Nonetheless, there is scarce information about the changes occurring during the geopedochemical weathering or, in other words, quantitative information about the transfer/concentration of elements, as well as the weathering routes that happen from the unweathered rock up to the soil surface (weathering profile). This information has great influence on the land use and conservation management of the soil, in addition to serve as a base for other local and regional research and development sectors.

Hence, studies on the geopedochemical weathering and pedogenic processes offer support for identifying the suitability and usage of soils, besides supplying information on the fundamental aspects for their conservation. They are particularly important for areas that are essential to preserve ecosystems' diversityon a global scale, such as Pampa and Atlantic Forest biomes. In this context, this study aimed to characterize both qualitatively and semi-quantitatively the primary and pedogenic minerals present in soils of important ecosystems in

Rio Grande do Sul. In addition, this research analyses the mineralogical alterations (weathering routes) and the geochemical balance of alteration profiles located in environments with no history of anthropic actions in southern Brazil.

7.3. Materials and Methods

7.3.1. Localization and classification of profiles

The climatic variables and the soil source materials, as well as the minimal anthropic action on them were primarily taken into account to select the weathering profiles (fresh rock – saprolite/alterite – pedogenic horizons) (Table 1). The locations selected for description and collection of the weathering profiles are located in the municipalities of São Borja, Taquara and Eldorado do Sul in the state of Rio Grande do Sul, Brazil (Figures 15 and 16). In the profile located in Eldorado do Sul it was not possible to collect rock samples due to the depth of the material. The soils were classified based on the Brazilian Soil Classification System (EMBRAPA, 2013), the Soil Taxonomy (Estados Unidos, 2014) and the World Reference Base (IUSS Working Group WRB, 2015) (Table 2).

Table1.General description of the weathering profiles.

Alteration profile	**Source material**	**Soil use**	**Climate type[1]**	**Average annual temperature**	**Average annual precipitation**
São Borja	Basalt	Native field	Cfa	20.1°C	1523 mm
Taquara	Basalt	Forest	Cfa	19.4°C	1521 mm
Eldorado do Sul	Gneiss	Native field	Cfa	21.4°C	1544 mm

[1] Koppen (1936)

Table 2. Taxonomic classification of the soils of the alteration profiles.

Alteration Profile	**SiBCS**	**Soil Taxonomy**	**WRB**
São Borja	Chernossolo Ebânico Carbonático vertissólico	Vertic Hapludolls	Chernozem
Taquara	Chernossolo Háplico Férrico típico	Typic Hapludolls	Phaeozem
Eldorado do Sul	Argissolo Vermelho Distrófico típico	Rhodic Paleudult	Acrisols

Figure 15. Location of the sampling sites.

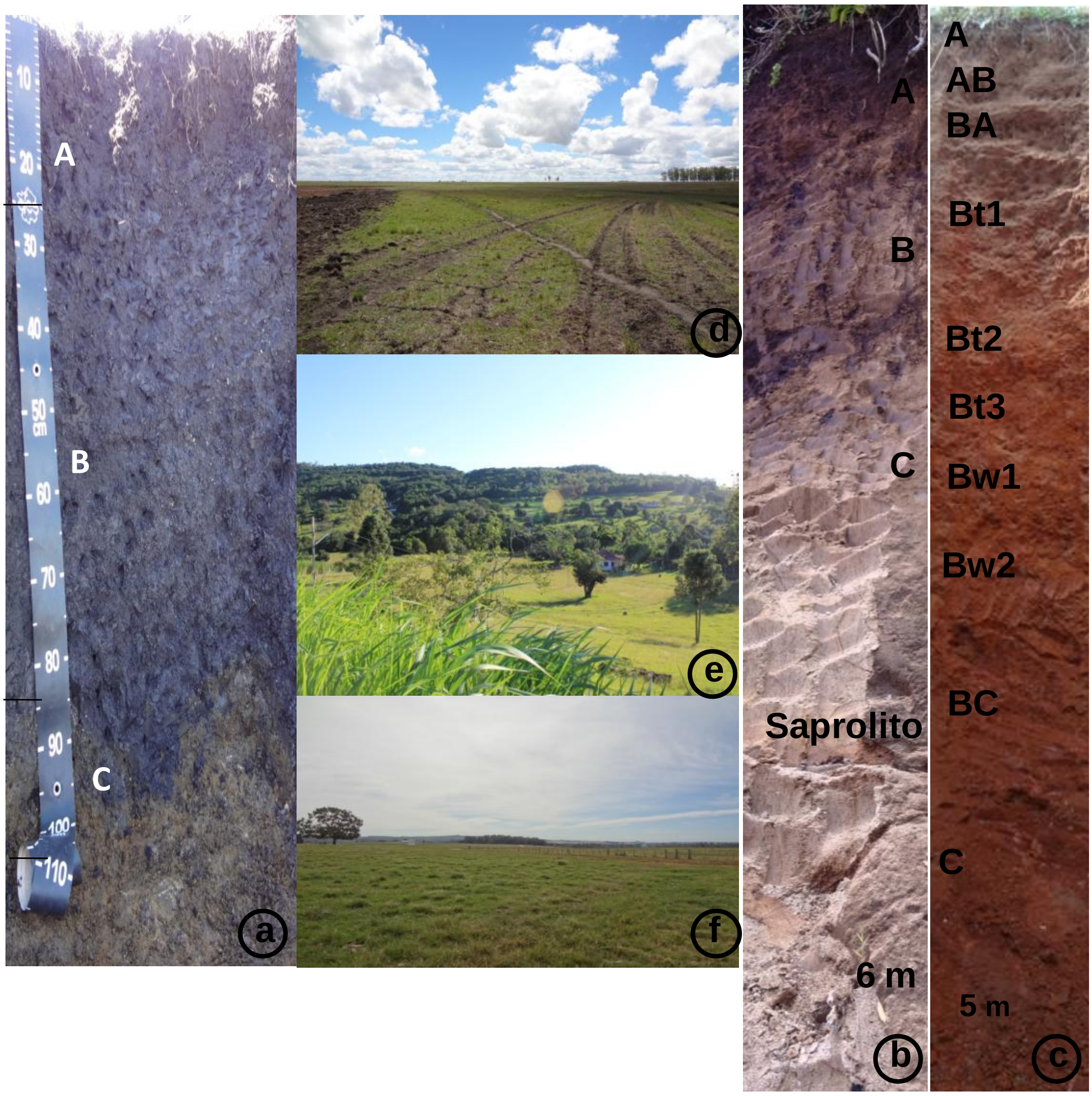


Figure 16. Alteration profiles sampled and local situation of the landscape in São Borja (a and d), Taquara (b and e) and Eldorado do Sul (c and f).

7.3.2. Characterization and environmental settings of sampled sites

7.3.2.1. Climate and lithology

According to the Köppen Climate Classification for the state of Rio Grande do Sul the subtype this is Cfa, Humid Subtropical Climate, in the locations of the three weathering profiles. The main climate variations in the east-west direction of RS are illustrated in Figure 17.

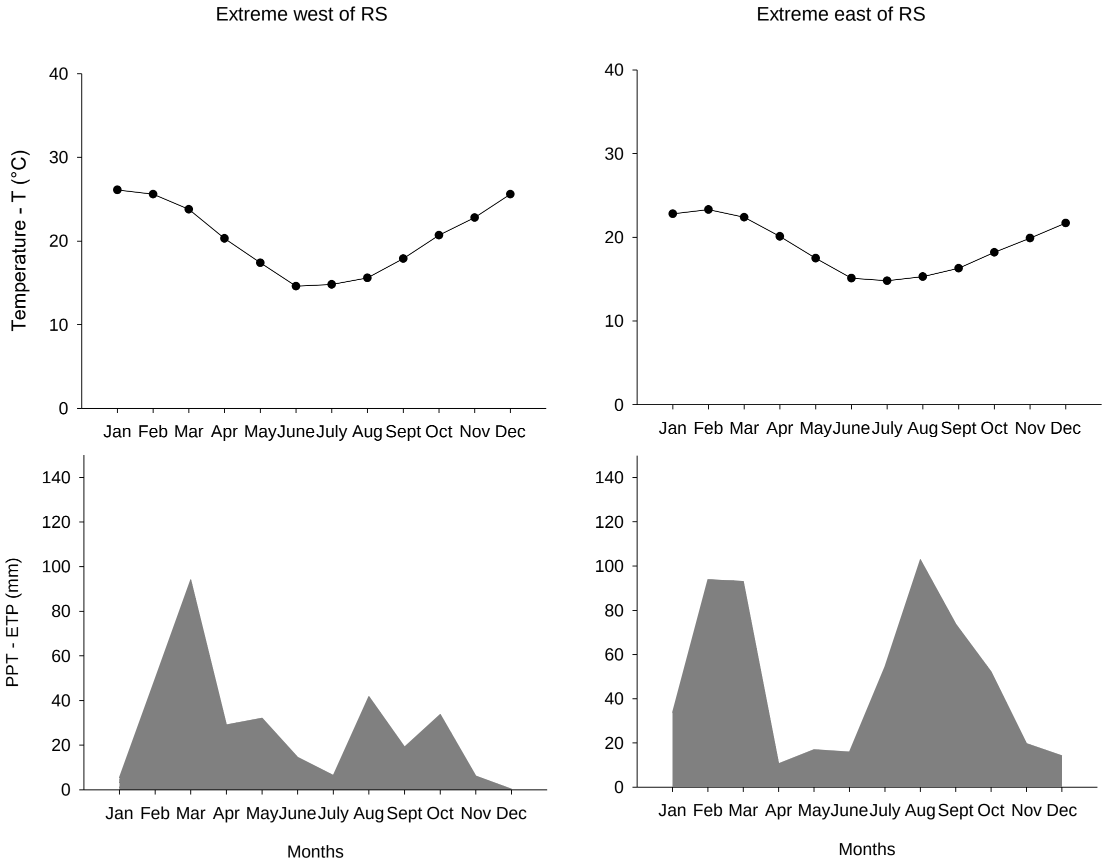


Figure 17. Climatic indexes representative of the variations in the east-west direction of RS.

The Planalto region, where São Borja (Vertic Hapludolls) and Taquara (Typic Hapludolls) profiles are located, covers a bundle of volcanic rock successions with basic (basalt) to acid compositions (dacites and rhyolites) of Serra Geral formation.The spill sequence within this area is identified by thresholds on slopes of valleys.This large volcanic manifestation, dating to the Cretaceous period (140-130 Ma), interrupted the sedimentation of Paraná Basin. The first volcanic derrames generally feature a basaltic composition, with predominance of elements such as Fe, Ca and Mg, while spills that are more recent feature a rhyolitic composition with more significant amounts of silicon and lower amounts of Fe, Ca and Mg. There are also intermediate types of spills with a dacitic composition (Nardy et al., 2008).

The Serra Geral formation is divided into eight distinct facies due to variation in chemical composition, textural characteristics and arrangement of the spills. Five facies are related to the mafic magmatism (Gramado, Paranapanema, Pitanga, Esmeralda, Campo Erê and Lomba Grande facies) and four are related to the intermediate to felsic magmatism (Palmas, Chapecó, Várzea do Cedro and Alegrete facies) (Figure 18). The area where Taquara profile was sampled corresponds to the Gramado facies, with a maximum thickness of about 300 meters. This facies represent the first volcanic manifestations over the sandy sediments of Botucatu desert (Peate et al., 1992). The region of sampling of São Borja profile is located at the western region of RS and corresponds to the Alegrete facies, characterized by and andesite/basalt outcrop with an average thickness lower than 100 meters (Martins et al., 2011).

Eldorado do Sul profile (Rhodic Paleudult) is inserted in the middle of the Gneissic Complex Arroio dos Ratos (Figure 18). This Complex was described in the 80’s (Fernandes et al., 1988) and is composed of biotite metatonalites and biotite metagranodiorites with subordinate occurrences of tonalitic and dioritic gneisses. Intrusion relationships were described within this Complex, where the less differentiated terms, predominantly tonalites, are cut by rocks of granodiorite composition, which, in turn, are intruded by granitic and trondhjemitic rocks. All of these rocks were affected by metamorphic conditions of upper amphibolite facies, thus featuring a main plot marked by an E-W sub-horizontal tectonic foliation (Fernandes et al., 1992).

In the northeastern region of RS, in areas where the altitude comprised between 300 and 500 meters, Serra Geral levels present a smooth wavy to mountainous relief. In the steepest portions, there is a predominance of Neossolos Litólicos/Regolíticos (Entisols), Chernossolos Argilúvicos (Molisols), Cambisolos Háplicos (Inceptisols), while there are Nitossolos Vermelhos (Ultisols or oxisols) in smooth wavy relief. Chernossolos Háplicos (Molisols) are found at the lower portions of the valleys.

In the west of RS, in Pampa region, soils are predominantly formed over basaltic rocks of Serra Geral formation, which are influenced by intercalated sandstones of Botucatu formation (sedimentary). This region is dominated by Neossolos Litólicos/Regolíticos (Entisols) mainly located in a smooth wavy relief. There is, however, the occurrence of Chernossolos Ebânicos (Molisols) occupying areas that are almost flat near river channels (Streck et al., 2008).

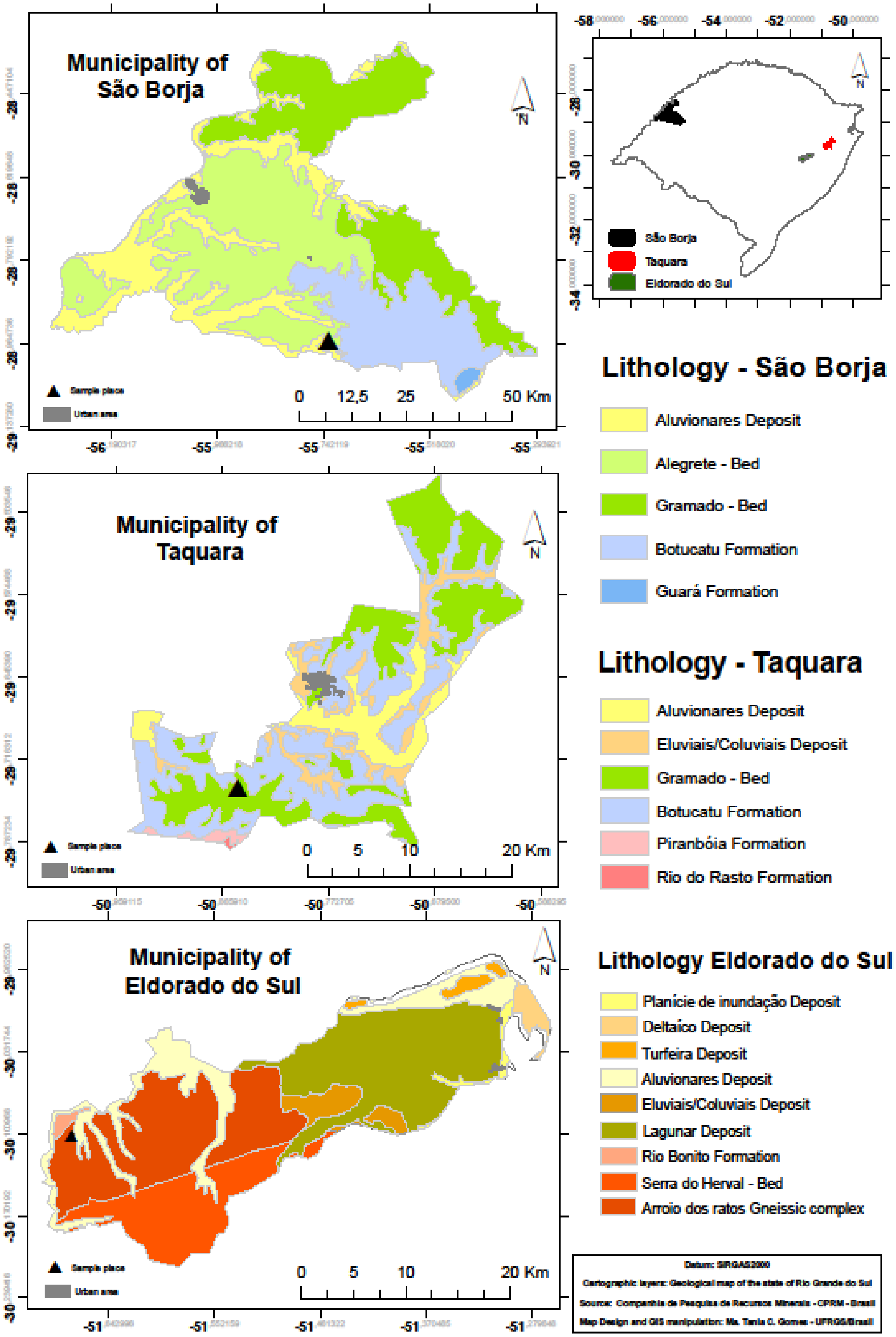


Figure 18. Lithological map of São Borja, Taquara and Eldorado do Sul municipalities.

7.3.2.2. Vegetation in the ecosystem context

Pradeira’s Domain (Pampa biome), where São Borja profile is located, is composed by natural landscapes with grassland vegetation prevailing, in an area of 178,243 km^2, according to the Map of Brazilian Biomes of IBGE (2004). This biome corresponds to 63% of the state’s territory and approximately 2% of the Brazilian territory. The vegetational diversity of the Pampa is due to the geopedological and climatic diversities (Vieira, 2014).

Araucaria’s Domain, where Taquara profile is located, is an ecosystem of the Atlantic Forest biome, characteristic of the southern region of Brazil and of some areas of the country’s southeastern region, which shelters a great variety of species, some of which are found exclusively within this ecosystem. Its natural physiognomy is characterized by the predominance of *Araucaria angustifolia*, which is among the officially endangered plant species of Brazil (Silva, 1996).

7.3.4. Morphological Description and Sampling

The morphology of the profiles was described (Annex 6) and collected in accordance with Santos et al. (2005). Samples were collected from all the pedogenic horizons, air dried, then the clods were broken up, and the material was passed through a 2mm mesh sieve, until obtaining the air-dried fine soil (ADFS) sample. The proportion of gravel was defined based on the material retained in the sieve. Undisturbed samples were collected at the main diagnostic and transitional horizons and placed in plastic containers (with approximate dimensions of 100 x 60 x 50mm). The materials that were not deformed were impregnated with orthophthalic resin in order to preserve the sample’s original features. After the drying, thin slices (30µm) were cut and placed in slides for optical microscopic analysis.

7.3.5. Physical analysis

The particle size distribution was determined after the dispersion of samples from the ADFS fraction with 1mol L^{-1} NaOH and mechanical stirring in a horizontal shaker for 4 hours at 120 oscillations per minute. The sand fraction was separated by humid sieving (0.053mm mesh sieve). The clay fraction was determined by the pipette method (Embrapa, 1997).

The specific surface area (SSA) of the ADFS fraction was estimated by the water adsorption method (Quirk, 1955). The samples were subjected to an atmosphere of 0% humidity (RH = 0%) in desiccators containing phosphorus pentoxide and were weighed afterwards. Subsequently, the samples were subjected to an atmosphere of 20% humidity (RH = 20%) in desiccators containing potassium acetate and were weighed again. Considering that one molecule of water covers 0.108nm^2, the SSA was calculated based on the following formula:

SSA m^2 g^{-1}= Avogadro's number (6.02214x1023) x 0.108nm^2 x (g water adsorbed/g sample)

7.3.6. Chemical analysis

The total organic carbon (TOC) was determined by dry combustion in the SHIMADZU Total Organic Carbon Analyzer. Ca^{2+}, Mg^{2+}, Al^{3+} and Na^+ were extracted with a KCl 1 mol L^{-1} solution, and quantified through Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). P was extracted based on the method described by Tedesco et al. (1995), where 3dm^{-3} of soil and 30mL of Mehlich-1 extraction solution (H2SO4 0.0125 mol L^{-1}+ HCl 0.05 mol L^{-1}) were used. The samples were shaken for 5 minutes in a horizontal shaker at 120 oscillations per minute, and after decanted for 16 hours. The determination of P in the extract was performed by colorimetry. For the quantification of K^+, the extraction was performed by Mehlich-1 and measured by ICP. From these data, the cation exchange capacity (CEC_{pH} 7.0), the sum of the bases (S), the saturation by aluminum (Al%), and the saturation by bases (V%) were calculated.

The total Fe in the ADFS (Fet) were extracted by acid attack (HF-HNO3-HClO4). The Fe of the pedogenic iron oxides (Fed) were extracted with sodium dithionite-citrate-bicarbonate at 80°C (Mehraand Jackson, 1960). The Fe of the iron oxides with low crystallinity (Feo) were extracted in the dark with an ammonium oxalate solution of 0.2 mol L^{-1} at pH 3 (Schwertmann, 1964). The Fet, Fed, Feo and Ald were quantified by ICP.

7.3.7. Mineralogical analysis

The mineralogical analysis was performed by X-ray diffraction (XRD), by randomly oriented powder samples (ADFS fraction) and oriented slides (clay fractions). The clay fraction (<2µm) was obtained by sedimentation after the oxidation of organic material with 5% H_2O_2v/v at 40°C and the dispersion with a 1 mol L^{-1} sodium chloride solution (3 saturations) after dispersion with ultrasound (~150W during 30s for 40mL).

The clay fractions were treated with 3-5 saturations with Ca ($CaCl_2$ 0.5 $molL^{-1}$) and K (KCl 1 $molL^{-1}$). After the saturation, the samples were washed in order to remove the excess of salts. Oriented slides were prepared by the deposition of a thin layer from the clay suspension in glass slides, which were then dried at room temperature (air-dried – 25°C). The slides saturated with $CaCl_2$ also went through an ethyleneglycol vapor solvation (EG) at 50°C, inside a desiccator for 16 hours. The slides saturated with KCl were analyzed after thermal treatments at 110, 330 and 550°C for 4 hours.

The XRD patterns were obtained from a Bruker D8 Advance equipment (radiation Cu Kα radiation) from 2.5 to 65° 2θ with steps of 0.012° 2θ and a counting time per step of 48s converted from scanning mode for randomly oriented of air-dried fine soil (ADFS) and of ground rock. The slides prepared with oriented clay were analyzed from 2.5 to 35° 2θ, with steps of 0.012° 2θ and a count time per step of 96s, converted by a scanning mode.

7.3.8. Weathering indexes

The total chemical analysis was performed in finely ground rock, saprolite and soil samples. After the acid attack (HF-HNO_3-$HClO_4$) the dissolution of the samples, the elements were determined by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), at Bureau Veritas - Mineral Laboratories (Canada). The major elements analyzed were expressed in oxides weigth percent in addition to the loss on ignition. The oxide weight percentageswere converted into molar cation values and were subsequently used to calculate the following parameters: 4Si (Si^{4+} cation number divided by 4 in order to refer to the general formula of phyllosilicates); M^+ (Na^++K^++2Ca^{2+}); R^{2+} (Mg^{2+}+Fe^{2+}+Mn^{2+}); and R^{3+} (Al^{3+}+Fe^{3+}) (Meunier et al.,2013). Afterwards, the Weathering Intensity Scale (WIS) was calculated by using the Δ4Si (the difference between the 4Si composition of the altered samples and unalteredrock) and the molar ratios R^{3+} / (R^{3+}+R^{2+}+M^+) (Meunier et al., 2013).

The Chemical Index of Alteration (CIA = [Al_2O_3 / (Al_2O_3+Na_2O+CaO+K_2O)] × 100), proposed by Nesbitt and Young (1982), was also calculated based on the molar data. The CIA is used to calculate the weathering intensity assuming that the main processes of weathering are the leaching of Ca^{2+}, Na^+ and K^+ and the accumulation of residual Al^{3+}.

The WIS combines the silicon loss and the accumulation of elements of very low mobility, such as Al^{3+} and Fe^{3+}, in order to estimate the intensity of the weathering. A high Δ4Si corresponds to an intense weathering of the silicates into clay minerals where 100% value for the complete alteration into kaolinite. High values for the relationship of R^{3+} / (R^{3+}, R^{2+}+M^+) represent a high degree of leaching of the alkaline and alkaline-earth cations, and the accumulation of Fe^{3+} and Al^{3+} in the form of oxi-hydroxides (goethite, hematite, gibbsite) (Meunier et al., 2013).

7.3.9. Microscopy

The microscope used for the observation of rock protolites was an automated Zeiss Axio Z2 with the help of the tools in the AutoScan System Py program. The microscope is equipped with a M_O= 10 objective and a M_L= 10 ocular, giving a final magnification of 100x.

7.3.10. Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR analysis was performed only on samples from the Taquara weathering profile. Samples of ground rock and clay from saprolites and pedogenic horizons were analyzed by Fourier Transform Infrared Spectroscopy (FTIR) (Shimadzu 8300), in KBrpellets (1:100), using 32 scans and a $4cm^-$

^{1}resolution at the spectral range of 4000 to 400cm^{-1}. The absorption bands were attributed according to Farmer (1974) and Tan (1996).

7.4. Results

7.4.1. General properties of the soil

The physical and chemical properties of the soils are presented in Tables 3 and 4, respectively. In the soils developed from basalt, the textural class varied from clay loam in the A horizons to silt loam and silty clay loam in the B horizons. In the soils developed from gneiss, the textural class ranged from sandy clay loam in the A horizon to clay in B horizon. According to the relationship fine sand/total sand in the soils developed on basalt the diameter of the sand particles decreases towards the surface, indicating an active weathering process (presence of weatherable primary minerals in the sand fraction) (Annex 3 and 4). In the soil developed from gneiss the relationship fine sand/total sand indicates a uniform size of sand particles throughout the whole profile, suggesting an absence of alterable minerals and the quartz predominance within this fraction, as indicated by the X-ray diffraction (Annex 5).

The weathering profile of São Borja, classified as Vertic Hapludolls (VH), is shallow (< 100cm) and dark in color (5Y 2,5/1) (Figure 16). The structure of this profile is made of angular and sub-angular blocks with numerous shrink/swell cracks (vertic properties). In the C horizon, the presence of calcium carbonate concretions, determined by effervescence with hydrochloric acid, was observed, thus characterizing a carbonaceous character. The relationship between silt and clay has high values throughout the profile, mainly in B and Chorizons, indicating a low degree of weathering. The high values of the specific surface area (SSA) in this soil, between 79 and 119m^{2}g^{-1}, are due to the expressive presence of 2:1 expandable clay minerals (smectites).

The weathering profile of Taquara, classified as Typic Hapludolls (TH), is deep (0cm to 190cm), and deeper there is saprolitic material present up to 7m depth, and usually has dark brown colors (2,5YR 3/4). The profile structure is predominantly composed of angular and sub-angular blocks. The values of the relationship between silt and clay were also high, but lower than those found on VH soil, suggesting a more advanced weathering degree in the TH soil (Table 3).

In the same manner, there was a reduction of the SSA values in the B and C horizons of this soil compared to the VH soil, also developed from basalt.

Table 3. Physical characterization of alteration profiles.

		Particle size distribution(g kg^{-1})					
Soil horizon	**Depth** (cm)	**Sand**	**Silt**	**Clay**	**FS/TS**[1]	**silt/clay**	**SSA**[2] (m^2 g^{-1})
			São Borja (Vertic Hapludolls - VH)				
A	0-25	290	390	320	0.62	1.22	79
B	25-85	210	660	130	0.48	5.08	119
C	85-100	310	600	90	0.35	6.67	118
			Taquara (Typic Hapludolls - TH)				
A	0-20	200	490	310	0.3	1.58	78
B	20-70	110	520	370	0.45	1.41	103
C	70-190	460	440	100	0.17	4.40	93
			Eldorado do Sul (RhodicPaleudult - RP)				
A	0-20	550	240	210	0.36	1.14	9
AB	20-35	510	200	290	0.33	0.69	14
BA	35-55	390	220	390	0.36	0.56	21
Bt1	55-90	330	200	470	0.33	0.43	27
Bt2	90-140	310	190	500	0.32	0.38	25
Bt3	140-165	330	220	450	0.33	0.49	18
Bw1	165-195	310	240	450	0.32	0.53	25
Bw2	195-230	310	240	450	0.32	0.53	26
BC	230-290	230	270	500	0.22	0.54	30
C	290-360	210	230	560	0.29	0.41	28

[1] FS/TS: relationship between fine sand and total sand
[2] SSA: Specific surface area

The weathering profile of Eldorado do Sul, classified as RhodicPaleudult (RP), is very deep (> 2m in depth), with saprolitic material reaching more than 6m depth. Clay contents increase in depth until the textural B horizon (Bt1, Bt2 and Bt3).This horizon was followed by a Latossolic B horizon (Bw1 and Bw2), with homogeneous clay contents. The low values of the relationship between silt and clay indicate an advanced weathering degree compared to the soils developed from basalt. This indication is evidenced by the low SSA values, between 9 and 30m^{2}g^{-1}, which were verified throughout the soil profile (Table 3).

For the soils derived from basalt, the organic C content was high (> 30g kg^{-1}) in surface and decreased with depth (Table 4). The pH$_{water}$ values indicated moderately acid (5.9) to moderately alkaline (7.8) for VH soils, while in TH soils they ranged from moderately acid (5.9) to practically neutral (6.7) (Embrapa, 2006).

The cation exchange capacity is high (CEC ≥ 15 cmol$_c$ kg^{-1}), with higher values for VH soil. The base saturation was higher than 70% in all horizons with predominant Ca^{2+} and Mg^{2+} cations, while the saturation by Al^{3+} was basically zero. The high Ca^{2+} content on the CEC reinforce the field observation of the occurrence of carbonate concretions in the VH soil.

In the soil derived from gneiss (RP), the organic C content was lower (< 12g kg^{-1}) and decreased with depth (Table 4). The soil pH was strongly acidic (4.3 to 5.3) throughout all the horizons. The CEC values ranged from low to medium with values lower than 8.1 cmol$_c$ kg^{-1}. Soil low base saturation ($V \leq 40\%$) was expressed by the low sum of the bases (≤ 2.2 cmol$_c$ kg^{-1}). The exchangeable Al^{3+} was high ($1.2 \leq Al \leq 3.7$ cmol$_c$ kg^{-1}), as well as the Al^{3+} saturation ($35 \leq m \leq 69\%$). These results characterize the RP soil as intensely leached and with an advanced degree of weathering.

Table4. Chemical characteristics of the sorption complex, organic C content and selective dissolutions of iron oxides.

Soil	pH water	Exchangeable cations cmol_c kg^{-1}					$H^+ + Al^{3+}$	S[1]	CEC	m[2]	V[3]	Organic C	Fet	Fed	Feo	Fed/Fet	Feo/Fed	Al(d)	Ald/(Ald+Fed)
horizon		Al^{3+}	Ca^{2+}	Mg^{2+}	Na^+	K^+				%		g kg^{-1}		---- g kg^{-1} ----				g kg^{-1}	
São Borja (Vertic Hapludolls – VH)																			
A	5,9	0,3	16,8	6,2	0,18	0,2	1,5	23,4	24,9	1	94	37,0	92,0	12,3	4,8	0,13	0,39	3,09	0,12
B	7,3	0	18,8	6,5	0,4	0,11	0,8	25,8	26,6	0	97	14,0	98,4	17,6	5,1	0,18	0,29	2,08	0,02
C	7,8	0	21,4	6,4	0,44	0,07	0,9	28,3	29,2	0	97	5,1	114,6	38,0	4,9	0,33	0,13	3,09	0,03
Taquara (Typic Hapludolls – TH)																			
A	5,9	0	7,4	4	0,11	0,14	5,1	11,7	16,8	0	70	30,0	118,5	85,8	29,1	0,72	0,34	8,85	0,09
B	5,7	0	7,1	6,1	0,26	0,14	3,7	13,6	17,3	0	79	4,6	95,1	43,9	6,3	0,46	0,14	7,56	0,09
C	6,7	0	9	7,7	0,3	0,11	1,2	17,1	18,3	0	93	3,8	80,6	24,4	2,7	0,30	0,11	2,38	0,04
Eldorado do Sul (Rhodic Paleudult - RP)																			
A	4,9	1,2	1,3	0,7	0	0,19	3,3	2,2	5,5	35	40	12,0	16,6	12,9	1,7	0,78	0,13	2,33	0,10
AB	4,7	2,3	0,7	0,4	0	0,05	3,9	1,2	5,1	66	24	8,9	22,2	16,5	1,8	0,74	0,11	4,03	0,14
BA	4,6	3,3	1,0	0,7	0	0,07	5,0	1,8	6,8	65	26	8,5	26,5	21,3	2,1	0,80	0,10	4,08	0,10
Bt1	4,8	3,7	1,2	0,9	0	0,10	5,9	2,2	8,1	63	27	7,9	33,7	25,3	2,3	0,75	0,09	3,98	0,06
Bt2	4,8	3,4	0,8	1,0	0	0,04	4,1	1,9	6,0	64	32	3,4	33,6	25,1	2,4	0,75	0,10	4,47	0,10
Bt3	5,1	3,0	0,8	1,1	0	0,03	3,6	2,0	5,6	60	36	2,7	30,5	23,1	2,1	0,76	0,09	3,75	0,09
Bw1	5,1	3,1	0,7	1,1	0	0,03	3,7	1,9	5,6	62	34	2,4	33,1	25,1	2,0	0,76	0,08	3,92	0,09
Bw2	4,9	3,1	0,6	1,2	0	0,03	3,4	1,9	5,3	62	36	1,3	33,0	24,7	1,8	0,75	0,07	3,38	0,08
BC	5,1	3,5	0,5	1,3	0	0,02	3,8	1,8	5,6	66	32	2,7	49,7	40,0	2,8	0,80	0,07	3,01	0,04
C	5,0	3,1	0,4	1,0	0	0,02	3,8	1,4	5,2	69	27	0,8	50,3	42,8	2,6	0,85	0,06	1,93	0,01

[1] Sum of base cations; [2] Al saturation; [3] Base saturation.

7.4.2. Chemical extractions

The Fe and Al contents determined after the selective dissolutions are shown in Table 4. The total iron content (Fet) was similar in the two soils derived from basalt, ranging from 80.6 to 114.6g kg^{-1} (Table 4). The pedogenic iron oxide (Fed) content was higher in the TH soil than in the VH soil. Therefore, the lower values of the Fed/Fet ratio in the VH soil indicate a lower degree of weathering compared to the TH soil, in which a higher proportion of Fe is already in the form of iron oxides. The Feo and Feo/Fed ratio showed similar contents in poorly crystallized forms of fe oxides in the two soils developed on basalt. However higher values of Feo in surface correspond to the higher concentration of organic binders which inhibit the crystallization of iron oxides (Almeida et al., 2000). Part of iron may be associated to organic matter as Fe-humus or Fe-Al-humus complexes in surface.

In the subsurface diagnostic B horizons, the higher substitution of Fe^{3+} for Al^{3+} in the structure of the iron oxides indicated by the relationship between Ald/(Ald+Fed) corroborates the more advanced weathering degree on the TH soil (Table 4).

In the soil derived from gneiss (RP), the Fet content was lower, ranging from 16.6 to 50.3g kg^{-1}. The Fed content increased in depth until reaching the Bt horizons, expressing the pedogenic process of clay lessivage. The Fed/Fet relationship indicated that approximately 75% of Fe is already in the form of pedogenic iron oxides in all horizons (Table 4). The low values of the Feo/Fed relationship (≤0.13) suggest a predominance of crystalline iron oxides (goethite, hematite, maghemite). The Fe^{3+} to Al^{3+} substitution of iron oxides, which is close to 0.10 mol mol^{-1} in most of the profile, associated to the large contents in iron oxides, reinforced the more advanced weathering degrees already observed of this soil compared the soils developed from basalt.

7.4.3. Mineralogy of the weathering profiles

7.4.3.1. Diffraction and optical microscopy

The minerals that were identified in the basalts, saprolites and soils were pyroxenes, potassium feldspars, plagioclases and quartz, in addition to secondary minerals, such as, 2:1 clay minerals, kaolinite and iron oxides (Figure 19). The mineral composition of the basalt that gave rise to the weathering profiles of São

Borja and Taquara were very similar. However, on the optical microscopy images, it was observed that the basalt from São Borja contains bigger and better preserved primary minerals than the basalt from Taquara (Figures 21A and 21B). The basalt from Taquara exhibited a finer granulometry, alterations localized to oxidation zones and the presence of vesicles, which are filled with clay mineral, possibly celadonite (clay mineral), a phyllosilicate which forms during the colling of the basalt. The biggest mineral particles within this basalt are plagioclases (Figure 21B).

The XRD of the ADFS fraction of the saprolite materials and the weathered soil basalts mainly differed by the presence of intense reflections of 2:1 clay minerals in the São Borja profile, including the horizons A and B, as well as the absence of kaolinite. In contrast, in the Taquara profile the reflections of 2:1 clay minerals decrease in intensity towards the soil surface, thus indicating the presence of kaolinite (Figure 19). The XRD of the ADFS fraction of the saprolite materials and the weathered soil gneisses was very similar throughout the alteration profile, being predominantly composed of quartz and kaolinite (Figure 20).

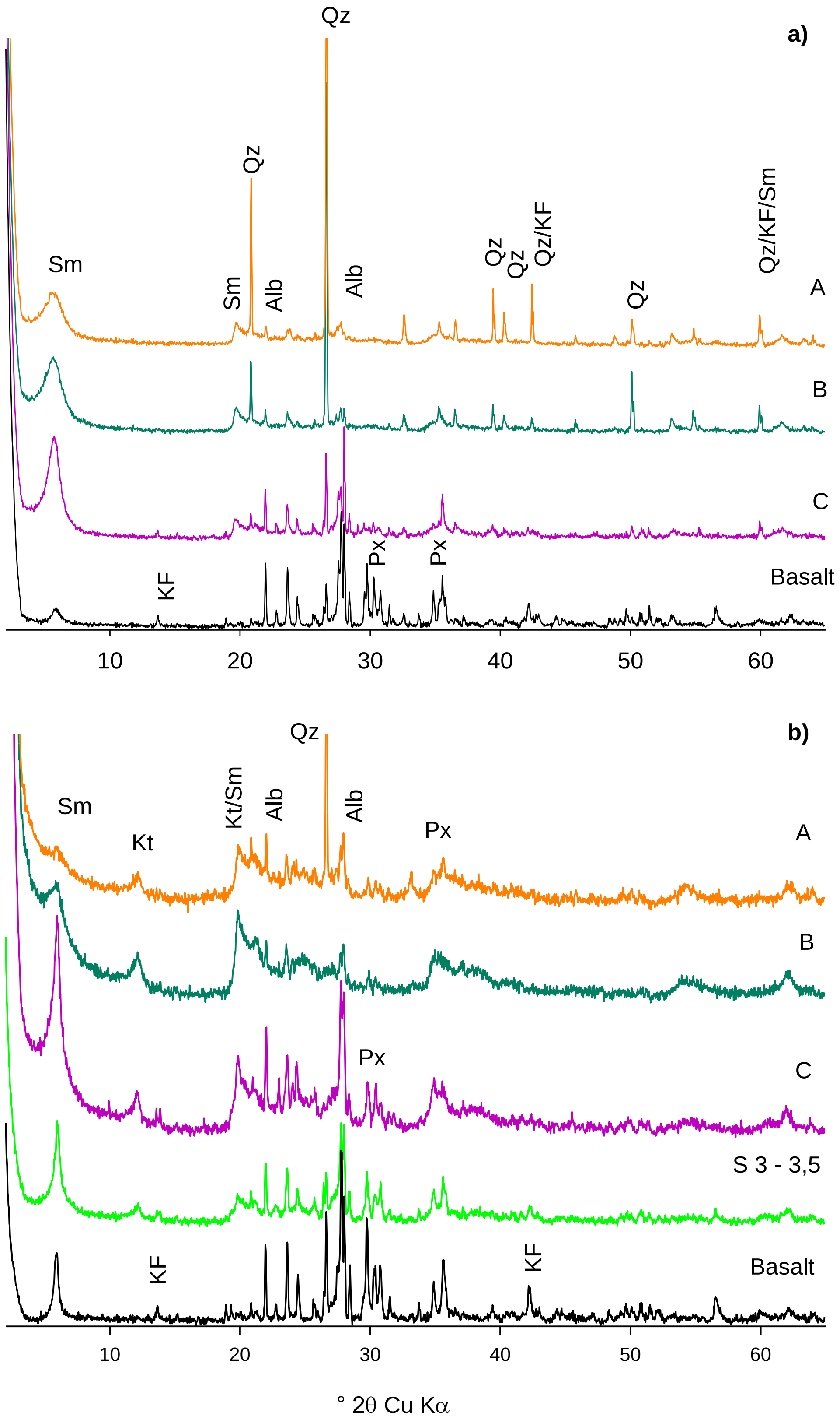


Figure 19. X-ray diffractograms of the fine air-dried earth of the materials rock, saprolite and the alteration profile soil of São Borja (a) and Taquara (b).Alb: albite; Qz: quartz; Sm: smectite; Kt: kaolinite; Px: pyroxene; KF: feldspar K.

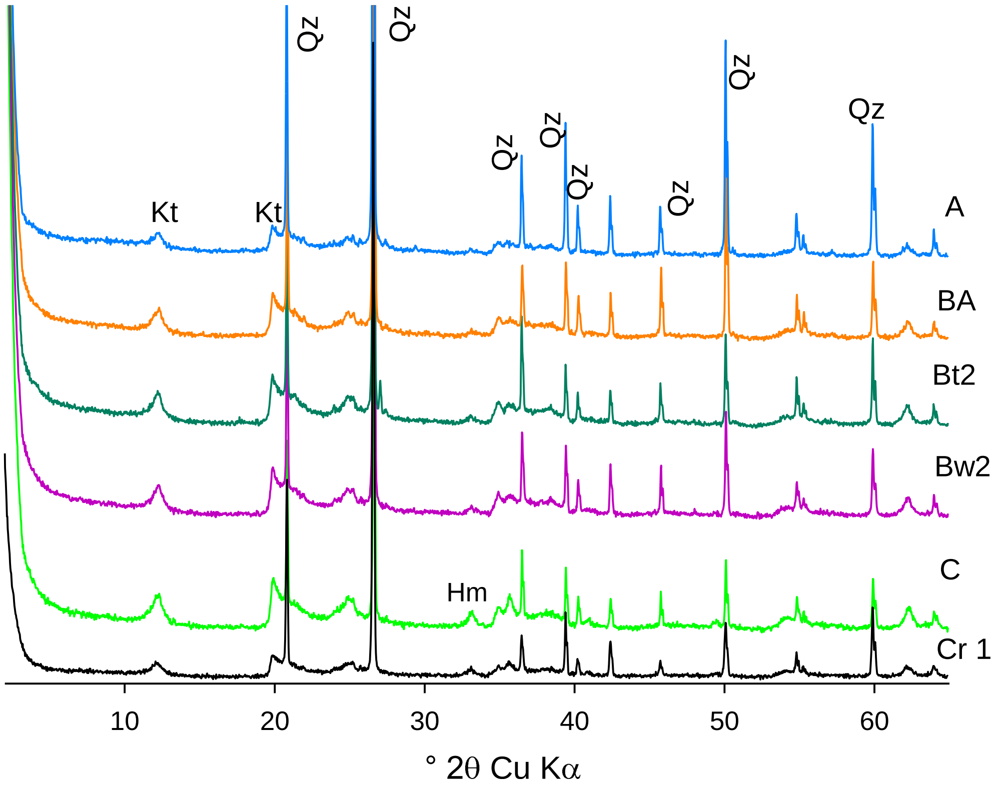


Figure 20. X-ray diffractograms of the fine air-dried earth of the materials saprolite and the alteration profile soil of Eldorado do Sul. Qz: quartz; Hm: hematite; Kt: kaolinite.

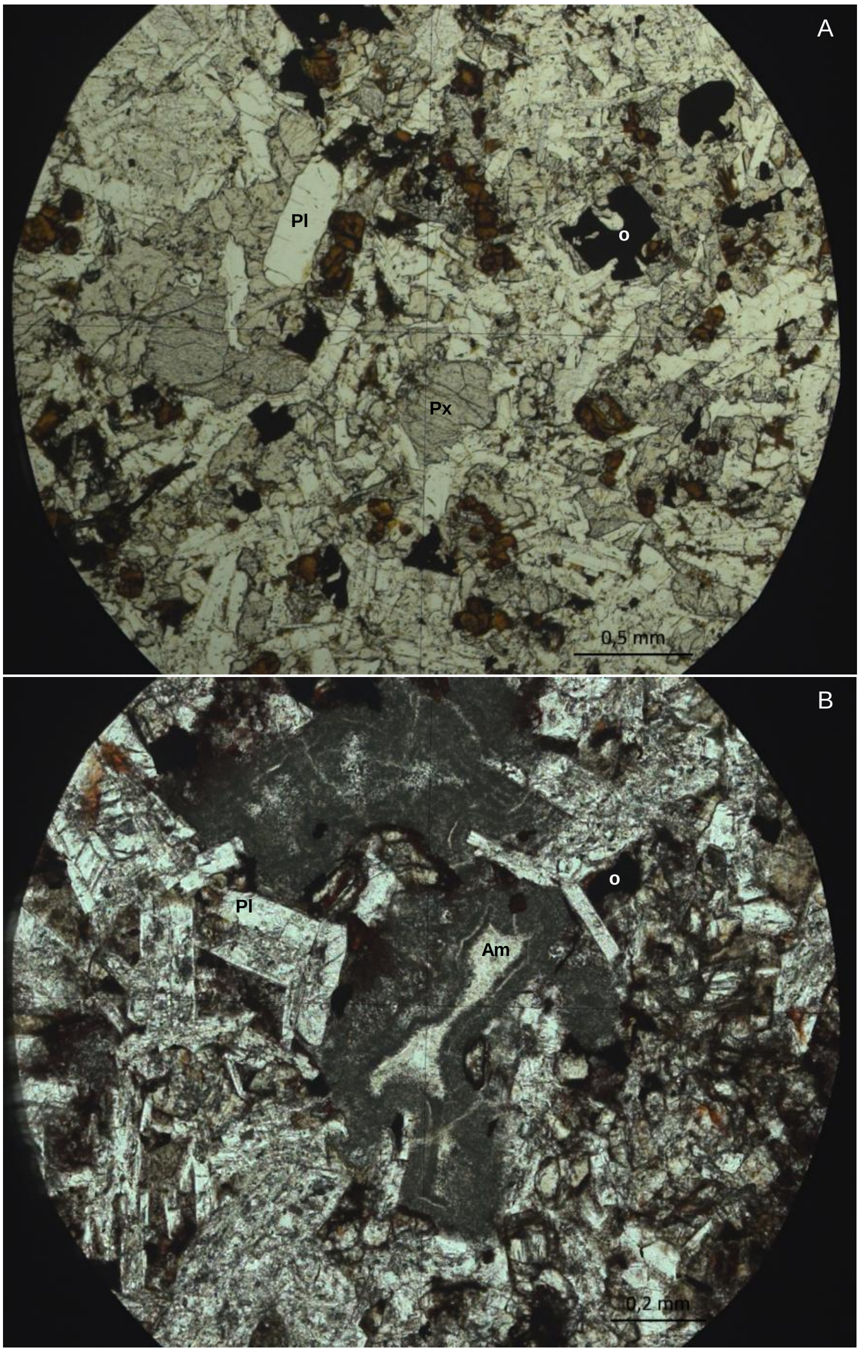


Figure 21. Micrographies of petrographic slides of the basalt from the weathering profile soil of São Borja (A) and Taquara (B). O: oxides; Am: vesicle; Px: pyroxene; Pl: plagioclase.

7.4.3.2. Diffraction of the clay fraction (< 2 µm)

The XRD patterns of the < 2 µm fractions of the Vertic Hapludolls (VH) soil in São Borja profile exhibited a 2:1 clay mineral predominance in all of the horizons, with small quartz reflections in A and B horizons (Figure 22). The presence of quartz in the superficial horizons has a possible origin associated to the intercalated

Botucatu sandstone and to the basaltic spills in the south of Brazil (Figure 18). The 2:1 clay minerals present in this soil belong to the smectite group (SAD), due to the expansion observed on the XRD froma d-spacing of about 15 Å toa d-spacing of about 17 Å after the solvation with ethyleneglycol (SEG) (Figure 22). After saturation with K followed by thermal treatments (110, 330 and 550ºC), the total displacement of the smectite related reflections for a d-spacing of about 10 Å, indicated an absence of intercalation of interlayers by hydroxyl-Al^{3+} polymers (XRD not shown). The dominance of expandable 2:1 clay minerals is characteristic of soils formed in regions with low quantities of available water for leaching or with deficient or impaired drainage (Kampf et al., 2012).

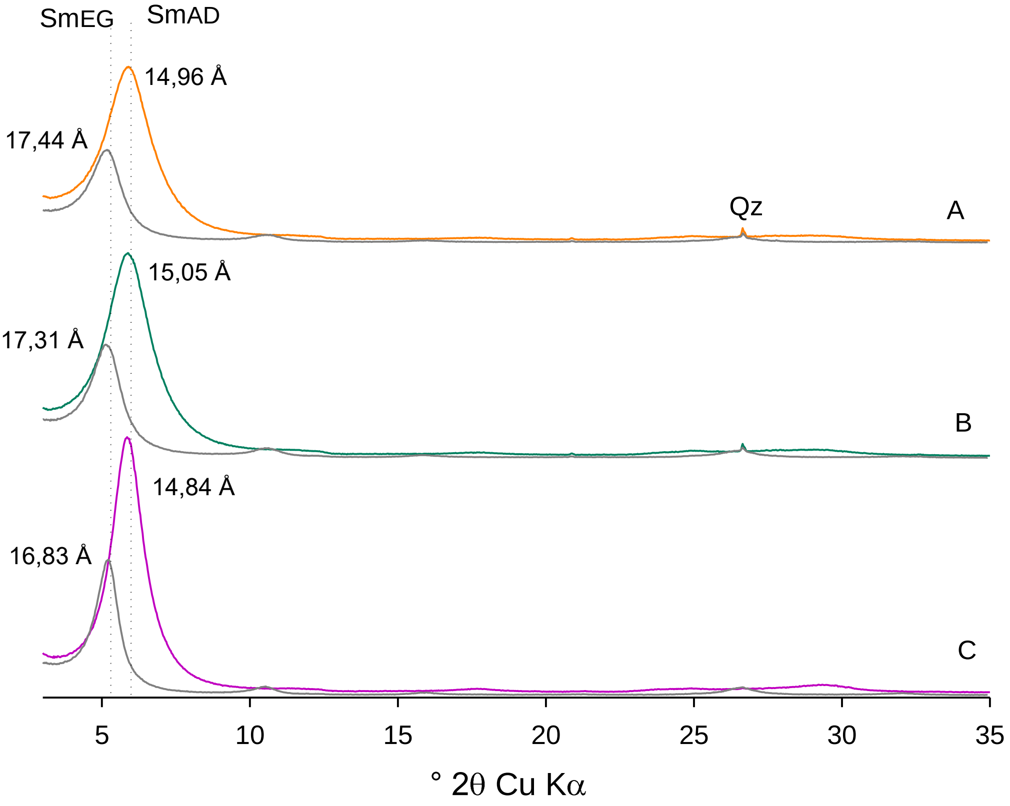


Figure 22. X-ray diffractograms of the < 2 µm fraction of the horizons of the alteration profile soil of São Borja after Ca saturation(SmAD) and solvatation with ethylene glycol (SmEG). Qz: quartz; Sm: smectite.

The XRDs of the < 2 µm fraction of the saprolite and the Typic Hapludolls (TH) soil of the Taquara profile showed intense reflections corresponding to the smectite and kaolinite presence (Figure 23). In addition, reflections with very low intensities regarding the quartz on the A horizon and feldspars in the saprolite at depth from 3 to 3.5m were observed. Unlike the São Borja profile, the XRD of the Taquara profile exhibited striking intensities of the smectite reflections on the saprolite layer and in C horizon, while they decreased in A and B horizons. On the other hand, the reflections related to kaolinite occurrence displayed an intensity increase towards the superficial horizons (A and B), thus suggesting that the formation of kaolinite in this profile partly form at the expense of the dissolution-neoformation/transformation of smectites.

On the XRD of the samples saturated with Ca and solvated with ethyleneglycol (SmEG), the smectites of the Taquara profile expanded less (d ~ 16,5 Å) than the smectites on the São Borja profile (d >17 Å). Furthermore, the saturation of the samples of A and B horizons with K and the thermal treatments did not induce the contraction for d-spacing of about 10 Å (Figure 24) indicating an aluminization of 2:1 clay minerals by the intercalation of hidroxyl-Al^{3+} polymers the interlayers as observed by Azevedo et al. (1996), Melo et al. (2009) and Caner et al. (2014). These observations when associated to the presence of kaolinite on this profile express the most advanced degree of weathering between the two soils formed from basaltic rocks.

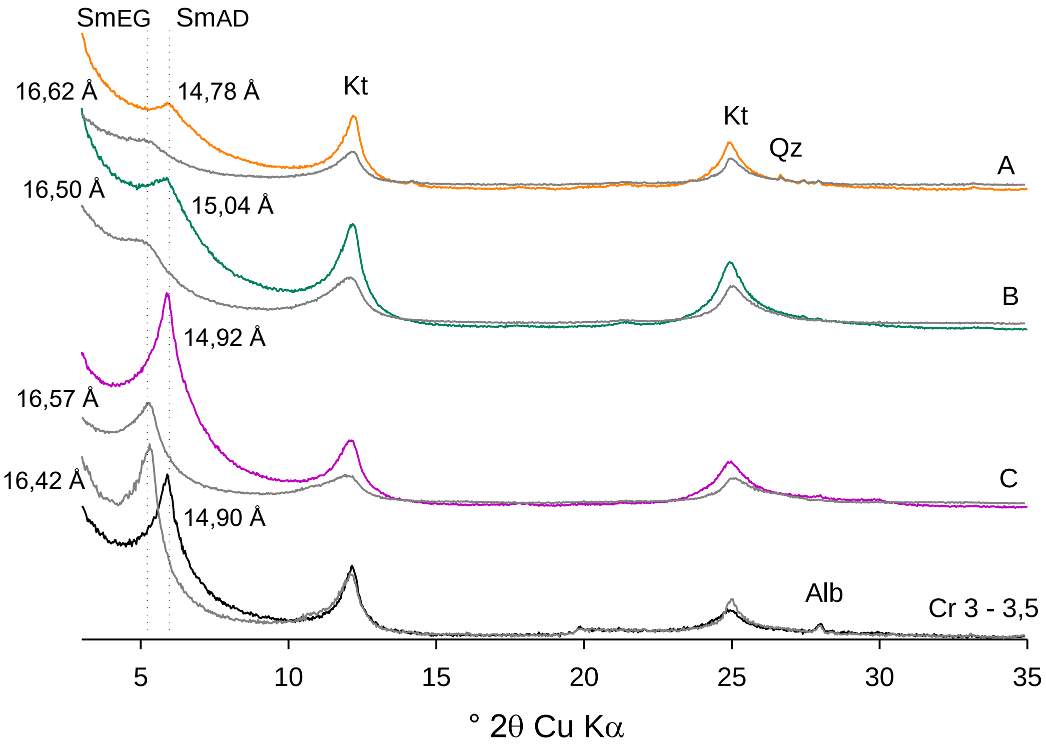


Figure 23. X-ray diffractograms of the <2 µm fraction of saprolite and horizons of the alteration profile soil of Taquara after saturation with Ca (SmAD) and solvatation with ethyleneglycol(SmEG). Qz: quartz; Sm: smectite; Kt: kaolinite; Alb: albite.

The XRD of the < 2 µm fraction of the Rhodic Paleudult (RP) soil of the Eldorado do Sul profile displayed reflections with higher intensity related to the occurrence of kaolinite and quartz (Figure 25). The reflections at a d-spacing of about 10 Å indicated the presence of mica (mica/illite) in the clay fraction, which content decreases towards the soil surface. Mica/illite was not identified in the sand and silt fractions. The clay fraction of the RP soil, developed from gneiss, is mainly composed of kaolinite, which gives it a more intense weathering degree among the three profiles evaluated in this study.

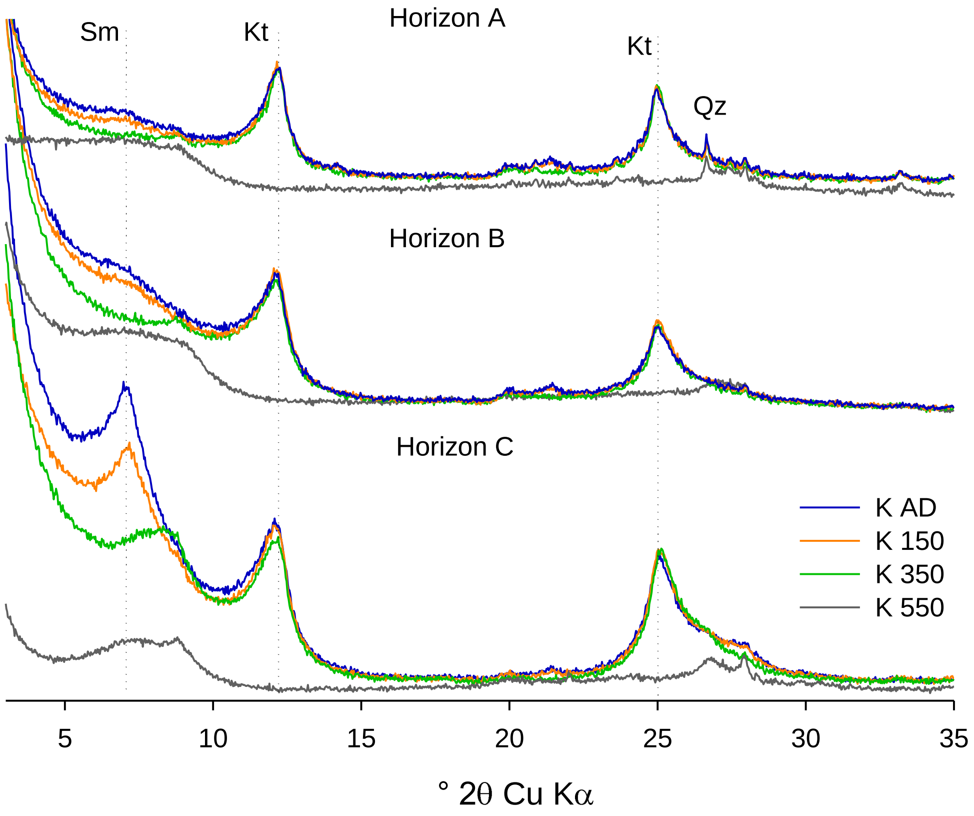


Figure 24. X-ray diffractograms of the < 2 µm fraction of the horizons of the weathering profile soil of Taquara after saturation with K (K AD) and heating (K 150, K 350 and K 550°C). Qz: quartz; Sm: smectite; Kt: kaolinite.

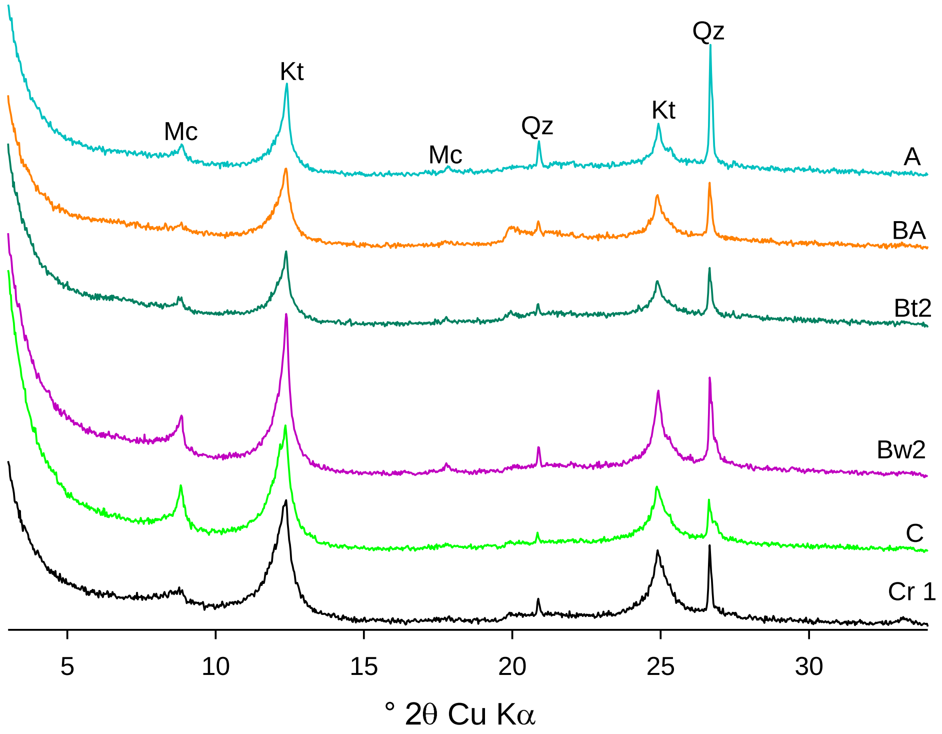


Figure 25. X-ray diffractograms of the< 2 μm fractions of the horizons of the weathering profile soil of Eldorado do Sul. Qz: quartz; Mc: mica; Kt: kaolinite.

7.4.3.3. Fourier Transform Infrared Spectroscopy (FTIR)

In the spectrum of Figure 26, corresponding to the clay sample of horizon A in the Taquara profile, the band at 3696cm^{-1} is attributed to the OH stretching of the hydroxyl on the kaolinite surface, while the 3616cm^{-1} band corresponds to the OH stretching of the internal hydroxyl (Farmer, 1974; Yahaya et al., 2012). The fact that there are only two bands in this region, in other words, the absence of bands around 3668 and 3652cm^{-1}, is indicative of a low crystallinity kaolinite (Balan et al., 2001), which is typical of soils. The band at 3596cm^{-1} is attributed to the Fe-OH stretching in kaolinite octahedrons and indicates the presence of Fe in the octahedral sites in substitution of Al^{3+}, as it has already reported in kaolinite the Amazon Basin (Balan et al., 2007). A band at 1638cm^{-1} results from the H-O-H deformation of the water molecule hydrating the minerals. A band at 1103cm^{-1}is attributed to the Si-O stretching, and the bands at 1029 and 1012cm^{-1} correspond to the stretching of the Si-O-Si of the kaolinite (Farmer, 1974; Balan et al., 2001). The band at 910cm^{-1} belongs to the deformation vibrations kaolinite Al_2OH groups (Saikia et al., 2012). The spectra of the clay fraction of B and C horizons (Figure 27) are similar to the clay fraction of horizon A (Figure 26) suggesting that the kaolinite in those horizons is relatively similar.

The bands situated at 540 and 470cm^{-1} indicate the Si-O-Si vibrations of deformation of the kaolinite. The intensity of such bands increases in surface, since it is related to the increase of the kaolinite proportion of the samples. The widest band at about 3420cm^{-1} corresponds to the water of hydration of the smectites. The FTIR results seem to indicate that the horizons at larger depths have trioctaedral smectites and the dominance of Al^{3+} smectites in surface, however it is not possible to clearly verify this based on the spectra (Figure 28). The band at 795cm^{-1} in the A and B horizons belongs to the Si-O-Si bonds of quartz possibly due to a Botucatu sandstone contribution.

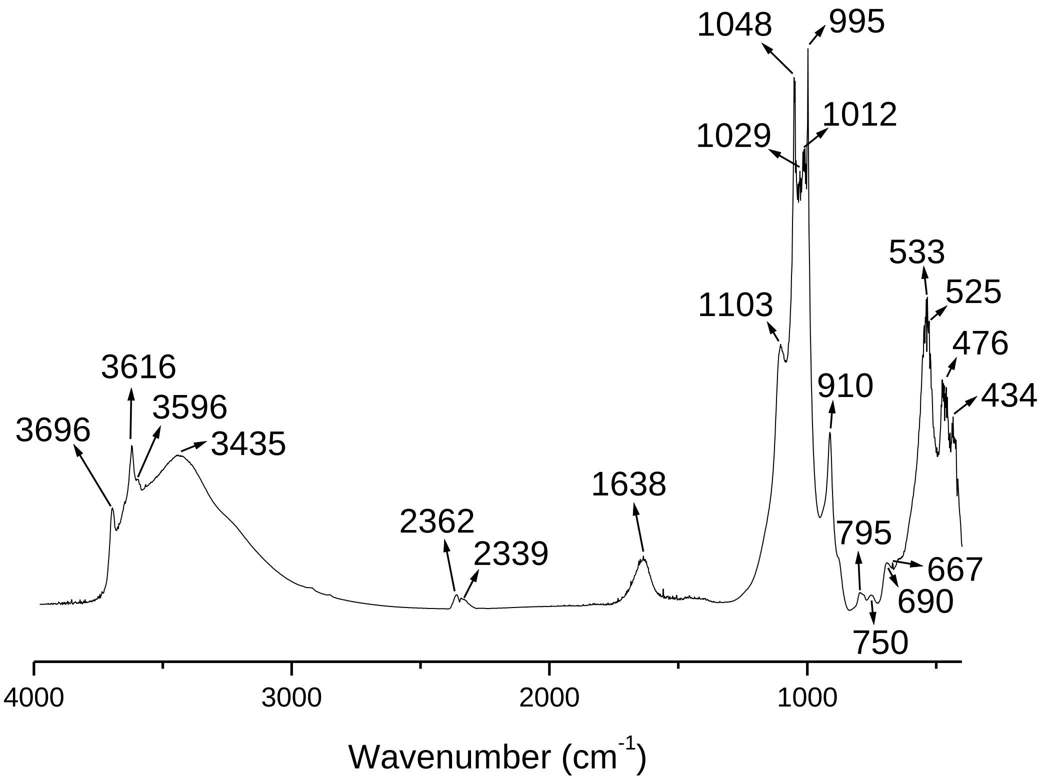


Figure 26. Fourier Transform Infrared Spectroscopy (FTIR) for the < 2 µm fraction of the horizon A of the alteration profile soil of Taquara.

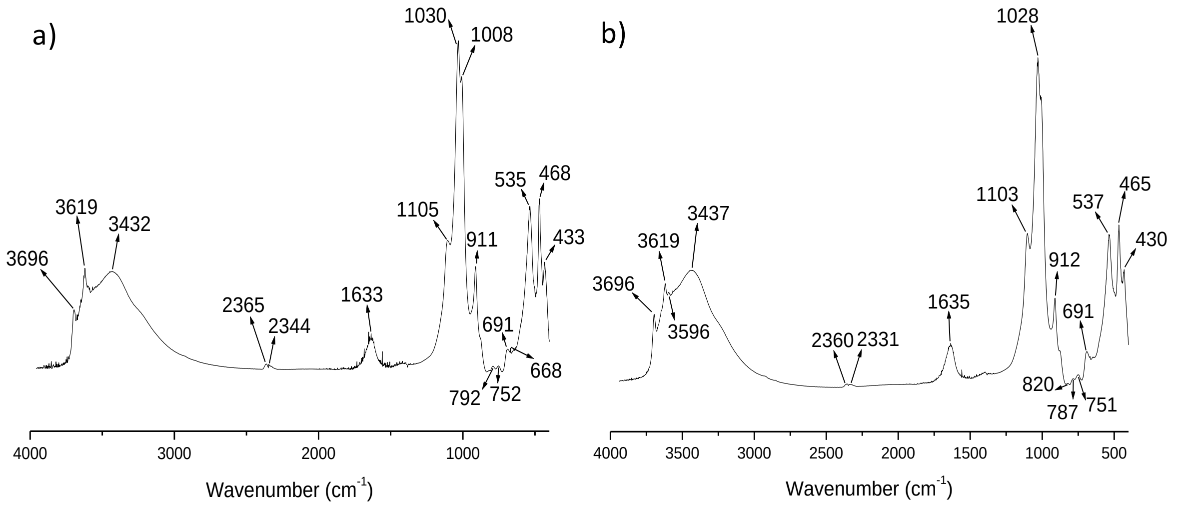


Figure 27. Fourier Transform Infrared Spectroscopy (FTIR) for the < 2 µm fraction of the horizons B (a) and C (b) of the alteration profile soil of Taquara.

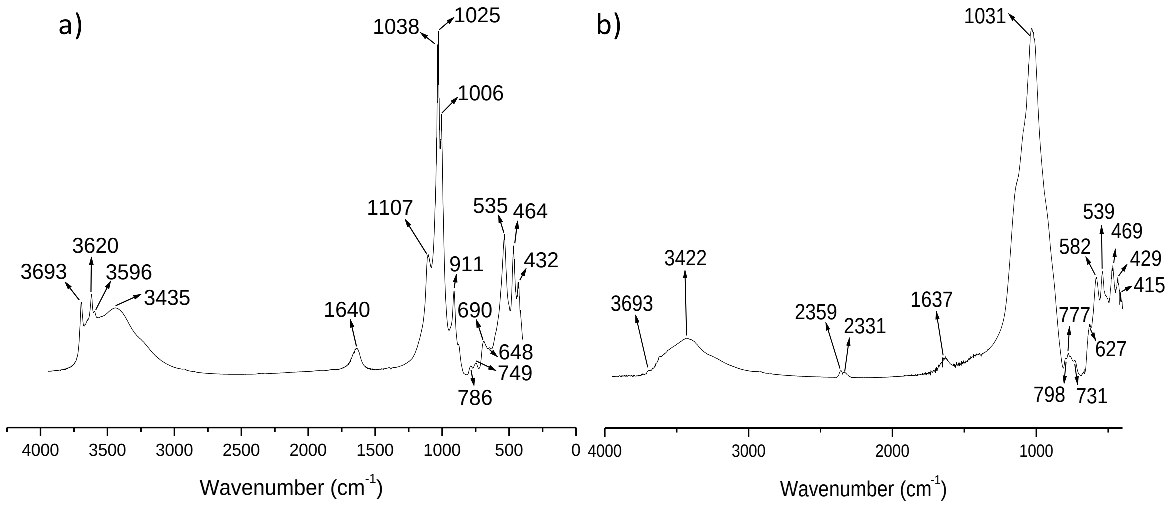


Figure 28. Fourier Transform Infrared Spectroscopy (FTIR) for the < 2 µm fraction of the saprolite S 3 - 3.5(a) and the rock (b) of the alteration profile of Taquara.

7.4.4. Total chemical analyses and weathering indices

The percentage of chemical elements throughout the weathering profiles and weathering indices are shown in Table 5. A similar concentration of the elements was observed for the two basalts, except in the Fe_2O_3 and TiO_2 contents, which were higher in the basalt of the São Borja profile. In this profile, the SiO_2, Fe_2O_3 and Al_2O_3 contents did not show significant variations, whereas the base cation contents decreased towards the soil surface. In the Eldorado do Sul profile, of gneissic origin, the SiO_2 concentrations are higher, reaching approximately 85 % in the Cr2 (saprolite

2), whereas the contents of Fe_2O_3 and Al_2O_3 are smaller when compared to the basalts. The base cation contents are very low both in the saprolites and along the soil horizons.

Table 5. Total elemental analysis data for ICP.

Soil	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	MnO	Cr_2O_3	P_2O_5	TiO_2	ZrO_2	LOI	Total	Δ4Si	$R^{3+}/(R^{3+}+R^{2+}+M^{+})$	CIA
horizon	%	%	%	%	%	%	%	%	%	%	%	%	%	%			
São Borja (Vertic Hapludolls – VH)																	
A	50,91	7,45	13,15	0,91	1,3	0,39	0,42	0,39	0	0,1	8,75	0,06	15,9	99,85	57	0,76	77,9
B	51,65	8,34	14,07	1,06	1,49	0,41	0,42	0,77	0	0,08	8,26	0,06	13,1	99,83	53	0,75	78,2
C	45,56	11,63	16,39	1,88	4,19	1,37	0,93	0,43	0	0,25	5,15	0,04	11,9	99,8	20	0,62	64,2
Basalt	48,65	13,28	14,98	5,26	8,77	2,48	1,23	0,2	0	0,41	3,06	0,03	1,3	99,77	0	0,45	51,6
Taquara (Typic Hapludolls – TH)																	
A	41,51	16,62	16,94	0,96	0,85	0,86	0,8	0,34	0,03	0,09	2,38	0,03	18,4	99,87	49	0,84	86,9
B	40,62	22,36	13,6	1,08	0,53	0,64	0,79	0,12	0,03	0,01	1,25	0,02	18,8	99,91	54	0,88	91,9
C	47,86	17,39	11,52	3,17	2,72	1,96	1,72	0,17	0,02	0,13	1,28	0,02	11,8	99,87	20	0,64	73,1
Cr 2-2,5	49,4	16,2	11,43	5,05	3,98	1,79	1,66	0,17	0,02	0,14	1,26	0,02	8,7	99,85	13	0,56	68,6
Cr 2-3	49,07	16,61	11,28	4,27	3,64	1,83	1,81	0,15	0,02	0,14	1,25	0,02	9,7	99,87	15	0,58	69,5
Cr 3-3,5	50,32	15,92	11,19	5,12	5,04	2,01	1,71	0,17	0,02	0,14	1,28	0,02	6,9	99,84	9	0,52	64,5
Cr 3,5-4	50,46	16,15	10,7	5,34	5,63	2,05	1,63	0,15	0,02	0,16	1,2	0,02	6,3	99,85	8	0,51	63,4
Cr 4-4,5	50,78	15,75	10,52	5,77	6,55	2,13	1,51	0,15	0,02	0,15	1,23	0,02	5,2	99,84	5	0,48	60,7
Cr 4,5-5	50,77	16	10,54	5,55	6,42	2,12	1,47	0,16	0,02	0,15	1,2	0,02	5,4	99,83	6	0,49	61,5
Cr 6+	50,66	15,83	10,31	5,54	7,01	1,94	1,23	0,16	0,02	0,15	1,11	0,02	5,8	99,83	5	0,48	60,9
AR	51,07	15,14	10,5	6,22	8,9	2,08	1,29	0,16	0,02	0,17	1,18	0,02	3	99,84	0	0,43	55,2
LAR	51,68	15,13	10,41	6,23	9,1	2,1	1,26	0,16	0,02	0,16	1,18	0,02	2,3	99,84	0	0,43	54,8
Basalt	51,94	14,95	10,34	6,29	9,33	2,15	1,29	0,15	0,02	0,16	1,17	0,02	1,9	99,83	0	0,42	53,9
Eldorado do Sul (Rhodic Paleudult – RP)																	
A	83,05	7,11	2,38	0,11	0,05	0,04	0,42	0,02	0,00	0,03	0,70	0,07	6,0	100,00		0,92	93,3
AB	78,48	10,00	3,18	0,13	0,04	0,04	0,45	0,02	0,00	0,03	0,74	0,07	6,8	99,98		0,94	95,0
BA	73,37	12,31	3,79	0,16	0,05	0,03	0,44	0,02	0,01	0,02	0,71	0,06	9,0	99,99		0,95	95,9
Bt1	67,71	15,76	4,82	0,20	0,05	0,03	0,51	0,02	0,01	0,04	0,76	0,06	10,0	99,96		0,95	96,4
Bt2	68,91	15,29	4,81	0,20	0,04	0,03	0,47	0,02	0,01	0,03	0,81	0,06	9,3	99,96		0,95	96,6
Bt3	72,20	13,95	4,36	0,19	0,03	0,03	0,41	0,01	0,01	0,04	0,78	0,06	7,9	99,98		0,95	96,7
Bw1	70,03	15,13	4,73	0,20	0,03	0,03	0,44	0,01	0,01	0,04	0,86	0,06	8,4	99,96		0,96	96,8
Bw2	71,27	14,47	4,72	0,20	0,03	0,02	0,37	0,01	0,01	0,04	0,90	0,07	7,9	99,98		0,96	97,2
BC	65,46	16,55	7,10	0,21	0,02	0,02	0,36	0,01	0,01	0,05	0,94	0,06	9,1	99,96		0,97	97,6
C	62,80	18,54	7,20	0,19	0,03	0,02	0,33	0,02	0,01	0,04	0,99	0,06	9,7	99,97		0,97	98,0
Cr 1	68,86	15,70	5,64	0,16	0,03	0,02	0,32	0,02	0,01	0,02	1,05	0,06	8,1	99,97		0,97	97,7
Cr 2	85,48	5,98	1,52	0,08	0,04	0,13	2,09	0,01	0,00	0,02	0,54	0,06	4,0	99,99		0,72	72,6

AR: altered rock; LAR: less altered rock; Cr: saprolite

On the basalt profiles, the loss on ignition (LOI) increased from the rock to the surface soil horizons due to the increase of the secondary clay minerals concentration. In the gneiss profile, the decrease of LOI on the surface A and AB horizons is due to the translocation of clays to the subsurface horizons.

In the weathering profiles developed from basalt, the values of the three analyzed weathering indices (Δ4Si; $R^{3+}/(R^{3+}+R^{2+}+M^{+})$; CIA) increased from the rock to the soil surface (Table 5), showing an advance of the weathering degree throughout the profile. Considering that the index values were similar in both basalts, the highest index values observed in the Taquara profile indicate a more advanced weathering degree when compared to the São Borja profile. In the profile derived from gneiss – excluding the saprolite Cr2, where the $R^{3+}/(R^{3+}+R^{2+}+M^{+})$ values and CIA were 0.72 and 72.6, respectively –, all other values were expressively elevated (higher than 0.92 and 93.3, respectively), thus characterizing a more advanced weathering degree of this profile compared to profiles developed from basalt. These results support the data obtained from the XRD analyses.

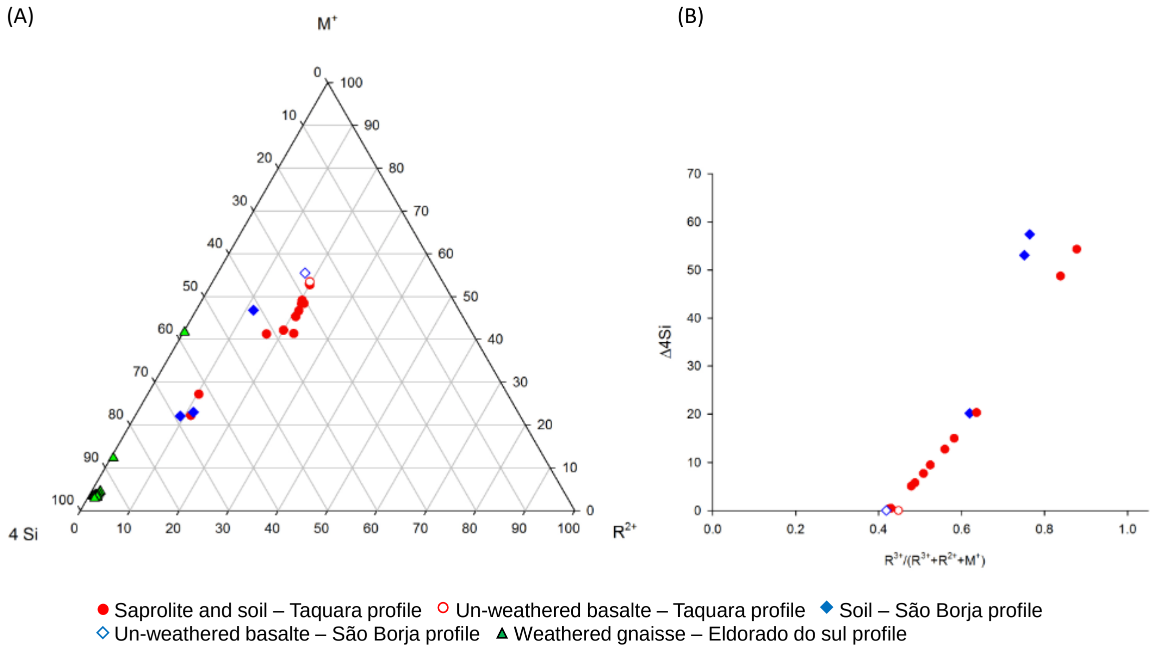


Figure 29. Chemiographic projections (A) and diagram 4 Si-M^{+}-R^{2+} a in the Δ4Si and $R^{3+}/(R^{3+}+R^{2+}+M^{+})$ (B).

Figure 29B shows a weathering sequence, especially in the saprolite layers of the Taquara profile. The surface horizons of the São Borja and Taquara profiles are different. However, there is a more intense leaching in surface with base cation losses and relative accumulation of Si, while there is not any significant changes in the mineralogy of the two profiles. In Figure 29A, the values for the Eldorado do Sul profile are close to the 4Si pole due to important losses of alkaline cations and earth alkaline. These values are in accordance with a mineralogy dominated by kaolinite mineralogy in this soil.

7.5. Discussion

7.5.1. Evolution of the pedogenic minerals

The mineralogy of the clay fraction (< 2 µm) of the two soil is different and especially in surface horizons. In the São Borja profile, in the absence of kaolinite, smectite was predominant due to smaller amount of available water as described in the western region of RS (Streck et al., 2008). In the Taquara profile, the mineralogy of the clay fraction is mostly composed of kaolinite, 2:1 clay minerals and 2:1 HI (HIS) as already found in the basaltic soil of RS (Bortoluzzi et al., 2012; Caner et al., 2014). In the Eldorado do Sul profile, a predominance of kaolinite and quartz with subordinate occurrence of mica was observed, as shown by other authors in soils of Escudo Rio-grandense (Inda et al., 2010; Fink et al., 2014a).

The chemical composition of the sorption complex and the mineralogy of the clay fraction of the profiles indicate a more intense weathering of the soil (kaolinite, 2:1 HI and oxi-hydroxides) in Taquara and Eldorado do Sul profiles, while moderate conditions of weathering (predominance of smectites) were observed in the São Borja profile.

The climatic conditions that characterize the subtropical climate of RS (an average temperature of 18°C and precipitation that ranges from 1,186 and 2,468 mm) favor different weathering rates, which result in differing intensities of desilication. One scenario involves the retention of a part of the silicon and base cations (Ca^{2+}, Mg^{2+} and K^{+}) due to elevated evapotranspiration (Figure 17) and to largest drainage due to the flatter relief, thus preserving the 2:1 clay mineral stability (São Borja and Taquara profiles); whereas the other involves a larger loss of silicon and a total loss of base cations (Eldorado do Sul profile).

The occurrence of expandable clay minerals (smectite) was a common characteristic among the soils of basaltic origin. However, in the São Borja profile these minerals remain stable throughout the profile, even without intercalation of Hydroxyl-Al^{3+} in the interlayers. On the contrary, in the Taquara profile the smectites suffer important alterations, mainly in the A and B horizons, reducing their swelling. The incomplete collapse after saturation with K and heating indicative of the aluminization process has been observed by several authors in soils of the southern region of Brazil (Inda et al., 2010; Bortoluzzi et al., 2012; Caner et al., 2014). The occurrence of 2:1 HI clay minerals is more common in surface horizons, in soils at higher altitudes, in tropical and subtropical areas. The surface horizons contained hydroxyl-Al-interlayered minerals most probably formed by the aluminization of smectite present in the saprolite. Acidic condition and high contents in organic matter in surface may promote the dissolution of residual primary minerals or clay minerals and release of aluminium, as shown by higher exchangeable values, and its incorporation into the interlayer of the 2:1 clay minerals to form HIMs at the expense of swelling minerals (Caner et al., 2011, 2014). Aluminization of clay minerals in surface appear to be a ‘natural’ process of evolution of the soils as acidification develops with important loss due to the subtropical climate (high mean annual P) and organic matter accumulation due to elevation. In the Taquara and Eldorado do Sul profiles, the kaolinite occurrence at greater depths demonstrates an intense weathering action within these profiles, even in the proximity of rocks.

The study highlight also a possible control by the rock composition additionned to the climatic conditions. The soils developed on basalt present 2;1 clay minerals as smectite and HIV/HIS present even in the surface horizons, whereas the soil developed on gneiss present only kaolinite even in the saprolite at 6 m depth. The presence of 2:1 clay minerals in the soils developed on basalt could be linked to the more basic composition compared to the gneiss and to the presence of celadonite in vesicles that is partly preserved during weathering. This must be taking into account by considering thelarge surface area covered by basalt in south Brazil.

7.5.2. Alteration intensities and weathering índices

The weathering indices (WIS and CIA) revealed the following increasing sequence of the weathering degree of the evaluated alteration profiles: São Borja < Taquara < Eldorado do Sul. When taking into account the mineralogical composition of the profiles, this sequence can also be written as follows: smectite composition <smectite-kaolinite composition <kaolinite composition.

In the Taquara profile, the presence of 2:1 HI clay minerals still occurs. The transformation from S to HIS was verified based on the horizon C towards the soil surface, where there was a clear reduction on the expansivity and contraction of the smectites (Figures 23 and 24). This corroborates the evidence of an environment with a moderate weathering intensity. The lowest weathering observed through the CIA in the São Borja profile is evidenced by a mineralogy dominated by smectites lacking aluminization and without kaolinite occurrence. Nonetheless, the difference within the weathering states among the basalts happens in the superficial layers of the soil, since the CIA exhibits very similar values for both rocks, which can also be verified through the diagram (WIS). This surface variation denotes the influence of the different climatic conditions form the east to the west of RS, since the chemical composition of the rocks is very similar. The chemiographic projection shows the progressive advancement of the weathering in the Taquara profile from the saprolitic layers with greater silicon losses and greater accumulation of iron oxides ($R^{3+}/(R^{3+}+R^{2+}+M^{+})$) towards the soil surface.

7.5.3. Environmental relevance and soil use

The study showed that the soils have important differences, even between those formed from the same parent material (such as Taquara and São Borja profiles) due to the climatic and relief differences. The soil of the eastern region of RS (Taquara profile) is located in Araucaria's Domain, which represents intermediate weathering conditions for the soils in southern Brazil, with elevated kaolinite concentration associated to 2:1 HI clay minerals (Bortoluzzi et al., 2012; Caner et al., 2014). In the western region of RS (São Borja profile), which is in the Pampa biome, in areas of small geographic expression, the soils exhibit specific mineralogical, chemical and physical characteristics, with expandable clay predominance with elevated SSA and CEC, neutral to basic soil reaction, high sums and base saturation, indicating a low degree of soil weathering. Even though they show high chemical fertility, the physical properties such as the contraction and expansion of soils and the low degree of flocculation of this type of clay represent and important limitation for agricultural use and exposes the fragility of these soils when managed inadequately. Thus, the attention to the conservation of these soils must be observed in a special manner, since it also comprehends the preservation and maintenance of the flora and fauna characteristic of the Pampa biome, a landscape of great ecosystemic importance and of scenic beauty in RS (Vieira, 2014).

The Taquara profile has high CEC values, which is important for the fertility of the soil (Ca^{2+}, Mg^{2+} and K^{+} retention), specifically on the saprolitic layer, representing a cation reservoir for plants, particularly arboreal species with root systems that develop at greater depth, thus having access to these elements. However, the fertility potential of these soils is affected by the great pressure exerted by agricultural use in southern Brazil, which has advanced over the forest regions, such as the araucaria plants, thus augmenting the deforestation in order to broaden the agricultural area and intensifying the grain production. The mineralogy of this profile reveals an aluminization of the 2:1 clay minerals at the surface causing a CEC decrease (Barnhisel and Bertsch, 1989; Meunier, 2007) and affecting the soil properties such as the nutrient availability, Al toxicity and acidification. The degree of aluminization of the 2:1 clay minerals is sensitive to agricultural use, which has presented changes when growing grapevines (Bortoluzzi et al., 2012) as well as in intensive grain cropping systems (Inda et al., 2010). Thus, these minerals are an important indicator of alterations in the pedoenvironment and changes in the physicochemical properties of the soil.

The Eldorado do Sul profile displayed some limitations for agricultural use due to its properties, both chemical (low CEC and nutrient retention) and physical (textural gradient), which are the result of the mineralogical composition of this profile. The limiting physical properties of this profile are associated to higher levels of sand at the surface and the clay accumulation at the subsurface, a typical behavior of this type of soils. Nonetheless, this situation gives fragility to this type of soil, thus requiring conservation and management care in order to avoid considerable losses due caused by erosion.

7.6. Conclusions

The São Borja (Vertic Hapludolls) and Taquara (Typic Hapludolls) basalt alteration profiles exhibit the same minerals, potassium feldspars, pyroxenes, plagioclases and oxide traces. The São Borja basalt profile has bigger and better preserved minerals, while the Taquara basalt presents amygdule facies with celadonite in its interior. The dominant minerals on these alteration profiles are smectites in the São Borja profile, kaolinite, smectite and smectite with hydroxyl-Al^{3+} in the Taquara profile, and kaolinite and quartz in the Eldorado do Sul profile.

The set of analysis performed indicated the following weathering sequence for the three alteration profiles: São Borja < Taquara < Eldorado do Sul. In the São Borja profile, the smectites are neoformed from the dissolution of pyroxenes, plagioclases and potassium feldspars. In the Taquara profile, the weathering sequence observed is: primary minerals (pyroxenes, plagioclases and potassium feldspars)→Smectite→HIS→Kaolinite + iron oxides. In the Eldorado do Sul profile, the kaolinite is formed by the transformation from mica/ilite and, possibly, by neoformation.

8. CHAPTER III – IMPACT OF AN INTEGRATED NO-TILL SOYBEAN-BEEF CATTLE PRODUCTION SYSTEM ON THE OXISOL MINERALOGY IN SOUTHERN BRAZIL

8.1. Abstract

Agricultural activities in the state of Rio Grande do Sul (RS), southern Brazil, have traditionally been quite intensive and led to decreased overall soil quality, and to depletion of soil organic matter and nutrients. There have been attempts at restoring soil quality by using integrated crop–livestock systems (ICLS). ICLS in association with no-tillage (NT) potentially increase soil organic matter content and nutrient supplies. In this work, we assessed the influence of grazing intensity in three different treatments [viz., intensive grazing (IG), moderate grazing (MG) and no grazing (NG)] on the mineralogy of an Oxisol in an integrated soybean–cattle beef production system in southern Brazil by using various types of methods and tests. Mineralogical XRD analyses of the clay fraction (< 2µm) showed it to consist mainly of kaolinite and 2:1 clay minerals of the hydroxy-interlayered mineral (HIM) type. The reflections for 2:1 clay minerals under the IG treatment were better defined than those for the minerals under NG, which suggests the prevalence of HIMs. The 2:1 clay minerals in the IG group exhibited expandable layers. Splitting the clay fraction into three subfractions according to size (< 0.05 µm, 0.05–0.1 µm and 0.1–2 µm) exposed considerable alterations. Thus, hydroxy-aluminum interlayered vermiculite (HIV-Al) was present irrespective of treatment. Also, the HIV-Al reflection was better defined under IG and MG than under NG, which suggests strong aluminization of 2:1 clay minerals. Chemical analyses revealed a decrease in total organic carbon (TOC) with increasing depth in all treatments. The decrease was especially marked under NG by effect of the absence of animals favoring accumulation of plant shoots. pH_{water} was higher under IG as a result of the removal of aluminum from the soil solution increased aluminization of 2:1 clay minerals. K concentrations in solution were low under IG as a result of the formation of HIMs and/or swelling layers with exchangeable K; by contrast, solution K levels under NG where high owing to the absence of HIMs. The presence of animals, which increases K availability through animal wastes, may have resulted in competition between exchangeable K^+ and Al^{3+} to form HIMs. Without splitting the clay fraction it would have been impossible to confirm the mineralogical alteration in 2:1 phyllosilicates due to the impact of ICLS systems.

Keywords: Clay mineralogy; subfractionation; hydroxy-interlayered minerals; aluminization.

8.2. Introduction

Brazil contributes an estimated 61 million tons of grain (average for the period 1993–2013) and about 187 million animal units of beef cattle (FAO, 2015) to global food production each year. Maintaining or even increasing these production levels has required intensifying agricultural activities, which has led to a decrease in overall soil quality. In fact, extractive farming practices diminish crop yields through erosion, and depletion of soil organic matter and nutrients (Lal, 2009).

Integrated crop–livestock production systems (ICLS) alternating grain crops and grazing for optimal crop and grass (fodder) production have traditionally been used in southern Brazil to reduce human impacts on agrosystems and raise farmers' benefits (Carvalho et al., 2010; Moraes et al., 2014). The combined use of ICLS and no-tillage (NT) soil management is known to increase soil organic matter content (Assmann et al., 2014), and also to improve soil fertility and nutrient supply (Martins et al., 2014). These management practices additionally reduce soil losses by erosion (Merten and Minella, 2013). Permanently protecting the soil surface through uninterrupted cultivation of pasture or annual crops under NT increases the moisture content of soil and decrease the temperature of its surface layer. These pedoenvironmental changes obviously alter existing natural conditions.

Studies in Rio Grande do Sul (RS), southern Brazil, have assessed the effects of ICLS on different soil types under variable conditions. Most have focused on soil chemical and physical properties, and on their potential influence on crops and soil (Assmann et al., 2014; Conte et al., 2011, Martins et al., 2014; Souza et al., 2009), and also on biological activity (Chavez et al., 2001). Martins et al. (2014) found the 0–40 cm layer of soils under ICLS for 9 years to be less acidic, and to have higher contents in base cations and lower aluminum saturation, than soils under no grazing. Souza et al. (2009) and Assmann et al. (2014) found moderate grazing intensities (20 cm and 40 cm of pasture sward height) in a ICLS under NT to increase total and particulate organic C and N.

In addition to altering soil properties, the pedoenvironmental changes caused by ICLS may affect soil mineralogy —particularly that of 2:1 phyllosilicates (Fink et al., 2014b; Inda et al., 2010; Officer et al., 2006). Vermiculite and smectite can easily expand and acquire a high specific surface area; as a result, they possess a high cation-exchange capacity (CEC) and play a key role in soil reactions (Malla, 2002; Reid-Soukup and Ulery, 2002; Wilson, 1999). Under moderately acidic conditions, 2:1 clay minerals can intercalate hydroxy-aluminum to form hydroxy-aluminum interlayered minerals (HIMs), which include hydroxy-interlayered vermiculite (HIV) and smectite (HIS) (Barnhisel and Bertsch, 1989; Meunier et al., 2007). The intercalation of aluminum dramatically decreases the expansibility and cation-exchange capacity of HIMs. The formation of 2:1 HIS/HIV clay minerals is favored by weathering, a moderately acid environment, a low organic matter content, and frequent wetting and drying cycles (Barnhisel and Bertch, 1989; Meunier, 2007; Rich, 1968). However, comprehensive structural studies such as that of Viennet at al. (2015), which focused on the influence of pedoenvironmental conditions on the degree of aluminization of 2:1 HIMs, are scant (Zanelli et al., 2007) and none has seemingly considered the effects of production systems combining annual crops and pasture (ICLS).

Inda et al. (2010) found no difference in Al polymerization in HIMs in a subtropical Oxisol under tillage and no-tillage cropping systems for 26 years. However, the chemical composition of the soil solution suggested slow intercalation and a gradual change from HI with extensive intercalation to HI with partial intercalation. Bortoluzzi et al. (2012) found grape cropping to reduce the clay fraction and the organic matter content of a Regosol, and also to change the degree of Al polymerization in HIMs, which they ascribed to increased weathering and susceptibility to anthropogenic pressure.

In hilly areas of southwestern New Zealand, Officer et al. (2006) found regeneration of the mica-rich complex in the upper layers of soil under pasture to be accompanied by the presence of poorly crystallized swelling 2:1 clay minerals. Fink et al. (2014b) also found dissolution and transformation of 2:1 clay minerals in an Ultisol under cattle-grazed native pasture with a high stocking rate.

Integrated crop–livestock systems (ICLS) under NT favor accumulation of plant residues at the surface and across the soil profile relative to conventional cropping systems (Kunrath et al., 2014) through the action of plant roots (Salton et al., 2002) and grazing. The formation of 2:1 HIMs may be affected by two major factors, namely: accumulation of animal wastes in soil (Silva et al., 2014) and grazing intensity. Available knowledge of the effects of ICLS on the mineralogy of tropical and subtropical soils is still incipient. In this work, we assessed the effect of grazing intensity on the mineralogy of an Oxisol in an integrated soybean–cattle beef production system in southern Brazil.

8.3. Material and methods

8.3.1. Soil selection, sampling and sample preparation

Soil samples were obtained from an integrated soybean–beef cattle production site located on Espinilho Farm, São Miguel das Missões municipality, Rio Grande do Sul state (RS), Brazil (28°57′23″S and 54°21′22″W, 465 m asl). The samples were collected in November 2013, 12.5 years after the start of the experiment (May 2001). The soil was a Rhodic Hapludox. Originally, the area was a native grass field typical of the upland region of RS consisting mainly of Paspalum spp and Axonopus spp but including stubs of Aristida spp. In 1993, an NT system was started with soybean (Glycine max L.) for grain production in summer and black oat (Avena strigosa Schreb.) in winter. This crop succession was maintained until the autumn of 2000, when the area was placed under cattle-grazing for several weeks and then seeded for winter crops, using a mixture of black oat and Italian ryegrass (Lolium multiflorum Lam.) —the latter reseeding naturally thereafter. The soil was analysed in November 2000, prior to the trial establishment (Table 1). Then, soybean was planted under NT during the summer. In May 2001, soybean was harvested and the ICLS experiment, which continues at present, was started.

The experiment treatments were as follows: (a) intensive grazing (IG) with 10 cm of average pasture sward height; (b) moderate grazing (MG) with 30 cm of average pasture sward height; and (c) no grazing (NG), the reference treatment, where the pasture was left undisturbed or never grazed. The average cattle stocking rate (live weight) was 600–1300 kg ha–1. The cattle used were young animals (10–12 months old when accessing the pasture for the first time), with initial average live weight of 190–200 kg. The pasture grass height at the beginning of the experiment was 25 cm. The amount of vegetation being left in the field after grazing for gradual decomposition and accumulation on the soil surface differed among treatments, and so did the amounts of urine and dung produced by the cattle, which also decompose and are incorporated onto the soil surface (Martins et al., 2015).

Table 6. Soil chemical properties before no-till integrated crop-livestock system (soybean-beef cattle) establishment (November 2000).

Layer	pH	OM[a]	Ca[b]	Mg[b]	Al[b]	H+Al	P[c]	K[c]	V[d]	m[e]
cm	H_2O	g kg^{-1}			mmol$_c$kg^{-1}			mg kg^{-1}		%
0-5	4.9	42.2	62	13	3	87	13.4	240	48	4
5-10	4.6	34.8	48	18	6	97	9.8	119	41	9
10-15	4.6	25.5	41	22	7	97	5.2	88	40	11
15-20	4.6	25.5	40	11	1	101	3.7	55	34	17

[a] Soil organic matter;[b] Exchangeable (KCl 1 mol L^{-1}) Ca, Mg and Al;[c] Available P and K (Mehlich-1); [d] Base saturation;[e] Al saturation.

8.3.2. Chemical analyses

Samples were collected from the 0–5, 5–10, 10-20 and 20–40 cm soil layers in November 2013 after the animals were removed from the area in order to plant soybean. The samples were air dried, crumbled and sieved (< 2 mm) to isolate the air dried fine soil (ADFS) fraction. Particle size analysis was done with the pipette method (Embrapa, 1997), using dispersions in 6% NaOH on a horizontal shaker at 120 oscillations/min for 4 h.

Total organic carbon (TOC) was determined by dry combustion on a Shimadzu VCSH carbon analyser. The soil pH in water, pHwater, was measured by using a 1:1.25 soil solution ratio. The concentrations of extractable Ca^{2+}, Mg^{2+}, Al^{3+} and $H^{+}+Al^{3+}$ were determined in air dried fine soil samples, using methods recommended by Embrapa (1997). The resulting concentrations were used to calculate sum of bases (S), cation-exchange capacity (CECpH7), base saturation (V), and aluminum saturation (m). P and K were extracted by using Mehlich-1 solution (0.0125 mol H2SO4 L^{-1} + 0.05 mol HCl L^{-1}) according to Tedesco et al. (1995).

Samples were shaken on a horizontal shaker at 120 oscillations/min for 5 min and then allowed to stand for 16 hr. P in the extract was determined with the colorimetric method of Murphy and Riley (1962), and K+ in the extract by ICP.

8.3.3. Mineralogical analyses

The clay size fractions smaller than 2 μm were extracted from the bulk soil samples without destroying organic matter. For this purpose, the bulk soil was dispersed into 1 mol NaCl L^{-1} solution (five saturations) and sonicated. The < 50 μm fractions were obtained by wet sieving, and the clay fraction (< 2 μm) by sedimentation and subsequent flocculation with addition of $CaCl_2$. Aliquots of the clay fraction were then Ca-saturated with 0.5 mol $CaCl_2$ L^{-1}or K-saturated with 1 mol KCl L^{-1} and washed to remove excess salt. Oriented clay preparations were made by depositing the clay suspensions onto glass slides that were allowed to dry at room temperature (air dried-AD). The slides were saturated with ethylene glycol (EG) vapor at 50 °C inside a desiccator for 16 hr. K-saturated clay slides were heated at 110, 330 or 550 °C. XRD patterns for the oriented clay preparations were recorded on a Bruker D8 Advance using Cu Kα radiation, the 2θ range from 2.5 to 35°, 2θ steps of 0.012° and a counting time per step of 96 s as converted from a scanning mode. Randomly oriented powder XRD patterns in the 2θ range from 2.5 to 65° were obtained for powdered fine earth samples (ADFS).

The clay fraction (< 2 μm) was subsequently split into three subfractions (< 0.05, 0.05–0.1 and 0.1–2 μm) by following the centrifugation procedures of Laird et al. (1991), and Hubert et al. (2009, 2012), on a Biofuge (R) Stratos centrifuge. The clay fraction was treated with a dithionite–citrate–bicarbonate (DCB) mixture to remove amorphous and/or crystalline Al/Fe oxy–hydroxides (Mehra and Jackson, 1960) prior to extraction. The different size fractions were obtained by repeated centrifugation at different relative centrifugal forces until the supernatant was clear (8–10 steps). The clay subfractions were Ca and K-saturated by using the same protocol as for the bulk < 2 μm fraction, after which they were freeze-dried and weighed.

8.3.4. Statistical analysis

Statistical inferences were made in R language (R CORE TEAM, 2015), using a completely randomized single-factor model. Data were subjected to analysis of variance (ANOVA) at $p < 0.05$, using the following two factors as fixed effects: grazing intensity (NG, MG and IG) and soil layer (0–5, 5–10, 10–20 and 20-40 cm).

8.4. Results

8.4.1. General soil properties

Soil properties exhibited some differences among layers and grazing intensities (Table 2). Despite the statistical differences in the body of soil layers among grazing intensities (viz., increased concentrations of sand, silt and clay under NG, IG and MG, respectively), the textural class was identical and typical of a clayey soil with an increase in clay contents starting in the 10–20 cm layer (Table 2).

All chemical parameters except pH changed across the soil profile (Table 2). Although pH values were similar in all soil layers, pHwater for the body of layers was higher under IG than it was under MG and NG. TOC contents only differed markedly among grazing intensities in the topmost layer (0–5 cm), where they were lower under IG and MG than under NG.

Nutrient availability and soil acidity in the form of available P, exchangeable Al and Ca, CEC, base saturation and aluminum saturation, differed little among grazing intensities. Exchangeable Mg exhibited a positive relationship with animal stocking rate, and was highest under IG and lowest under NG. Finally, K availability in all soil layers was lower with the two grazing treatments (IG and MG) than with NG.

Table 7. Soil chemical and textural attributes of an Oxisol after 12 years of integrated crop-livestock (soybean-beef cattle) system establishment under different grazing intensities in southern Brazil.

Grazing intensity	**Soil layer**	**TOC$^{(1)}$**	**pH**		**Available$^{(2)}$**		**Exchangeable$^{(3)}$**			**CEC**	**V$^{(4)}$**	**m$^{(5)}$**	**Sand**	**Silt**	**Clay**
			KCl	**H_2O**	**P**	**K**	**Al**	**Ca**	**Mg**						
	cm	**g kg^{-1}**			**mg kg^{-1}**	-----------------------	**cmol$_c$ kg^{-1}**	-----------------------			-------- **%** -------		------------	**g kg^{-1}**	------------
Intensive	0-5	30.9 aB	4.30	5.27	13.8	0.35	0.43	4.77	2.10	12.2	61	7	237	375	388
	5-10	20.9 b	4.38	5.27	4.7	0.15	0.60	5.33	2.57	12.6	58	10	202	404	394
	10-20	16.4 bc	4.10	5.17	2.4	0.10	0.80	4.07	2.20	11.2	55	15	181	358	461
	20-40	13.4 c	3.83	4.73	1.6	0.05	2.03	1.93	1.13	8.8	25	40	166	334	500
	Average	20.4	4.15	5.10 A	5.6	0.16 B	0.97	4.03	2.00 A	11.2	52	18	197 B	367 A	436 B
Moderate	0-5	31.7 aB	4.07	4.87	10.6	0.52	0.73	3.70	1.70	11.6	51	11	238	351	411
	5-10	21.0 b	4.02	4.83	4.9	0.30	0.87	3.63	1.77	11.5	50	13	196	351	453
	10-20	16.3 b	3.80	4.73	3.1	0.13	1.53	2.67	1.50	10.1	43	27	181	309	510
	20-40	14.7 b	3.80	4.60	1.9	0.05	2.00	1.40	0.80	8.0	28	47	164	299	537
	Average	20.9	3.92	4.76 B	5.1	0.25 B	1.28	2.85	1.44 AB	10.3	43	25	195 B	328 B	477 A
No grazing	0-5	38.1 aA	4.00	4.70	15.4	0.77	0.40	3.80	1.60	13.4	46	6	276	359	365
	5-10	18.9 b	4.12	4.63	6.8	0.38	0.87	2.93	1.37	11.8	40	16	242	351	407
	10-20	13.4 bc	4.17	4.77	3.1	0.32	0.93	2.77	1.40	10.6	42	17	226	298	476
	20-40	10.0 c	4.32	4.80	1.7	0.17	1.10	2.07	1.10	7.8	42	27	245	269	486
	Average	20.1	4.15	4.73 B	6.8	0.41 A	0.83	2.89	1.37 B	10.9	42	17	247 A	320 B	433 B
Average	0-5	33.6	4.12	4.94	13.3 a	0.55 a	0.52 b	4.09 a	1.80 a	12.4 a	52 a	8 b	251 a	362 ab	388 b
	5-10	20.3	4.17	4.91	5.5 b	0.28 b	0.78 b	3.97 a	1.90 a	12.0 a	50 ab	13 b	214 ab	368 a	418 b
	10-20	15.4	4.02	4.89	2.9 bc	0.18 bc	1.09 b	3.17 ab	1.70 ab	10.6 a	47 ab	20 b	196 b	321 bc	483 a
	20-40	12.7	3.98	4.71	1.8 c	0.09 c	1.71 a	1.80 b	1.01 b	8.2 b	35 b	38 a	192 b	301 c	507 a
	Average	20.5	4.08	4.87	5.8	0.27	1.03	3.26	1.60	10.8	46	20	213	338	449

TOC: total organic carbon; CECpH7: cátion exchange capacity; V: base saturation; m: aluminium saturation;*Lower case letters distinguish the soil layers in each grazing intensity; upper case letters distinguish the grazing intensities in each soil layers; absence of letters=no significant difference (Tukey test, $p<0.05$).

8.4.2. Clay Mineralogy and submicrometric fractionation

The clay minerals identified in the bulk < 2 µm fraction of soil under NG and IG included kaolinite (7.14 and 3.57 Å) and 2:1 clay minerals (14.2 and 4.74 Å). The fact that the peak at 14.7 Å remained fairly unchanged following solvation with ethylene glycol suggests the absence of swelling layers (Cecagno et al., 2016). The peak can be assigned to vermiculite or hydroxyl-interlayered minerals (Fig. 1).

Mass contributions from each submicrometric fraction were calculated from gravimetric recoveries normalized to 100% (see Fig. 1). The coarser fraction (0.1–2 µm) was the dominant fraction irrespective of treatment and accounted for 45–54 % of the < 2 µm fraction under NG and for 36–41 wt% under IG. The proportion of this subfraction increased with increasing soil depth. The finest subfraction (< 0.05 µm) contained the lowest proportion with all treatments and accounted for 16–18 wt% of the < 2 µm fraction under NG and for 23–25 wt% under IG. The proportions differed little among soil layers. Finally, the intermediate fraction (0.05–0.1 µm) accounted for 30-39 wt% of the bulk < 2 µm fraction; its proportion was slightly higher under IG than under the other two treatments and increased with increasing soil depth.

The outcome of the submicrometric particle size fractionation was similar to that previously reported by Hubert et al. (2012). Thus, the finer fractions were almost devoid of 2:1 clay minerals and contained poorly crystallized kaolinite as suggested by the width of the reflections at 7.14 and 3.57 Å for all treatments and depths. By contrast, the coarser fraction (0.1–2 µm) exhibited well-defined, strong reflections for kaolinite and 2:1 clay minerals. The intermediate fraction (0.05–0.1 µm) exhibited broader kaolinite reflections than the coarser fraction in addition to ill-defined reflections for 2:1 clay minerals (Figs 1 and 2).

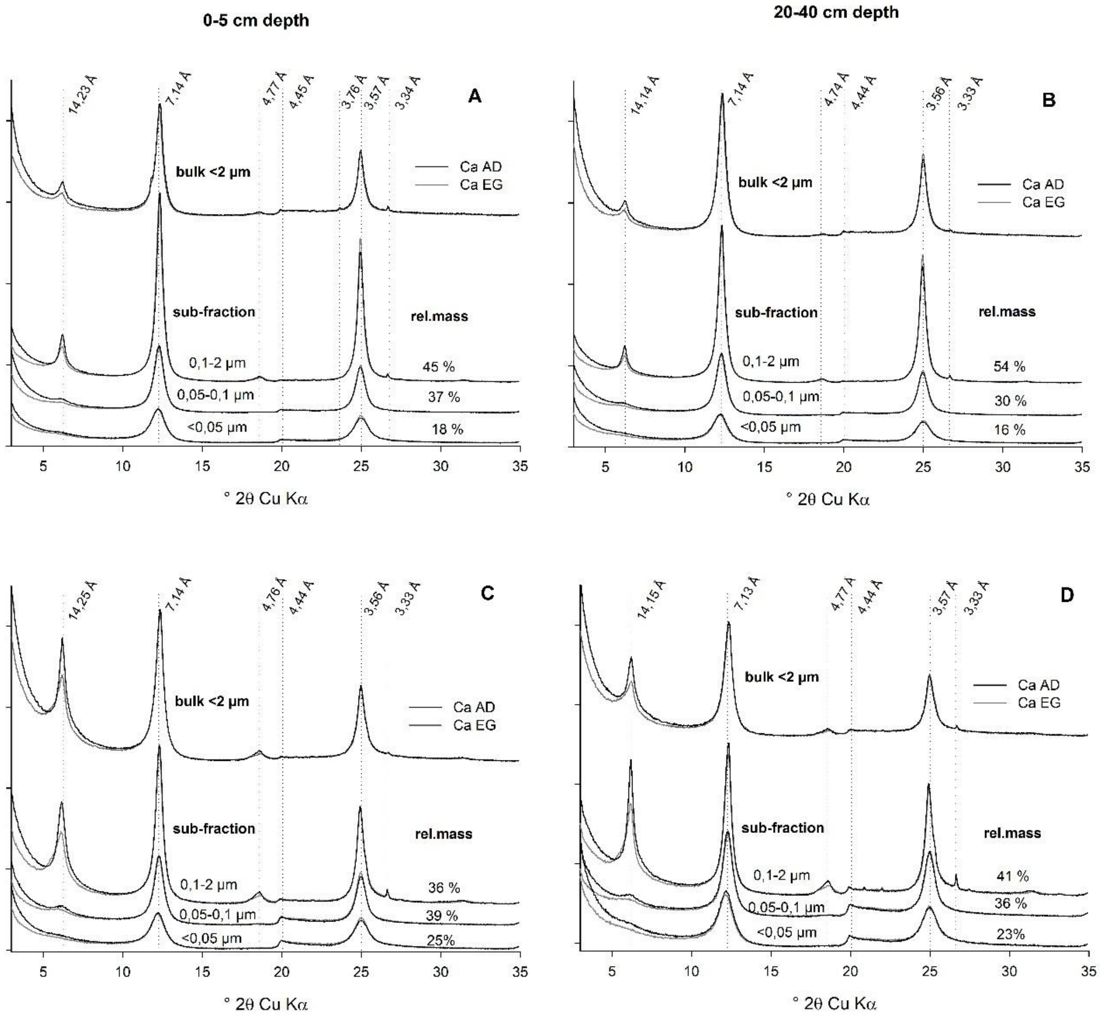


Figure 30. Experimental XRD patterns of the bulk <2µm fraction and subsequent sub-fractions. (A) and (B) No grazing; (C) and (D) Intensive grazing. Comparison of Ca-saturated AD (solid line) and Ca-saturated EG (gray line) patterns. AD: air dried; EG: ethylene-glycol. The relative mass (rel. mass) of each sub-fraction shown in (a) was normalized to 100%.

The 2:1 clay mineral reflections in the patterns for the NG treatment were weaker than the kaolinite reflections irrespective of fraction (bulk or submicrometric). The reflections for 2:1 clay minerals shifted slightly upon EG solvation, which suggests the presence of few swelling layers (Figs 1A and B). The patterns for the IG samples exhibited increased reflections for 2:1 clay minerals relative to kaolinite (especially in the 0.1–2 µm fraction, where the intensity of the 001 reflection for 2:1 clay minerals was similar to that for kaolinite) (see Figs 1C and 1D).

Like NG, the EG treatment caused no appreciable shifts in the reflections other than a slight change in the 003 reflection at 4.76 Å. The XRD patterns for the < 0.05 µm fraction of the NG and IG samples contained no reflections for 2:1 clay minerals (Fig. 1); therefore, no patterns for the K-saturated and heated samples in this fraction are shown. Reflections for 2:1 clay minerals were indeed present in the > 0.05 µm fractions that were stronger and better defined in the coarser fraction (Fig. 2). The proportion of 2:1 clay minerals in NG and IG samples was highest in the 0.1–2 µm fraction. K saturation and heating caused a collapse from 14.1 to 10 Å (0–5 and 20–40 cm layers) in the 0.1–2 µm fraction from IG (Figs 2D and 2H) that suggests the presence of vermiculite and the absence —or presence of only small amounts— of HIV.

8.4.3. No grazing (NG)

The intensity of the reflection at 14 Å for the 0.05–0.1 µm fraction of the 0–5 cm layer of soil under NG was reduced by K saturation and heating; also, it exhibited gradual asymmetric expansion at high 2ɵ angles (Fig 2A). This result suggests occupation of interlayers by hydroxy-Al hindering complete contraction of 2:1 clay minerals at 10 Å. In the 0.1–2 µm fraction of soil under NG, K saturation and heating caused a progressive collapse from 13.9 Å to lower d-values. Heating at 350 and 550 °C led to incomplete collapse and the resulting pattern exhibited a broad band with two maxima at 11.3 and ca. 10 Å (0–5 cm layer, Fig. 2B). Heating also led to weaker, broader reflections at both soil depths. The samples contained vermiculite in the layers fully collapsing upon K saturation and heating, and hydroxy-aluminum interlayered vermiculite (HIV-Al) in those incompletely collapsing by effect of aluminum intercalation. The patterns for the 20–40 cm layer (Fig. 2F) exhibited an identical trend; however, heating K-saturated samples considerably reduced reflection intensities.

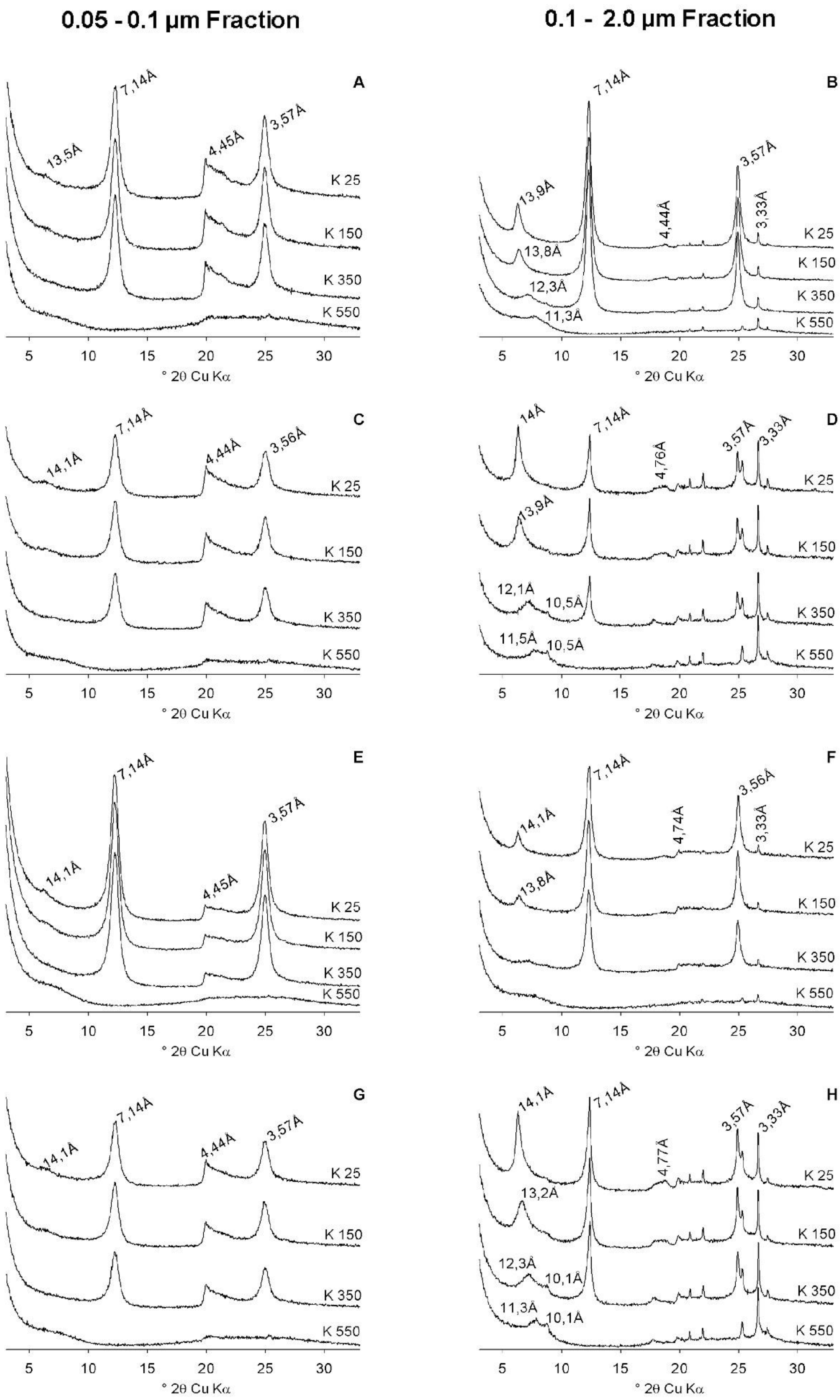

0.05 - 0.1 µm Fraction
0.1 - 2.0 µm Fraction
A
7,14Å
3,57Å
13,5Å
4,45Å
K 25
K 150
K 350
K 550
B
7,14Å
3,57Å
13,9Å
4,44Å
3,33Å
13,8Å
12,3Å
11,3Å
K 25
K 150
K 350
K 550
C
7,14Å
14,1Å
4,44Å
3,56Å
K 25
K 150
K 350
K 550
D
14Å
7,14Å
4,76Å
3,57Å
3,33Å
13,9Å
12,1Å
10,5Å
11,5Å
10,5Å
K 25
K 150
K 350
K 550
E
7,14Å
3,57Å
14,1Å
4,45Å
K 25
K 150
K 350
K 550
F
7,14Å
3,56Å
14,1Å
4,74Å
3,33Å
13,8Å
K 25
K 150
K 350
K 550
G
7,14Å
3,57Å
14,1Å
4,44Å
K 25
K 150
K 350
K 550
H
14,1Å
7,14Å
3,57Å
3,33Å
4,77Å
13,2Å
12,3Å
10,1Å
11,3Å
10,1Å
K 25
K 150
K 350
K 550
5
10
15
20
25
30
° 2θ Cu Kα

Figure 31. Experimental XRD patterns of the different sub-fractions obtained after K saturation (K 25) and heating at 150°C (K 150), 350°C (K 350) and 550°C (K 550). (A) No grazing 0-5 cm depth; (B) No grazing 0-5 cm depth; (C) Intensive grazing 0-5 cm depth; (D) Intensive grazing 0-5 cm depth; (E) No grazing 20-40 cm depth; (F) No grazing 20-40 cm depth; (G) Intensive grazing 20-40 cm depth; (H) Intensive grazing 20-40 cm depth.

8.4.4. Intensive grazing (IG)

Like NG, IG led to increasingly strong and narrow reflections with increasing particle size. The clay mineral assembly was similar to that observed under NG. The reflection at 14.3 Å for the 0.1–2 µm fraction in the samples from the 0–5 cm layer of soil under IG underwent no shift upon EG solvation; by contrast, the reflection at 4.76 Å changed with solvation (Fig. 1C), which suggests the presence of a small amount of swelling layers. K saturation and heating at 350 and 550 °C caused the reflection at 14.2 Å (Ca AD) to collapse and split into two at 11.5 and 10.5 Å respectively (0–5 cm IG layer). These results suggest that 2:1 clay minerals were vermiculite (complete collapse to 10 Å) and HIV (partial collapse). The reflection at 10 Å was better defined than in the NG samples, thus suggesting weaker aluminization of HIMs.

The 20–40 cm layer exhibited the same trend but less marked collapse upon K saturation and heating, which suggests the presence of greater amounts of HIVs or a higher degree of aluminization of HIMs than in the soil surface. The intensity of the 001 reflection for 2:1 clay minerals in the 0.1–2 µm fraction was similar to that for the 001 reflection of kaolinite. Whereas the reflection at 14.3 Å was unaffected by EG solvation, that at 4.76 Å for the 0.1–2 µm fraction of the 20–40 cm layer under IG was slightly different following EG solvation, thus suggesting the presence of very small amounts of swelling layers.

CEC values were slightly higher in the grazing treatments, which can be ascribed to the higher organic matter content of the soil (Table 2). CEC levels under intensive grazing (IG) were very similar to those under no grazing (NG), possibly as a result of the presence of 2:1 minerals.

8.5. Discussion

The amount of pedogenic soil minerals (i.e., phyllosilicates and oxides), and their chemical and structural characteristics, vary with the source material, weathering intensity, soil solution composition and drainage conditions (Karathanasis, 2002); also, it may be affected by soil management practices (Fink et al., 2014b; Silva Neto et al., 2008).

According to Churchman (1980), in acidic systems containing chelating organic acids, chlorites, whether mafic or pedogenic, are dissolved and transformed into vermiculite. Malcolm et al. (1969) found chelating organic compounds to remove aluminum incorporated into hydroxy-Al interlayered clay minerals (HIV-HIS) and form montmorillonite. These organic acids can also influence Al hydrolysis and precipitation reactions, Al hydroxide types (Huang & Violante, 1986; Kodama & Schnitzer, 1980; Kwong & Huang, 1979) and iron oxyhydroxide forms (Schwertmann et al., 1986).

Overall, total organic carbon (TOC) decreased with increasing soil depth in all treatments. NG samples exhibited higher TOC levels (especially in the soil surface) layer by effect of the absence of animals allowing greater accumulation of plant shoots at the end of the grazing season. Similar results were previously reported by Assmann et al. (2014). The decreased mass proportion of the 0.1–2 µm fraction from the 0–5 cm layer relative to the 20–40 cm layer may have resulted from depolymerization of interlayer Al by organic binders and subsequent instabilization and dissolution of clay minerals in that layer.

Irrespective of grazing intensity, pHwater in the intermediate soil layers was higher under IG by effect of the decreased content in exchangeable Al resulting from stronger aluminization of interlayer 2:1 minerals. Our results suggest that increased alumination of HIMs helps fix aluminum from the soil solution and raises pH as found under intensive grazing (IG) conditions.

The 0.1–2 µm fraction from the 0–5 and 20–40 cm layers of soil under IG contained 2:1 clay minerals that collapsed to 10.1–10.5 Å and others that collapsed only partially to 11.3–11.5 Å following K saturation and heating at 550 °C. The samples contained a population of HIMs (partial collapse) and one of 2:1 clay minerals with expandable layers accommodating exchangeable cations (quasi-complete collapse). The increased intensity of the reflections under IG suggests the presence of higher proportions of those minerals than under NG.

Also, the more marked collapse upon K saturation and heating in HIMs under IG suggests a low degree of aluminization relative to NG.

Ferreira et al. (2011) found K cycling to increase with increasing grazing intensity, 274 kg K ha^{-1} being cycled under IG and 164 kg K ha^{-1} coming from animal waste. Haynes and Williams (1993) found most K ingested by the animals (up to 90%) to be returned to soil and the dominant excreted form (70–90%) to be soluble K^+ in urine. Thus, the presence of animals increases K availability to plants in soil (Fink et al., 2014a; Officer et al., 2006). According to Jarvis (2000), the K surplus not absorbed by plants is likely lost from the system.

Some chemical properties of the 0–5 and 20–40 cm soil layers such as organic matter content, acidity, and Ca^{2+}, K^+ and aluminum (Al^{3+} or hydroxylated forms) availability, are closely related to soil management. Thus, high contents in organic matter, moderately acidic conditions and strong weathering all favor the release of aluminum that is partly fixed by 2:1 clay minerals to form HIMs (Caner et al, 2014). Also, grazing by animals, and their manure, increases the availability of cations such as Ca^{2+} and K^+. Under such conditions, Al and K or Ca may compete for sorption in the interlayer or by 2:1 clay minerals to form HIMs or vermiculite, respectively. Accordingly, HIM formation or instabilization may be Al- or K/Ca-dependent and hence linked to soil use (IG/NG).

Submicrometric particle fractionation allowed the identification of major changes in the soil clay fraction even after 13 years of agricultural management. Such anthropogenically mediated changes are difficult to detect by analysing the mineralogy and chemical composition of the bulk clay fraction (Bortoluzzi et al. 2012; Cecagno et al. 2016; Fink et al., 2014b; Inda et al. 2010).

This line of mineralogical changes merits further study, particularly as regards the formation of 2:1 mineral interlayers in relation to competition between chelating organic compounds, hydroxy-aluminum polymers and exchangeable cations.

8.6. Final Considerations

The clay fractionation highlights the importance of a careful and appropriate methodological sequence for the characterization of mineralogical changes in the soil clay fractions. Without the use of clay extraction and Fe oxides removal, as well as the infra-micrometric fractionation of clay fraction, it was not possible to reveal the trend of mineralogical changes of the 2:1 phyllosilicates due to the anthropic impact.

This line of mineralogical changes deserves further study, specifically to investigate the processes involved in the formation of 2:1 minerals interlayers, especially with regard to competition between organic complexing compounds and polymers of hydroxy-aluminum. Further research concerning abundance and type of iron oxides in this type of soil is also deserved.

8.7. Conclusions

The results obtained in this work allow us to draw three main conclusions, namely:

The soil clay fraction was mineralogically similar irrespective of treatment, with a prevalence of kaolinite and 2:1 HI minerals. However, after 12 years under an integrated soybean–beef cattle production system, ungrazed soil contained smaller amounts of 2:1 minerals. On the other hand, soil under intensive or moderate grazing was similar in this respect owing to the increased aluminization of interlayer 2:1 minerals.

The increased aluminization observed under intensive and moderate grazing may have resulted from aluminum being drained from the soil solid phase and hence made less available —and more toxic— to plants.

The effect of grazing intensity on soil mineralogy can only be confirmed by a comprehensive study of the clay fraction necessarily including its subfractions. It is therefore highly advisable to fractionate clay, especially when studying 2:1 interlayer minerals.

9. GENERAL CONCLUSIONS

The soils of subtropical regions from Rio Grande do Sul and Santa Catarina, present a low proportion of 2:1 clay minerals, that are absent in the soil from tropical regions of Brazil. However, such minerals, even in low proportions, are key factors for the fertility of the soils of these regions. South Brazil is a region with a very intensive agriculture and the pressure on soil use is considerably more intense than in the Amazonian region. In Amazonian region, the biggest challenge is to limit and to control the deforestation advance. In South Brazil the challenge is to maintain favorable conditions of soil fertility for a sustainable crop production.

The study showed that the soils have important differences, even between those formed from the same parent material (such as Taquara and São Borja profiles) due to the climatic and relief differences. The soil of the eastern region of Rio Grande do Sul (Taquara profile) is located in Araucaria’s Domain, which represents intermediate weathering conditions for the soils in southern Brazil, with elevated kaolinite concentration associated to 2:1 HI clay minerals. In the western region of Rio Grande do Sul (São Borja profile), which is in the Pampa biome, in areas of small geographic expression, the soils exhibit specific mineralogical, chemical and physical characteristics, with expandable clay predominance with elevated specific surface area and cation exchange capacity, neutral to basic soil reaction, high sums and base saturation, indicating a low degree of soil weathering;

After 12 years under an integrated soybean–beef cattle production system, the ungrazed areas presented lower intensity of 2:1 minerals. On the other hand, areas under intensive grazing and moderate grazing presented similar behaviour due to the higher aluminization of the interlayer of 2:1 minerals. The higher aluminization under intensive and moderate grazing managements may be a drain on aluminum in the soil solid phase, making it less available to plants and decreasing its phytotoxicity. The certification of the effect of grazing intensity on soil mineralogy can only be verified with a detailed study of the clay fraction, which necessarily includes its fractionation. Therefore, it is highly recommended to perform the clay fractionation, especially when studying 2:1 interlayer minerals.

10. BIBLIOGRAPHIC REFERENCES

AB'SÁBER, A. A. Um conceito de geomorfologia a serviço das pesquisas sobre o quaternário. **Geomorfologia**, São Paulo, v.18, 1969.

ALMEIDA, J. A. Solos dos Pampas. In: ALVAREZ V. V. H.; FONTES, L. E. F.; FONTES, M. P. F. (Ed.). **O solo nos grandes domínios morfoclimáticos do Brasil e o desenvolvimento sustentado**. Viçosa: Sociedade Brasileira de Ciência do Solo, Universidade Federal Viçosa, 1996. p.289-306

ALMEIDA, J. A.; MAÇANEIRO, K. C.; KLAMT, E. Mineralogia da fração argila de solos vermelhos com horizontes superficiais brunados do Planalto de Lages (SC). **Revista Brasileira de Ciência do Solo**, Campinas, v. 24, n. 4, p. 815-828, 2000.

ANDRADE, F. D. R. et al. Terra sólida: minerais e rochas. In: TEIXEIRA, W. et al. (Ed.). **Decifrando a Terra.** São Paulo: Companhia Editora Nacional, 2009.

ANGHINONI, I. et al. Benefícios da integração lavoura-pecuária sobre a fertilidade do solo em sistema plantio direto. In: FERTILIDADE do solo e nutrição de plantas no sistema plantio direto. Ponta Grossa: AEACG/ Inpag, 2011. p. 1-31

ASSMANN, J. M. et al. Soil carbon and nitrogen stocks and fractions in a long-term integrated crop–livestock system under no-tillage in southern Brazil. **Agriculture, Ecosystems e Environment**, Amsterdam, v. 190, p. 52-59, 2014.

AZEVEDO, A.C. **Efeito da calagem na dinâmica evolutiva de Latossolo Bruno distrófico.** 1993. 95p. Dissertação (Mestrado) - Curso de Pós-Graduação em Ciência do Solo, Programa de Pós-Graduação em Agronomia, Faculdade de Agronomia, Universidade Federal do Rio Grande do Sul, Porto Alegre, 1993.

AZEVEDO, A.C.; KÄMPF, N.; BOHNEN, H. Alterações na dinâmica evolutiva de Latossolo Bruno pela calagem. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 20, p. 191-198, 1996.

BALAN, E. et al. Inheritance vs. neoformation of kaolinite during lateritic soil formation: a case study in the middle amazon basin. **Clays and Clay Minerals**, Oxford, v.55, n.3, p.253–259, 2007.

BALAN, E. et al. First-principles modeling of the infrared spectrum of kaolinite. **American Mineralogist**, Washington, v.86, p.1321–1330, 2001.

BARNHISEL, R. I.; BERTSCH, P. M. Chlorites and hydroxy-interlayered vermiculite and smectite. In: MINERALS in Soil Environments. Madison: SSSA, 1989. p. 729-788

BARRÉ, P. et al. Which 2: 1 clay minerals are involved in the soil potassium reservoir? Insights from potassium addition or removal experiments on three temperate grassland soil clay assemblages. **Geoderma**, Amsterdam, v.146, n.1, p.216-223, 2008.

BATISTA, I. et al. Teores e estoque de carbono em frações lábeis e recalcitrantes da matéria orgânica do solo sob integração lavoura-pecuária no bioma Cerrado. **Semina:** CiênciasAgrárias, Londrina, v. 34, n. 6, p. 3377-3388, 2013.

BORNYASZ, M. A.; GRAHAM, R. C.; ALLEN, M. F. Ectomycorrhizae in a soil-weathered granitic bedrock regolith: Linking matrix resources to plants. **Geoderma**, Amsterdam, v. 126, p. 141-160, 2005.

BORTOLUZZI, E. C. et al. Mineralogical changes caused by grape production in a regosol from subtropical Brazilian climate. **Journal of Soils and Sediments**, Berlin, v. 12, n. 6, p. 854-862, 2012.

BRANTLEY, S. L. 5Reaction kinetics of primary rock-forming minerals under ambient conditions. In: TREATISE on Geochemistry. Oxford: Elsevier, 2003. p. 73–117,

BRASIL, Ministério da Agricultura. **Levantamento de reconhecimento dos solos do estado do Rio Grande do Sul.** Recife: convênio MA/DPP – SA/ DRNR, 1973. 431p. (BoletimTécnico, 30).

BRICKER, O.P.; JONES, B.F.; BOWSER, C.J. Mass-balance approach to interpreting weathering reactions in watershed systems. In: TREATISE on Geochemistry. v. 5, Surface and Ground Water, Weathering, and Soils, New York: Elsevier, 2003. Chapter 4, p. 119–132

BRIMHALL, G. H; DIETRICH, W. E. Constitutive mass balance relations between chemical composition, volume, density, porosity, and strain in metasomatic hydrochemkai systems: Results on weathering and pedogenesis. **Geochimica et Cosmochimica Acta**, London, v. 51**,** p. 657-587, 1986.

BROWN, G. et al. The structures and chemistry of soil clay minerals. In: THE CHEMISTRY of soil constituents. Chichester: John Wiley & Sons, 1978. p.29-178.

CANER, L. et al. Basalt and rhyo-dacite weathering and soil clay formation under subtropical climate in southern Brazil. **Geoderma**, Amsterdam, v. 235–236, p. 100-112, 2014.

CARVALHO, A. P. Caracterização, distribuição e utilização dos solos da Estação Experimental Zootecnica de Uruguaiana. 1976. 150 f. Dissertação (Mestrado) - Curso de Pós-Graduação em Agrnomia, Faculdade de Agronomia, Universidade Federal do Rio Grande do Sul, Porto Alegre, 1976.

CARVALHO, P. C. et al. Managing grazing animals to achieve nutrient cycling and soil improvement in no-till integrated systems. **Nutrient Cycling in Agroecosystems**, Dordrecht, v. 88, n. 2, p. 259-273, 2010.

CARVALHO, P. et al. Integração soja-bovinos de corte no Sul do Brasil. Porto Alegre: Universidade Federal do Rio Grande do Sul, 2011. 60 p. (Boletim Técnico)

CECAGNO, D. et al. Least limiting water range and soybean yield in a long-term, no-till, integrated crop-livestock system under different grazing intensities. **Soil and Tillage Research**, Amsterdam, v. 156, p. 54-62, 2016.

CHADWICK, A. O; BRIMHALL, G.H; HENDRICKS, D. M. From a black to a gray box a mass balance interpretation of pedogenesis. **Geomorphology**, Amsterdam, v. 3, n.3-4, p. 369-390, 1990.

CHADWICK, O. A.; GRAHAM, R. C. Pedogenic processes. In: SUMNER, M. (Ed.). **Handbook of Soil Science.** New York: CRC Press, 2000. p. E41– E73.

CHÁVEZ, L. F. et al. Diversidade metabólica e atividade microbiana no solo em sistema de integração lavoura pecuária sob intensidades de pastejo. **Pesquisa Agropecuária Brasileira,** Brasília, v. 46, p. 1254-61, 2011.

CHEMALE JR., F. Evolução Geológica do Escudo Sul-rio-grandense. In: HOLZ, M.; DE ROS, L. F. (Ed.) **Geologia do Rio Grande do Sul.** Porto Alegre: CIGOUFRGS, 2000. p. 13-52

CHOROVER, J. et al. Soil biogeochemical processes within the critical zone**. Elements**, Quebec, v.3, n.5, p.321-326, 2007.

CHURCHMAN G.J. Relevance of different intercalation tests for distinguishing halloysite from kaolinite in soils. **Clays and Clay Minerals**, Oxford, v.38, p.591-599, 1990.

CHURCHMAN, G.J. Clay minerals formed from micas and chlorites in some New Zealand soils. **Clay Minerals**, London, v. 15, p. 59-76, 1980.

CHURCHMAN, G.J. The alteration and formation of soil minerals by weathering. In: SUMNER, M.E. (Ed.). **Handbook of soil science**. Boca Raton: CRC Press, 2000. p.F3-F76.

CLAYTON, J.L. Nutrient supply to soil by rock weathering. In: IMPACT of Intensive Harvesting on Forest Nutrient Cycling. New York: State University of New York, College of Environmental Science and Forestry, Syracuse, 1979. p. 75–96

COGO, N.P. **Morfologia e gênese de solos escuros formados sobre basalto na Campanha-oeste do Rio Grande do Sul.** 1972. 130p. Dissertação (Mestrado) – Programa de Pós-Graduação em Ciência do Solo, Faculdade de Agronomia, Universidade Federal do Rio Grande do Sul, Porto Alegre, 1972.

CONTE, O. et al. Evolução de atributos físicos de solo em sistema de integração lavoura-pecuária. **Pesquisa Agropecuária Brasileira,** Brasília, v. *46,* n*.* 10, p. 1301-1309, 2011.

DA SILVA, F. D. et al. Soil carbon indices as affected by 10 years of integrated crop–livestock production with different pasture grazing intensities in Southern Brazil. **Agriculture, Ecosystems e Environment**, Amsterdam, v. 190, p. 60-69, 2014.

DE MORAES, A. et al. Integrated crop–livestock systems in the Brazilian subtropics. **European Journal of Agronomy**, Amsterdam, v. 57, p. 4-9, 2014.

DE OLIVEIRA FERREIRA, E. V. et al. Ciclagem e balanço de potássio e produtividade de soja na integração lavoura-pecuária sob semeadura direta. **Revista Brasileira de Ciência do Solo,** Viçosa, v. 35*,* n. 1, p. 161-169, 2011.

DEMATTÊ, J. L. I. et al. Estimativa da evolução do intemperismo mediante ganhos e perdas de íons numa seqüência de solos desenvolvidos de diabásio e influenciados pela drenagem em Piracicaba, SP**. Revista Brasileira de Ciência do Solo**, Campinas, v. 15, p. 69-73, 1991.

DIXON, J.B. Kaolin and serpentine group minerals. In: DIXON, J.B; WEED, S.B. (Ed.). **Minerals in soil environments.** Madison: Soil Science Society of America, 1989. p. 467-525.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA. Centro Nacional de Pesquisa de Solos. **Manual de métodos de análise de solo**. 2. ed. Rio de Janeiro: Embrapa, 1997. 212 p.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA. Centro Nacional de Pesquisa de Solos. **Sistema Brasileiro de Classificação de Solo**. 2. ed. Rio de Janeiro: Embrapa, 2006. 412p.

EMPRESA BRASILEIRA DE PESQUISA AGROPECUÁRIA. Centro Nacional de Pesquisa de Solos. **Sistema Brasileiro de Classificação de Solo**. 3. ed. Rio de Janeiro: Embrapa, 2013. 353p.

ESTADOS UNIDOS. Department of Agriculture. Soil Survey Division. Soil Conservation Service. Soil Survey Staff. **Keys to Soil Taxonomy**. 12th ed. Washington, DC: USDA-Natural Resources Conservation Service, 2014.

FARMER, V. C. (Ed.). **The Infrared Spectra of Minerals**. London: Mineralogical Society, 1974.

FERNANDES, L. A. D.; TOMMASI, A.; PORCHER, C. C. Deformation patterns in the southern Brazilian branch of the Dom Feliciano Belt: a reappraisal. **Journal of South American Earth Sciences**, Oxford, v. 5, n. 1, p. 77-96, 1992.

FERNANDES, L. A. D. et al. Mapa geológico de parte das folhas de Quitéria e Várzea do Capivarita - RS, Quitéria, folha SH 22-Y-B-I-4, estado do Rio Grande do Sul, Várzea do Capivarita, folha SH 22-Y-B-I-3, estado do Rio Grande do Sul. Porto Alegre, 1988. 1 mapa, preto e branco. Escala 1:50.000.

FERREIRA, E. V. D. O. et al. Ciclagem e balanço de potássio e produtividade de soja na integração lavoura-pecuária sob semeadura direta. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 35, n. 1, p. 161-169, 2011.

FILIPPI, P. et al. Monitoring and Modeling Soil Change: The Influence of Human Activity and Climatic Shifts on Aspects of Soil Spatio temporally – A Review. **Advances in Agronomy,** San Diego, v.139, p. 153-2014, 2016.

FINK, J. R et al. Chemical and mineralogical changes in a Brazilian Rhodic Paleudult under different land use and managements. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 38, p. 1304-1314, 2014a.

FINK, J.R. et al. Mineralogy and phosphorus adsorption in soils of south and central-west Brazil under conventional and no-tillage systems. **Acta Scientiarum Agronomy**, Maringá, v. 36, p. 379-387, 2014b.

FONTES, M. P. F. Intemperismo de rochas e minerais. In: PEDOLOGIA: fundamentos. Viçosa, MG: SBCS, 2012.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. [Informações obtidas no site]. [2015]. Disponível em: <http:/ http://www.fao.org/economic/ess/ess-fs/>. Acesso em: 30 set 2015.

FORMOSO, M. L.L. Some topics on geochemistry of weathering: a review. **Anais da Academia Brasileira de Ciências,** Rio de Janeiro, v. 78, n. 4, p. 809-820, 2006.

GESSLER, P. E., CHADWICK, O. A., CHAMRAN, F., ALTHOUSE, L., & HOLMES, K. Modeling soil–landscape and ecosystem properties using terrain attributes. **Soil Science Society of America Journal**, 64(6), 2046-2056. 2000.

GOBAT, J.M.; ARAGNO, M.; MATTHEY, W. **Le sol vivant**. Lausanne, 568p. 2003.

HARRIS, W.; WHITE, G.N. X-ray diffraction techniques for soil mineral identification. In: METHODS of Soil Analysis, Part 5**,** Mineralogical Methods. Madison, Wisconsin: Soil Science Society of America, 2008. p. 81–115.

HAYNES, R. J.; WILLIAMS, P. H. Nutrient cycling and soil fertility in the grazed pasture ecosystem. **Advances in agronomy,** San Diego, v.49, p.119-199, 1993.

HOOSBEEK, M. R.; BRYANT, R. B. Towards the quantitative modeling of pedogenesis – a review. **Geoderma**, Amsterdam, v. 55, n. 3-4, p. 183-210, 1992.

HUANG, P.M.; VIOLANTE, A. Influence of organic acids on crystallization and surface properties of precipitation products of aluminum. In: HUANG, P.M.; SCHNITZER, M. (Ed.). **Interactions of soil minerals with natural organics and microbes.** Madison: Soil Science Society of America, 1986. p.159-222.

HUBERT, F. et al. Unraveling complex< 2 µm clay mineralogy from soils using X-ray diffraction profile modeling on particle-size sub-fractions: Implications for soil pedogenesis and reactivity. **American Mineralogist**, Washington, v. 97, n. 2-3, p. 384-398, 2012.

HUBERT, F. et al. Advances in characterization of soil clay mineralogy using X-ray diffraction: from decomposition to profile fitting. **European Journal of Soil Science**, Oxford, v. 60, n. 6, p. 1093-1105, 2009.

IBGE. **Mapa de Biomas do Brasil, primeira aproximação**. Rio de Janeiro: IBGE, 2004. Disponível em:<www.ibge.gov.br>. Acesso em: 26 out 2016.

INDA JUNIOR, A.V.; KÄMPF, N. Variabilidade de goethita e hematita via dissolução redutiva em solos de região tropical e subtropical. **Revista Brasileira de Ciência do Solo**, Viçosa, v.29, p.851-866, 2005.

INDA, A. V. et al. Aluminum hydroxy-interlayered minerals and chemical properties of a subtropical Brazilian Oxisol under no-tillage and conventional tillage. **Revista Brasileira de Ciência do Solo,** Viçosa, v. 34, n. 1, p. 33-41, 2010.

IUSS WORKING GROUP WRB. **World Reference Base for Soil Resources 2014, update 2015 International soil classification system for naming soils and creating legends for soil maps.** Rome: FAO, 2015. (World Soil Resources Reports, n.106)

JARVIS, S. C. Progress in studies of nitrate leaching from grassland soils. **Soil use and Management**, Oxford, v. 16, (s1), p. 152-156, 2000.

KÄMPF, N. Die Eisenoxidmineralogie einer Klimasequenz von Böden aus Eruptiva in Rio Grande do Sul, Brasilien. 1981. 271p.Tese (Doutorado) - Freising, Technische Universität München, 1981.

KÄMPF, N.; CURI, N. Formação e evolução do solo (Pedogênese). In: KER, J. C. et al. (Ed.). **Pedologia:** Fundamentos. Viçosa: Sociedade Brasileira de Ciência do Solo, 2012. 1 v. p. 207-302.

KÄMPF, N.; CURI, N.; MARQUES, J. J. Intemperismo e ocorrência de minerais no ambiente do solo. In: MELO, V. F.; ALLEONI, L. R. F. (Ed.). **Química e mineralogia do solo**. Viçosa: Sociedade Brasileira de Ciência do Solo, 2009. 1 v. p. 333-426.

KÄMPF, N.; KLAMT, E. Mineralogia e gênese de Latossolos (Oxisols) e solos podzólicos da região nordeste do Planalto Sul Riograndense. **Revista Brasileira de Ciência do Solo**, Campinas, v. 2, p. 68-78, 1978.

KÄMPF, N.; MARQUES, J. J.; CURI, N. Mineralogia de solos brasileiros. In: KER, J. C. et al. (Ed.). **Pedologia**: fundamentos. Viçosa: Sociedade Brasileira de Ciência do Solo, 2012. 1 v. p. 81-146.

KÄMPF, N.; SCHNEIDER, P.; MELLO, P. F. Alterações mineralógicas em sequência Vertissolo-Litossolo na região da Campanha no Rio Grande do Sul. **Revista Brasileira de Ciência do Solo**, Campinas, v. 19, n. 3, p. 349-357, 1995.

KÄMPF, N.; SCHWERTMANN, U. Goethite and hematite in a climosequence in Southern Brazil and their application in classification of kaolinitic soils. **Geoderma**, Amsterdam, v.29, p.27-39, 1983.

KARATHANASIS, A. D. Compositional and solubility relationships between aluminum-hydroxyinterlayered soil-smectites and vermiculites. **Soil Science Society of America Journal**, Madison, v. 52, p. 1500-1508, 1988.

KARATHANASIS, A. D. Seasonal variation in solution composition and mineral stability of two Kentucky Alfisols. **Soil Science Society of America Journal**, Madison, v. 55, n. 3, p. 881-890, 1991.

KARATHANASIS, A. D.; DIXON, J. B.; SCHULZE, D. G. Mineral equilibria in environmental soil systems. In: SOIL mineralogy with environmental applications. [Madison]: SSSA, 2002. p.109-151

KODAMA, H.; SCHNITZER, M. Effect of fulvic acid on the crystallization of Fe (III) oxides. **Geoderma,** Amsterdam, v. 19, n. 4, p. 279-291, 1977.

KODAMA, H.; SCHNITZER, M. Effect of fulvic acid on the crystallization of aluminum hydroxides. **Geoderma**, Amsterdam, v. 24, n. 3, p. 195-205, 1980.

KÖPPEN, W. Das Geographische System der Klimatologie. Berlin, 1936. 44 p.

KUNRATH, T. R. et al. Management targets for continuously stocked mixed oat× annual ryegrass pasture in a no-till integrated crop–livestock system. **European Journal of Agronomy**, Amsterdam, v. 57, p. 71-76, 2014.

KWONG, N.K.K.F.; HUANG, P.M. The relative influence of low-molecular-weight complexing organic acids on the hydrolysis and precipitation of aluminum. **Soil Science**, Baltimore, v. 128, p. 337-342, 1979.

LAIRD, D. A. et al. Chemistry of smectitic and illitic phases in interstratified soil smectite. **Soil Science Society of America Journal**, Madison, v. 55, n. 5, p. 1499-1504, 1991.

LAL, R. Soils and food sufficiency. A review. **Agronomy for Sustainable Development**, Paris, v. 29, n. 1, p. 113-133, 2009.

LOSS, A. et al. Bulk density and soil fertility under no-tillage systems and crop-livestock integration in the Cerrado. **Revista de Ciências Agrárias**, Belem, v. 55, n. 4, p. 260-268, 2012.

MACEWAN, D.M.C.; WILSON, M.J. Interlayer and intercalation complexes of clay minerals. In: BRINDLEY, G.W.; BROWN, G. (Ed.). **Crystal Structures of Clay Minerals and their X-ray Identification**. London: Mineralogical Society, 1980. p. 197-248

MALCOLM, R.L.; NETTLETON, W.D.; MCCRACKEN, R.J. Pedogenic formation of montmorillonite from a 2:1-2:2 Intergrade clay mineral. **Clays and Clay Minerals**, Oxford, v. 16, p. 405-414, 1969.

MALLA, P.B. Vermiculites. In: DIXON, J.B.; SCHULZE, D.G. (Ed.). **Soil Mineralogy with Environmental Applications.** Madison: SSSA, 2002. p. 501-530.

MALUF, J. R. T. Nova classificação climática do Estado do Rio Grande do Sul. **Revista Brasileira de Agrometeorologia**, Santa Maria, v. 8, n. 1, p. 141-150, 2000.

MARCHÃO, R. L. et al. Qualidade física de um Latossolo Vermelho sob sistemas de integração lavoura-pecuária no Cerrado. **Pesquisa Agropecuária Brasileira**, Brasília, v. 42, n. 6, p. 873-882, 2007.

MARQUES, J. J. et al. Mineralogy of soils with unusually high exchangeable Al from the western Amazon Region. **Clay Minerals**, Oxford, v.37, n.4, p.651-661, 2002.

MARTINS, A. P. et al. Soil acidification and basic cation use efficiency in an integrated no-till crop–livestock system under different grazing intensities. **Agriculture, Ecosystems e Environment**, Amsterdam, v. 195, p. 18-28, 2014.

MARTINS, A.P. et al. Integração soja-bovinos de corte no sul do Brasil. 2ª. ed. Porto Alegre, RS: Gráfica RJR, 2015. 104 p.

MARTINS, L. C.; WILDNER, W.; HARTMANN, L.A. Estratigrafia dos derrames da província vulcânica Paraná na região oeste do Rio Grande do Sul, Brasil, com base em sondagem, perfilagem gamaespecrométrica e geologia de campo. **Pesquisas em Geociências**, Porto Alegre, v. 38, n. 1, p. 15-27, 2011.

MCLENNAN, S.M. Weathering and global denudation. **Journal of Geology**, Chicago, v. 101, p. 295–303, 1993.

MEHRA, O. P.; JACKSON, M. L. Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate. **Proceedings Clays and Clay Minerals Conference,** London, v.7, p.317-327, 1960.

MELFI, A. J.; PEDRO, G. Estudo geoquímico dos solos e formações superficiais do Brasil: caracterização e repartição dos principais tipos de evolução geoquímica. **Revista Brasileira de Geociências**, São Paulo, v. 7, p. 271-286, 1977.

MELFI, A.J. et al. Tropical Soils: Genesis, distribution and degradation of lateritic pedological systems. In: FORMOSO, M.L.L.; CERRI, C.C. **Academia Brasileira de Ciências**, Rio de Janeiro, p. 7– 30, 1999. (Workshop on Tropical Soils)

MELO, V. F.; WYPYCH, F. Caulinita e Haloisita. In: MELO, V. F.; ALLEONI, L. R. F. (Ed.). **Química e mineralogia do solo**. Viçosa: Sociedade Brasileira de Ciência do Solo, 2009. 1 v. p. 427-504.

MERTEN, G. H.; MINELLA, J. P. The expansion of Brazilian agriculture: soil erosion scenarios. **International Soil and Water Conservation Research**, [S.l.], v. 1, n. 3, p. 37-48, 2013.

MEUNIER, A. Soil hydroxy-interlayered minerals: A re-interpretation of their crystallo chemical properties. **Clays and clay minerals**, Oxford, v. 55, n. 4, p. 380-388, 2007.

MEUNIER, A. et al. The Weathering Intensity Scale (WIS): an alternative approach of the chemical index of alteration (CIA). **American Journal of Science**, New Haven, v. 313, p. 113–143, 2013.

MEUNIER, A.; BORTOLUZZI, E.C; MEXIAS, A.S. **Le monde des argiles** = O mundo das argilas. Porto Alegre: Editora da UFRGS, 2016.

MORAES, A. et al. Research on integrated crop-livestock systems in Brazil**.** **Revista Ciência Agronômica**, Fortaleza, v.45, p.1024-1031, 2014.

MOTA, F.S. Estudo do clima do Estado do Rio Grande do Sul, segundo o sistema de W. Köeppen. **Revista Agronômica,** Porto Alegre, n. 193-198, p. 132-141, 1953.

MOTERLE, D. F. et al. Impact of potassium fertilization and potassium uptake by plants on soil clay mineral assemblage in South Brazil. **Plant and Soil**, The Hague, v.406, n.1-2, p.157-172, 2016.

MOTTA, P.E.F.; KÄMPF, N. Iron oxide properties as support to soil morphological features for prediction of moisture regimes in Oxisols of Central Brazil. **Zeitschriftfür Pflanzenernährung und Bodenkunde**, Weinheim, v. 155, n. 5, p. 385-390, 1992.

NESBITT, H. W.; YOUNG, G.M. Formation and diagenesis of weathering profiles. **The Journal of Geology**, Chicago, v.97, n.2, p. 129-147, 1989.

NESBITT, H.W.; YOUNG, G.M. Early Proterozoic climates and plate motions inferred from major element chemistry of lutites. Nature, London, v. 299, p. 715-717, 1982.

OFFICER, S.J. et al. Variability of clay mineralogy in two New Zealand steep-land topsoils under pasture. **Geoderma**, Amsterdam, v. 132, n. 3, p. 427-440, 2006.

PEDRON, F. A. **Mineralogia, morfologia e classificação de saprólitos e Neossolos derivados de rochas vulcânicas no Rio Grande do Sul**. 2007. 160 f. Tese (Doutorado em Ciência do Solo) - Universidade Federal de Santa Maria, Santa Maria, 2007.

PEDRON, F. A.; AZEVEDO, A. C.; DALMOLIN, R. S. D. Alteração mineralógica de Neossolos em uma climo-litossequência no Planalto do Rio Grande do Sul. **Ciência Rural**, Santa Maria, v. 42, n. 3, p. 451-458, 2012.

PRICE, J. R; VELBEL, M. A. Chemical weathering indices applied to weathering profiles developed on heterogeneous felsic metamorphic parent rocks**. Chemical Geology**, Amsterdam, v. 202, n. 3-4, p.397-416, 2003.

QUIRK, J. P. Significance of surface areas calculated from water vapour sorption isotherms by use of the BET equation. **Soil Science**, Madison, v. 80, n. 6, p. 423-430, 1955.

R CORE TEAM. **R: A Language and Environment for Statistical Computing**. Vienna, Austria: R Foundation for Statistical Computing, [2015]. Disponível em:<http://www.R-project.org/>. Acesso em: 02 nov. 2015.

REID-SOUKUP, D.; ULERY, A. Smectites. In: Dixon, J.; SCHULZE, D. (Ed.). **Soil Mineralogy with Environmental Applications**. Madison: Soil Science Society of America, 2002. p. 467–499

RICH, C.I. Hydroxy interlayers in expansible layer silicates. **Clays and Clay Minerals**, Oxford, v. 16, p. 15-30, 1968.

RIEU, R. et al. Climatic cycles during a Neoproterozoic "snowball" glacial epoch. **Geology**, Boulder, v. 35, p. 299-302, 2007.

RIGHI, D.; MEUNIER, A. Characterization and genetic interpretation of clays in an acid brown soil (Dystrochrept) developed in a granitic saprolite. **Clays and Clay Minerals**, Oxford, v. 39, n. 5, p. 519-530, 1991.

RUSSELLE, M.P.; ENTZ, M.; FRANZLUEBBERS, A.J. Reconsidering integrated crop– livestock systems in North America. **Agronomy Journal**, Madison, v. 99, p. 325–334, 2007.

SAIKIA, B.J.; PARTHASARATHY, G. Fourier Transform Infrared spectroscopic characterization of kaolinite from Assam and Meghalaya, Northeastern India. **Journal of Modern Physics**, v.1, n.4, p. 206-210, 2010.

SALTON, J.C. et al. Pastoreio de aveia e compactação do solo. **Revista Plantio Direto**, Passo Fundo, v. 69, p.32-34, 2002.

SANTOS, R.D. et al. **Manual de descrição e coleta de solo no campo.** 5.ed. Viçosa, MG: SBCS/EMBRAPA/CNPS, 2005. 100 p.

SCHAEFER, C.E.G.R.; FABRIS, J.D.; KER, J.C. Minerals in the clay fraction of Brazilian Latosols (Oxisols): a review. **Clay Minerals**, Oxford, v. 43, n. 1, p. 137-154, 2008.

SCHEFFLER, K.; HOERNES, S.; SCHWARK, L. Global changes during Carboniferous-Permian glaciation of Gondwana: linking polar and equatorial climate evolution by geochemical proxies. **Geology**, Boulder, v. 31, p. 605-608, 2003.

SCHWERTMANN, U. Differenzierung der eisenoxide des bodens durch extraktion mit ammoniumoxalat-lösung. **Zeitschrift für Pflanzenernährung und Bodenkunde,** Weinheim, v. 105, n. 3, p. 194-202, 1964.

SCHWERTMANN, U. Solubility and dissolution of iron oxides. In: CHEN, Y.; HADAR, Y. (Ed). **Iron nutrition and interactions in plants**. Dordrecht: Kluwer Academic, 1991. p.3-27.

SCHWERTMANN, U.; KÄMPF, N. Properties of goethite and hematite in kaolinitic soils of southern and central Brazil. **Soil Science**, Baltimore, v.139, p.344-350, 1985.

SCHWERTMANN, U.; KODAMA, H.; FISCHER, W.R. Mutual interactions between organics and iron oxides. In: HUANG, P.M.; SCHNITZER, M. (Ed.). **Interactions of soil minerals with natural organics and microbes.** Madison: Soil Science Society of America, 1986. p. 223-250.

SCHWERTMANN, U.; LATHAM, M. Properties of iron oxides in some New Caledonian Oxisols. **Geoderma**, Amsterdam, v. 39, p. 105–123, 1986.

SILVA NETO, L.F. et al. Iron oxides in tropical and subtropical Brazilian oxisols under long-term no-tillage. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 32, n. 5, p. 1873-1881, 2008.

SILVA, G. M. O desenvolvimento sustentado na região do domínio da floresta com Araucária. In: ALVAREZ V. V. H.; FONTES, L. E. F.; FONTES, M. P. F. (Ed.). **O solo nos grandes domínios morfoclimáticos do Brasil e o desenvolvimento sustentado**. Viçosa: Sociedade Brasileira de Ciência do Solo, Universidade Federal Viçosa, 1996. p.217-232

SOUZA, E.D. et al. Carbono orgânico e fósforo microbiano em sistemas de integração agricultura-pecuária submetidos a intensidades de pastejo em plantio direto. **Revista Brasileira de Ciência do Solo**, Viçosa, v. 32, p. 1273-1282, 2008.

SOUZA, E.D.D. et al. Estoques de carbono orgânico e de nitrogênio no solo em sistema de integração lavoura-pecuária em plantio direto, submetido a intensidades de pastejo. **Revista Brasileira de Ciência do Solo,** Campinas, v. 33, n. 6, p. 1829-1836, 2009.

SOUZA, P.A.; MARQUES-TOIGO, M. Progress on the Palynostratigraphy on the Permiam astrata on the Rio Grande do Sul State, Paraná Basin, Brazil. **Anais da Academia Brasileira de Ciências**, Rio de Janeiro, v. 77, n.2, p. 353-365.

STERNBERG, P. D. et al. Root distribution and seasonal water status in weathered granitic bedrock under chaparral. **Geoderma**, Amsterdam, v.72, n.1, p.89-98, 1996.

STILES, C.A.; MORA, C.I.; DRIESE, S.G. Pedogenic processes and domain boundaries in a Vertisol climosequence: evidence from titanium and zirconium distribution and morphology. **Geoderma**, Amsterdam, v. 116, p. 279– 299, 2003.

STRECK, E.V. et al. **Solos do Rio Grande do Sul**. 2.ed. rev. e ampl. Porto Alegre: Emater/RS, 2008. 222p.

STÜRMER, S.L.K. **Infiltração de água em Neossolos Regolíticos do rebordo do planalto do Rio Grande do Sul**. 2008**.** 104 f. Dissertação (Mestrado) - Universidade Federal de Santa Maria, Santa Maria, 2008.

SZABO, G.A.J.; TEIXEIRA, W.; BABINSKI, M. Magma e seus produtos. In: TEIXEIRA, W. et al. (Ed.). **Decifrando a Terra.** São Paulo: Companhia Editora Nacional, 2009.

TAN, K.H. Infrared spectroscopy. In: SOIL sampling, preparation and analysis. New York: Marcel Dekker, 1996. p. 278-298

TEDESCO, M. J. et al. **Análise de solo, plantas e outros materiais**. 2.ed. Porto Alegre: Departamento de Solos da Universidade Federal do Rio Grande do Sul, 1995. 174 p. (Boletim Técnico de Solos, 5)

TESKE, R.; ALMEIDA, J.A.; ANDREY. Caracterização mineralógica dos solos derivados de rochas efusivas no Planalto Sul de Santa Catarina, Brasil. **Revista de Ciências Agroveterinárias**, Lages, v. 12, n. 2, p. 187-198, 2013.

TOLEDO, M.C.M.; OLIVEIRA, S.M.B.; MELFI, A.J. Intemperismo e formação do solo. In: TEIXEIRA, W. et al. (Ed.). **Decifrando a Terra.** São Paulo: Oficina de Textos, 2000.

VELDE, B.; BARRÉ, P. **Soils, plants and clay minerals: mineral and biologic interactions.** Berlin: Springer, 2010. 333 p.

VIEIRA, L. F. S. **A valorização da beleza cênica da paisagem do Bioma Pampa do Rio Grande do Sul**: proposição conceitual e metodológica. 2014. 251p. Tese (Doutorado) - Programa de Pós-Graduação em Geografia, Instituto de Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre, 2014.

VIENNET, J. C. et al. Investigation of clay mineralogy in a temperate acidic soil of a forest using X-ray diffraction profile modeling: Beyond the HIS and HIV description. **Geoderma**, Amsterdam, v.241, p.75-86, 2015.

VOLKOFF, B.; MELFI, A.J.; CERRI, C.C. Solos podzólicos e cambissolos eutróficos do Alto Rio Purús (Estado do Acre). **Revista Brasileira de Ciência do Solo**, Campinas, v. 13, p. 363-372, 1989.

WHITE, A. F; BLUM, A. E. Effects of climate on chemical, weathering in watersheds. **Geochimica et Cosmochimica Acta**, London, v. 59, n. 9, p.1729-1747, 1995.

WILSON, M. J. The origin and formation of clay minerals in soils: past, present and future perspectives. **Clay Minerals**, London, v. 34, n. 1, p. 7-25, 1999.

WILSON, M. J. The origin and formation of clay minerals in soils: past, present and future perspectivesd. **Clay Minerals**, London, v. 34, n. 1, p. 7-25, 1999.

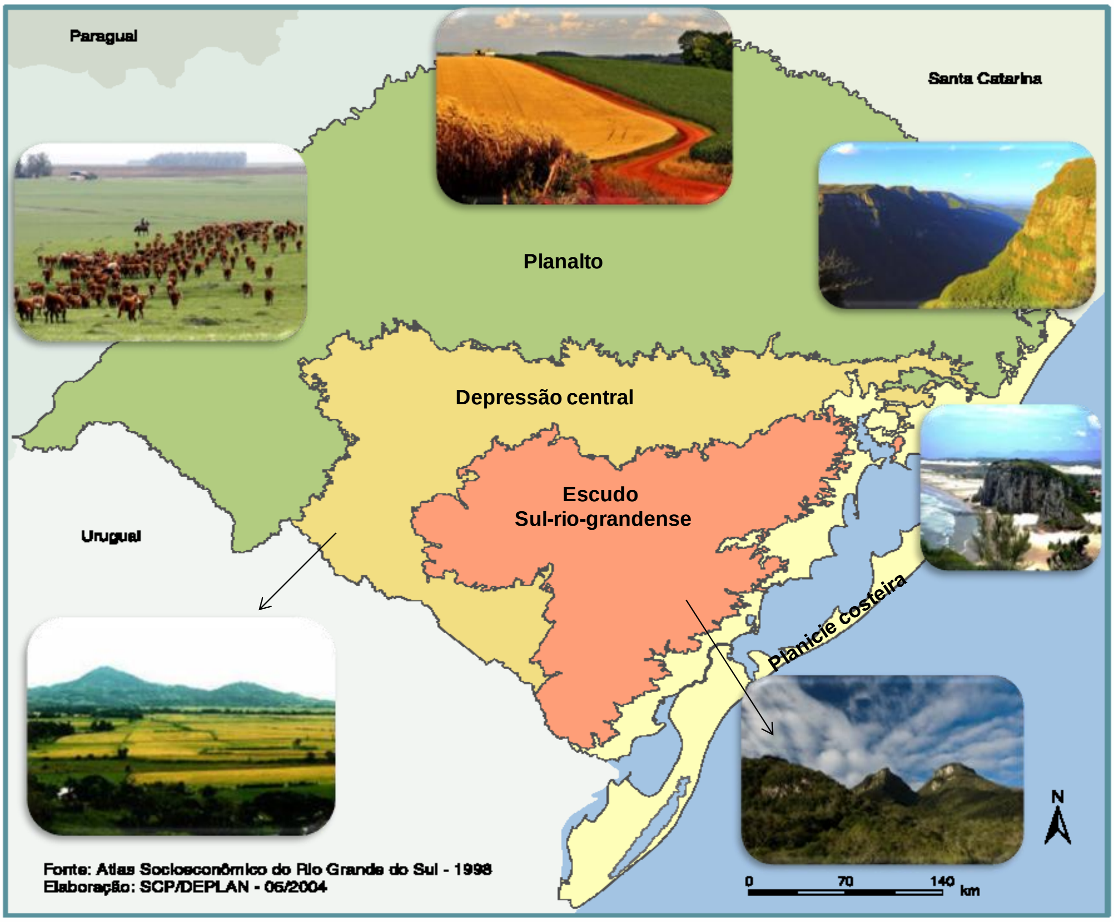
WITTY, J. H. et al. Contributions of water supply from the weathered bedrock zone to forest soil quality. **Geoderma**, Amsterdam, v. 114, n.3, p.389-400, 2003.

YAHAYA, L. E. et al. Natural Rubber/ Organoclay Nanocomposite from Tea (Camellia Sinensis) Seed Oil Derivative. **American Journal of Materials Science**, [S.l.], v.2, n.2 p. 1-5, 2012.

YOUNG, A. **Tropical Soils and Soil Survey**. London: Cambridge University Press, 1976. 468 p.

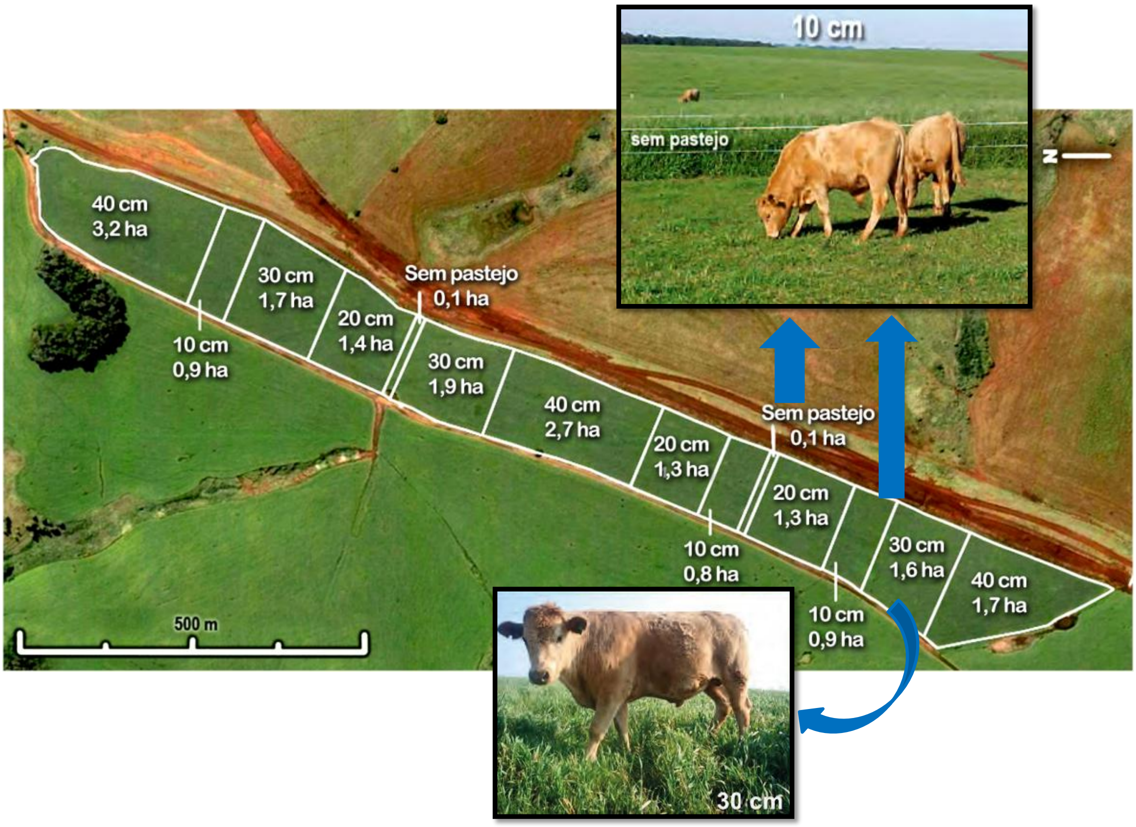
11. ANNEXES

Annex 1. Geomorphological configuration of Rio Grande do Sul State.

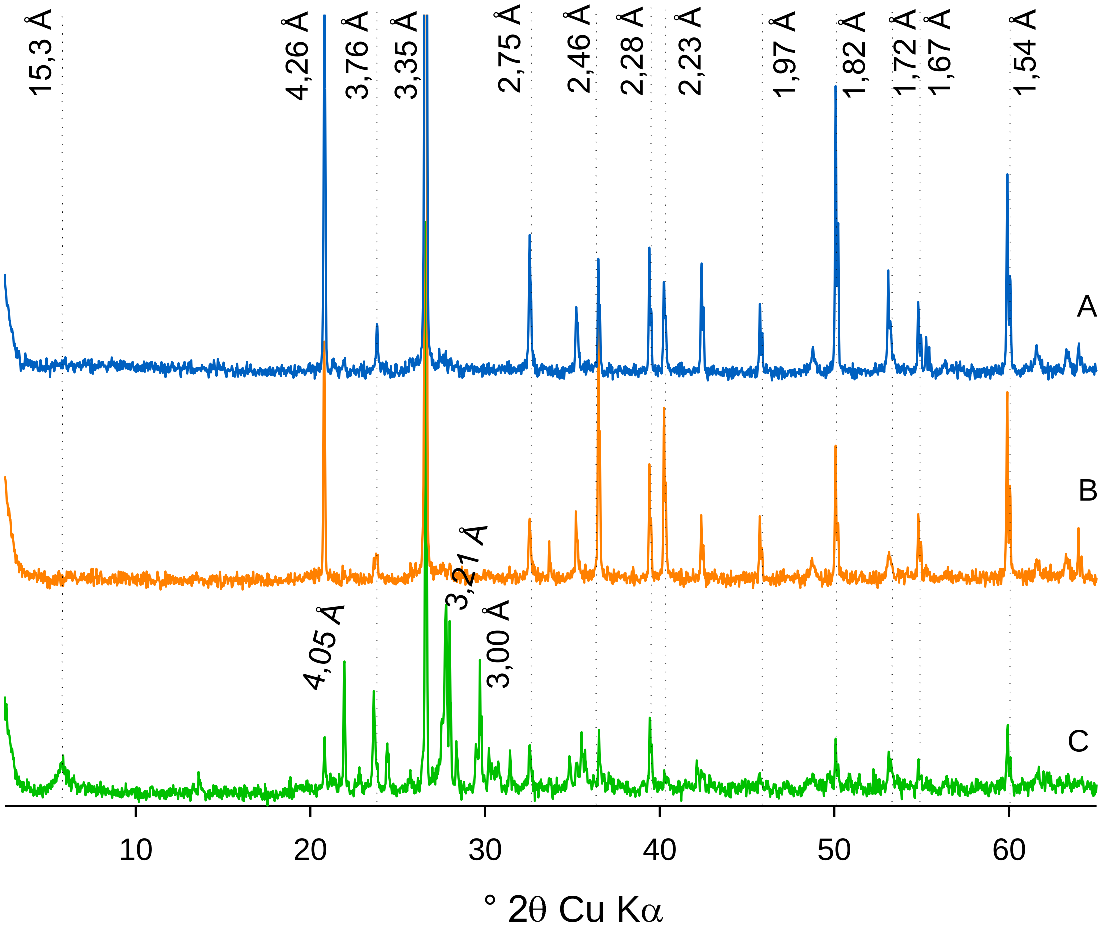


Fonte: Atlas Socioeconômico do Rio Grande do Sul - 1998
Elaboração: SCP/DEPLAN - 06/2004

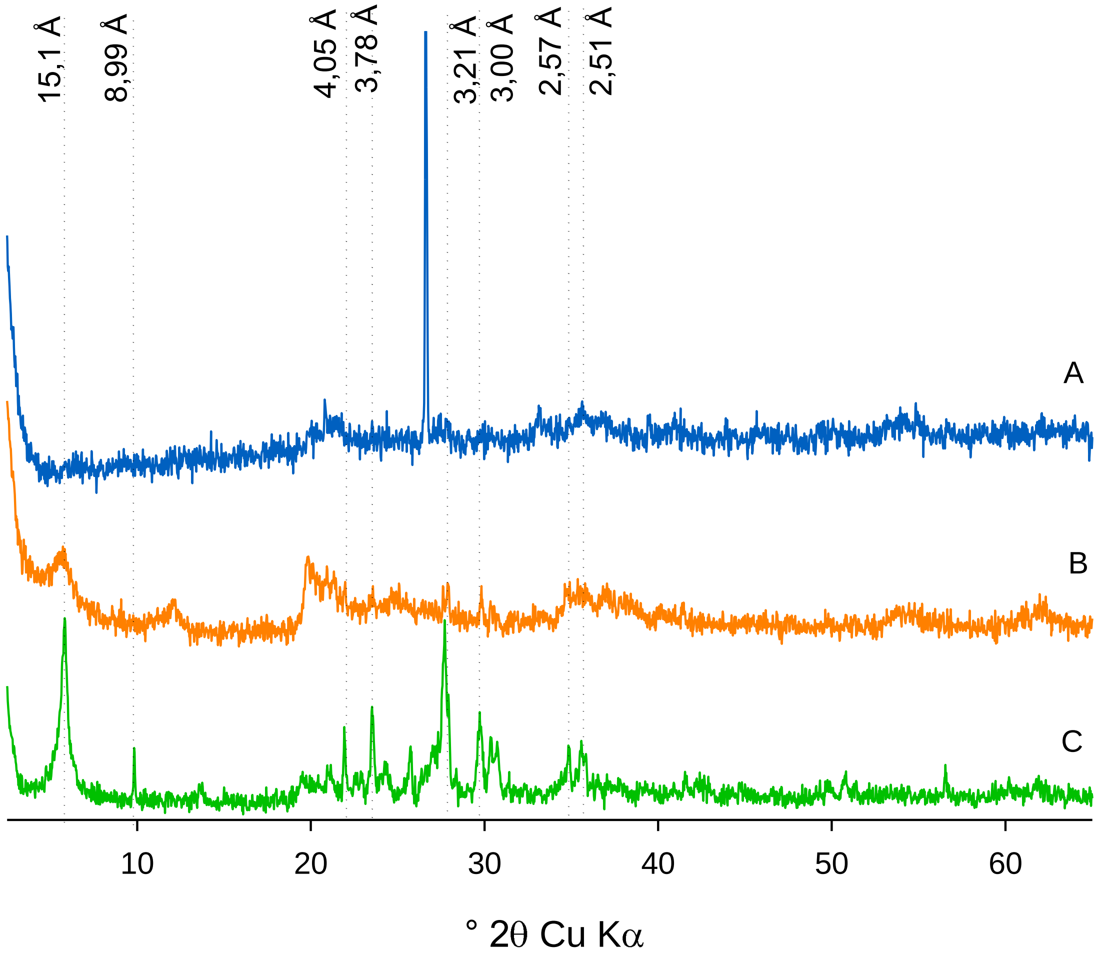
Annex 2. Experimental design with diferents grazing intensities in São Miguel das Missões.



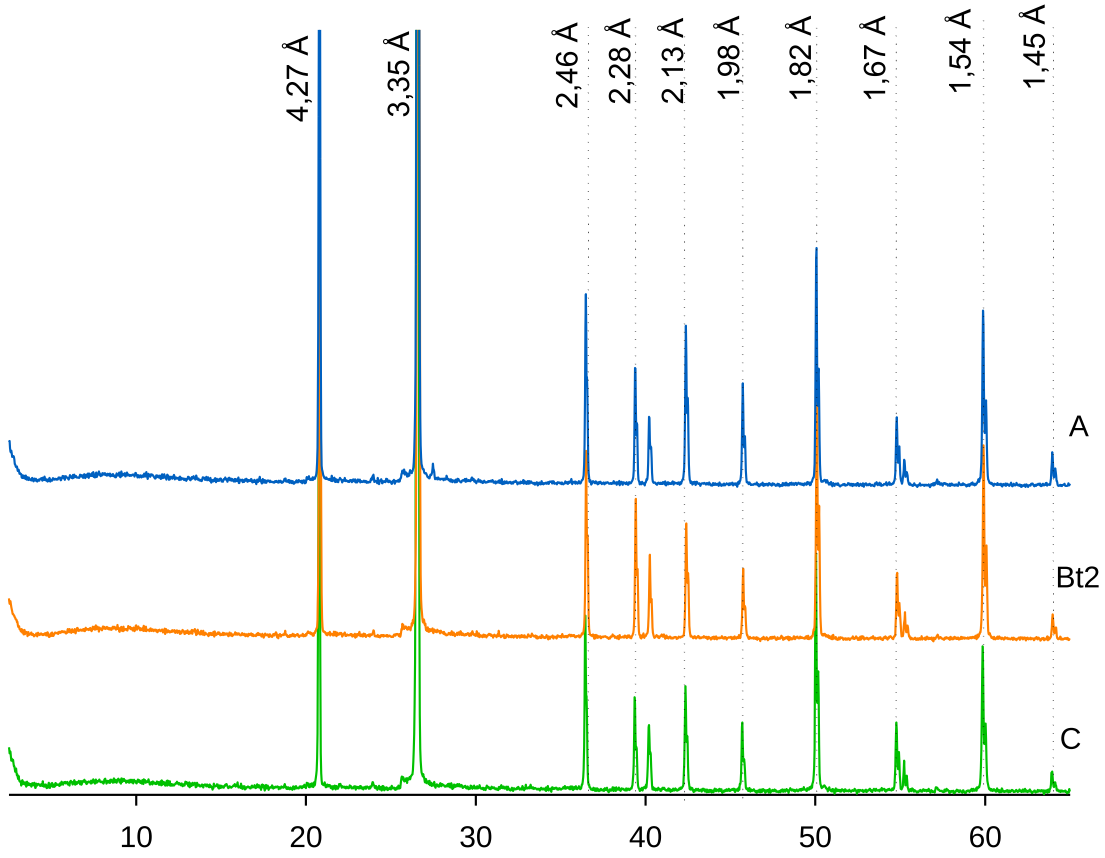
Annex 3. X-ray diffractograms of the sand fraction in the alteration profile of São Borja.



Annex 4. X-ray diffractograms of the sand fraction in the alteration profile of Taquara.



Annex 5. X-ray diffractograms of the sand fraction in the alteration profile of Eldorado do Sul.



Annex 6. Soil morphology.

Perfil do solo descrito e amostrado em São Borja

A) DESCRIÇÃO GERAL

Classificação: Chernossolo Ebânico Carbonático vertissólico
Localização e município: Rincão de São Lucas/ São Borja.
Coordenadas: 28°57’29.77” S/55°43’59.83” O
Situação, declive e cobertura vegetal sobre o perfil: Terço superior de coxilha; sob Campo nativo.
Altitude:105 m
Litologia e cronologia: Rochas ígneas extrusivas básicas (basalto).
Material originário: Produtos da alteração de basaltos.
Relevo local: suave ondulado a plano.
Relevo regional: suave ondulado a plano.
Erosão: Laminar ligeira a moderada.
Drenagem: moderadamente drenado.
Vegetação primária: Campo nativo.
Uso atual: Campo nativo.
Clima: Cfa (Koeppen).
Descrito e coletado por: Vanessa Bertolazi; Jessica Oliveira; Leonardo Bertolazi

B) DESCRIÇÃO MORFOLÓGICA

A 0-25 cm, (5Y 2,5/1, úmido); argila; fraca a moderada; blocos angulares e subangulares; pouco poroso; friável a firme, plástico e pegajoso; transição plana e clara.

B 25-85 cm, (5Y 2,5/1, úmido); argilosa; moderada média e grande blocos subangulares; poroso; cerosidade moderada e comum; friável, plástico e pegajoso; transição ondulada e gradual.

Cr 85/100 cm, bruno-forte (5Y 2,5/1, úmido); muito argilosa; forte pequena a média blocos subangulares; poroso; cerosidade forte e comum; firme, plástica e ligeiramente pegajosa; transição clara e ondulada.

Observações: Raízes muitas no A.

Perfil do solo descrito e amostrado em Taquara

A) DESCRIÇÃO GERAL

Classificação: Chernossolo Háplico Férrico típico
Localização e município: Rodovia RS-020, Sentido Cachoeirinha – Taquara, Coordenadas:
Situação, declive e cobertura vegetal sobre o perfil: Terço superior de coxilha; declividade local de 10 %, sob florestamento de Pinus sp.
Altitude: 219 m
Litologia e cronologia: Rochas ígneas extrusivas básicas (basalto).
Material originário: Produtos da alteração de basaltos.
Relevo local: ondulado.
Relevo regional: ondulado a forte ondulado.
Erosão: Laminar ligeira a moderada.
Drenagem: Bem drenado.
Vegetação primária: Floresta subtropical perenifólia.
Uso atual: Florestamento de Pinus sp. e pastagem.
Clima: Cfa (Koeppen).
Descrito e coletado por: Alberto Inda, Laurent Caner, Vanessa Bertolazi

B) DESCRIÇÃO MORFOLÓGICA

A 0-20 cm, bruno-avermelhado-escuro (5 YR 3/2, úmido); argila; moderada pequena e média blocos subangulares; poroso; muito friável, plástico e pegajoso; transição plana e clara.
B 20-70 cm, bruno-avermelhado-escuro (2,5 YR 3/4, úmido); argila; moderada média e grande blocos subangulares; poroso; cerosidade moderada e comum; friável, plástico e pegajoso; transição ondulada e gradual.
Cr 70/190 cm, bruno-forte (7,5 YR 4/6, úmido); muito argilosa; forte pequena a média blocos subangulares; poroso; cerosidade forte e comum; firme, plástica e ligeiramente pegajosa; transição clara e ondulada.
S1 190/450 cm.
S2 450-700 cm.

Observações: Raízes muitas no A, comuns no B, raras no Cr e ausentes no S1 e S2.

Perfil do solo descrito e amostrado em Eldorado do Sul

A) DESCRIÇÃO GERAL

Classificação: Argissolo Vermelho Distrófico típico
Localização e município: Estação agronômica da faculdade de Agronomia UFRGS – Eldorado do Sul.
Coordenadas: 30°51’31” S - 51°40’16” O
Altitude: 57 m
Litologia e cronologia: Rochas metamórfica (gnaisse).
Material originário: Metamorfismo de material granítico.
Relevo local: suave ondulado.
Relevo regional: suave ondulado a ondulado.
Erosão: Laminar moderada a forte.
Drenagem: Bem drenado.
Vegetação primária: Campo nativo.
Uso atual: Campo nativo.
Clima: Cfa (Koeppen).
Descrito e coletado por: Vanessa Bertolazi, Jessica Oliveira e Alberto Inda

B) DESCRIÇÃO MORFOLÓGICA

A 0-20 cm, bruno-escuro (7,5 YR 3/3, úmido); franco-argilo-arenosa; ligeiramente pegajosa, ligeiramente plástica.
AB 20-35 cm, bruno-escuro(7,5 YR 3/4, úmido); argilo-arenosa; ligeiramente pegajosa, ligeiramente plástica.
BA 35-55 cm, bruno-avermelhado-escuro(5 YR 3/3, úmido); argilo-arenosa; ligeiramente pegajosa, ligeiramente plástica.
Bt1 55-90 cm, bruno-avermelhado-escuro(5 YR 3/4, úmido); argilo-arenosa a argilosa; ligeiramente pegajosa, ligeiramente plástica.
Bt2 90-140 cm,vermelho(2,5 YR 4/7, úmido); franco arenosa; ligeiramente pegajosa, ligeiramente plástica.
Bt3 140-165 cm,vermelho(2,5 YR 4/8, úmido); franco argilosa; ligeiramente pegajosa, ligeiramente plástica.
Bw1 165-195 cm,vermelho(2,5 YR 4/8, úmido); franco argilosa; ligeiramente pegajosa, ligeiramente plástica.
Bw2 195-230 cm,vermelho(2,5 YR 4/8, úmido); franco argilosa; ligeiramente pegajosa, ligeiramente plástica.
BC 230-290 cm,vermelho(2,5 YR 4/8, úmido); mesclado/franco-argilo-arenosa; não pegajosa, não plástica.
C 290-360 cm,vermelho-escuro(10 R 3/4, úmido); franca; não pegajosa, não plástica.

Observações: Raízes comuns no A.