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CLAUDETE GINDRI RAMOS

POTENCIAL DE ROCHAS VULCÂNICAS SILICÁTICAS PARA REMINERALIZAÇÃO DE SOLOS

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RESUMO

A presente tese apresenta estudos de caracterização física, petrográfica, química e mineralógica e de disponibilidade de elementos nutrientes e potencialmente tóxicos em meios aquosos de resíduos gerados (subprodutos) nos processos de extração e britagem de rochas vulcânicas, provenientes de mineradoras localizadas no Distrito Mineiro do município de Nova Prata, no estado do Rio Grande do Sul. Além de realizar experimentos em casa de vegetação com aveia preta e milho para avaliar o potencial uso do subproduto como re-mineralizador do solo. A descrição petrográfica foi realizada em seções finas polidas por microscopia ótica. As fases mineralógicas foram identificadas por difração de raios-X (DRX). A composição química dos resíduos foi determinada por fluorescência de raios-X (FRX), espectrometria de emissão atômica por plasma indutivamente acoplado (ICP-AES) e espectrometria de massa com plasma indutivamente acoplado (ICP-MS). A composição geoquímica adicional foi realizada utilizando microscópio eletrônico de varredura (MEV) e de transmissão (MET), equipados com espectrômetros de raios-X de energia dispersiva (EDS). Para avaliar a disponibilidade de elementos nutrientes e elementos potencialmente tóxicos, foram realizados testes de lixiviação em diferentes meios aquosos e, posteriormente, as concentrações de Al, Ca, Fe, K, Mg, Na, P, S, Si, Mn, Li, Be, B, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Ba, La, Ce, Nd, Hf, Ta, W, Pb, Th e U foram determinadas na fase líquida por técnicas de ICP-MS e ICP-AES. As culturas de aveia-preta e, sequencialmente, de milho foram cultivadas em solo tratado com o subproduto em uma estufa agronômica. Cinco doses de subprodutos (0, 906, 1813, 3625 e 7251 kg ha-^{1}) foram adicionadas em vasos contendo solo, cada um com sete repetições. As respostas aos tratamentos foram avaliadas a partir da produção de matéria seca, estado nutricional das culturas e nas mudanças das propriedades do solo, após 70 dias de cada cultivo. Os resultados obtidos pela descrição petrográfica e DRX mostraram que os resíduos da mineração consistem em plagioclásio, K-feldspato, zeólita, esmectita e minerais opacos com apatita como mineral acessório. Os elementos maiores identificados nos resíduos via FRX, foram em média, SiO_2 (65%), Al_2O_3 (13,2%), Fe_2O_3 (7,1%), CaO (3,5%), K_2O (3,5%), Na_2O (3,1%) e, com menor concentração, o P_2O_5 (0,25%). Diversos macro e micronutrientes como Ca, Mg, P, K, Cu e Zn foram disponibilizados para os meios aquosos, indicando o potencial destas partículas para o desenvolvimento e manutenção da vida vegetal. Os teores dos elementos potencialmente tóxicos foram baixos não oferecendo riscos de contaminação ambiental. A adição de 3625 e 7251 kg ha^{-1} de subproduto aumentou substancialmente o rendimento de matéria seca das folhas de milho. A absorção de Ca pelas folhas de milho cultivadas em solo com 7251 kg ha^{-1} de subproduto foi significativamente maior que nas outras doses, e todas as doses de subprodutos promoveram altas concentrações de Mg e Ca. As quantidades acumuladas de Ca, K, Mg e P foram suficientes para suprir as necessidades nutricionais do milho. Melhorias nas propriedades do solo, como altos níveis de Ca, K e P, e baixos níveis de saturação de Al e Al trocáveis foram observados. O uso desses materiais geológicos é apresentado como uma alternativa para aumentar a produtividade agrícola e reduzir os impactos ambientais causados pelo uso excessivo de fertilizantes altamente solúveis. Os estudos aqui desenvolvidos pretendem contribuir para o processo de implementação de tecnologias limpas e preservação do meio ambiente, por meio do uso de resíduos derivados da mineração de rochas vulcânicas como insumo agrícola.

Palavras-chave: pó de rochas vulcânicas, resíduos da mineração, segurança ambiental, remineralizador de solos.

ABSTRACT

The present work describes studies of physical, petrographic, chemical and mineralogical characterization and of nutrient availability in aqueous media of mining of volcanic rocks wastes (by-products) from four companies located in the Mineiro District of the municipality of Nova Prata, Rio Grande do Sul Sul. In addition, to conducting a greenhouse experiments with black oats and corn to evaluate the potential use of the by-product as the soil re-mineralizer. The petrographic description was performed in thin sections polished by light microscopy. The mineralogical phases were identified by X-ray diffraction (XRD). The chemical composition of the residues was determined by X-ray fluorescence (FRX), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS). The additional geochemical composition was performed using scanning electron microscopy (SEM) and transmission (TEM), equipped with dispersive energy X-ray spectrometers (EDS). In order to evaluate the availability of nutrients and potentially hazardous elements, leaching tests were carried out in different aqueous media and, subsequently, the concentrations of Al, Ca, Fe, K, Mg, Na, P, S, Si, Mn, Li, Be, B, Sc, V, Cr, Co, Ni, Cu, Zn, Ga, Ge, As, Rb, Sr, Zr, Nb, Mo, Sn, Ba, La, Ce, Nd, Hf, Ta, Pb, Th, and U were determined in the liquid phase by ICP-MS and ICP-AES techniques. Black oats and sequentially maize crops were grown in soil treated with the byproduct in an agronomic greenhouse. Five doses of byproducts (0, 906, 1813, 3625 and 7251 kg ha-^{1}) were added to pots containing soil, each with seven replicates. Responses to treatments were evaluated from dry matter yield, crop nutritional status and changes in soil properties after 70 days of each crop. The results obtained by the petrographic description and XRD showed that the residues consist of plagioclase, potassium feldspar, zeolite, smectite and opaque minerals with apatite as an accessory mineral. The major elements found in the residues via XRF were SiO_2 (65%), Al_2O_3 (13,2%), Fe_2O_3 (7,1%), CaO (3,5%), K_2O (3,5%), Na_2O (3,1%) and P_2O_5 (0,25%). Several macro and micronutrients calcium, magnesium, potassium, phosphorus, cooper and zinc were available for the aqueous media, indicating the potential of these samples for the development and maintenance of plant life. The levels of the potentially toxic elements were low, offering no risk of environmental contamination. The addition of 3625 and 7251 kg ha^{-1} of byproduct substantially increased the dry matter yield of corn leaves. Ca uptake by corn leaves cultivated in soil with 7251 kg ha^{-1} of byproduct was significantly higher than in the other doses, and all doses of byproducts promoted high concentrations of Mg and Ca. The accumulated amounts of Ca, K, Mg and P were enough to supply the nutritional needs of maize. Improvements in soil properties such as high levels of Ca, K and P, and low levels of exchangeable Al and Al saturation were observed. The use of these geological materials is presented as an alternative to increase agricultural productivity and reduce the environmental impacts caused by excessive use of highly soluble fertilizers. The studies developed here intend to contribute to the process of implementation of clean technologies and preservation of the environment, using residues derived from the mining of volcanic rocks as agricultural input.

Keywords: volcanic rock powders, mining waste, environmental safety, soil remineralizers.

SUMÁRIO

1 INTRODUÇÃO

Os fertilizantes minerais solúveis são os principais responsáveis pela expansão e intensificação da agricultura, uma vez que fornecem os nutrientes (primários: N, P, K e/ou secundários: Mg, Ca, S, Na, B, Mn, Fe, Ni, Cu, Zn, Mo), que são removidos dos solos, tanto por absorção pelas plantas, quanto por lixiviação natural (CICERI et al., 2017). Alguns aspectos relevantes relacionados ao uso de fertilizantes minerais de alta solubilidade, na produção de alimentos, envolvem a qualidade nutricional das culturas, segurança alimentar e os impactos negativos causados pelo seu uso excessivo (MANNING e THEODORO, 2018). Um exemplo comum deste fato está relacionado à eutrofização das águas, causada pelo excesso de nutrientes ricos em fósforo e nitrogênio, que provocam o desenvolvimento de algas e, consequente, diminuição no teor de oxigênio dissolvido nos corpos d’água afetando os organismos dos recursos hídricos (HOU et al., 2013). Além disso, a maioria dos fertilizantes nitrogenados faz com que o solo se acidifique, afetando significativamente a biota do solo e a disponibilidade de nutrientes às plantas (HUANG et al., 2017).

É evidente que medidas globais precisam ser tomadas para reduzir os danos ambientais e econômicos da agricultura moderna e intensiva em insumos externos, especialmente em fertilizantes altamente solúveis (KORCHAGIN et al., 2019). Uma das medidas adotadas no Brasil, na década de 1970, por Leonardos et al. (1976) e Fyfe e Leonardos (1978), foi adicionar pó de rochas vulcânicas para recuperar a fertilidade do solo.

Diversos estudos demonstraram resultados positivos do uso de pó de rocha como remineralizadores de solo, tais como: uma única aplicação pode ser eficaz por até quatro ou cinco anos (MACHADO et al., 2016); os teores de P, K, Ca e Mg aumentam gradativamente ao longo do tempo com produtividade semelhante ou superior à da adubação solúvel (THEODORO; LEONARDOS, 2014); dimimuem a disponibilidade de elementos potencialmente tóxicos (PTEs) e alumínio (RAMOS et al., 2017); diminuem o risco de contaminação ou eutrofização de fontes de água, porque a rocha moída tem uma solubilidade gradual, ao contrário de fertilizantes altamente solúveis. Esta é uma questão relevante, uma vez que a aplicação contínua de fertilizantes, especialmente superfosfato simples, resultou na toxicidade associada ao cádmio em solos em todo o mundo (GREGER et al., 2016).

Outras vantagens do uso de pó de rochas como fertilizante dos solos, são a ampla distribuição de rochas vulcânicas na crosta terrestre (GILL, 2010), podendo ser utilizado como minerado (*in natura*) e não necessitando de processamento químico (SILVA et al., 2013).

No processo de extração e beneficiamento de rochas, em geral, são geradas quantidades consideráveis de materiais na forma de pó (DALMORA et al., 2016). No Brasil, o destino desses materiais tem sido, na maioria das vezes, a disposição inadequada em áreas de descarte das minerações, resultando em impactos ambientais que podem comprometer o ecossistema (SIMSEK et al., 2005). De acordo com Korchagin et al. (2019), esses resíduos também conhecidos como subprodutos, são acumulados em pilhas de material estéril ao longo de diferentes pedreiras, que precisam de uma disposição final ambientalmente adequada.

A aplicação destes subprodutos na agricultura deve ser considerada como uma alternativa para remineralizar solos esgotados de nutrientes e para reduzir o impacto ambiental desses materiais, requerendo a caracterização mineralógica e química e uma avaliação de seu desempenho agronômico (KORCHAGIN et al., 2019). Essa abordagem contribui tanto para resolver questões ambientais associadas à mineração de rochas quanto para criar uma alternativa mais limpa de fertilização dos solos.

Vale ressaltar, também, a importância estratégica para o Brasil encontrar alternativas sustentáveis à produção agrícola, tanto do ponto de vista ambiental e de qualidade do produto, como também de diminuir a dependência do país pela importação de insumos agrícolas. O fato da inclusão dos remineralizadores como nova categoria de insumo destinado à agricultura, através da Lei Nº 12.890/2013, deve ser visto como um marco a indicar mudanças de paradigma também na política da produção agrícola. A referida lei federal brasileira permite que os remineralizadores sejam usados para a nutrição das culturas, com especificações claramente definidas por regulamentação apropriada (BRASIL, 2016a, b). Os remineralizadores de solo são todos materiais minerais que possuem apenas redução de tamanho e classificação de tamanho por processos mecânicos e que alteram os índices de fertilidade do solo pela adição de macro e micronutrientes para culturas e melhoria das propriedades físicas ou físico-químicas ou da atividade biológica dos solos (BRASIL, 2013). Este cenário fornece um modelo alternativo e sustentável para que outros países possam explorar fontes geológicas locais e reduzir o uso de fertilizantes de alta solubilidade (MANNING; THEODORO, 2018).

Neste contexto, a presente tese pretende contribuir para o processo de implementação de tecnologias limpas e preservação do meio ambiente, através do uso de resíduos/subprodutos derivados da mineração de rochas vulcânicas como insumo agrícola.

Esta tese está organizada em seis seções. Na seção 1 a proposta da aplicação de pó de rochas vulcânicas na remineralização de solos é introduzida, são apresentados os objetivos deste trabalho e a integração dos artigos científicos. As seções 2, 3, 4 e 5 apresentam os artigos científicos intitulados "Chemical characterization, nano-particle mineralogy and particle size distribution of basalt dust wastes", autores: Dalmora, A. C., Ramos, C. R., Oliveira, M. L. S., Teixeira, E. C., Kautzmann, R. M., Taffarel, S. R., Brum, I. A. S., Silva, L. F. O. publicado no periódico Science of The Total Environment, em 2016; "A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer", autores: Ramos, C. G., Querol, X., Oliveira, M. L. S., Pires, K., Kautzmann, R. M., Oliveira, L. F. S. publicado no periódico Science of The Total Environment, em 2015; "Evaluation of the potential of volcanic rock waste from southern Brazil as a natural soil fertilizer", autores Ramos, C. G., Querol, X., Dalmora, A. C., Pires, K., Schneider, I. A. H., Oliveira, L. F. S., Kautzmann, R. M. publicado no periódico Journal of Cleaner Production, em 2017; "Evaluation of Soil Re-mineralizer from By-Product of Volcanic Rock Mining: Experimental Proof Using Black Oats and Maize Crops", autores: Ramos, C.G., dos Santos de Medeiros, D., Gomez, L. Silva, L. F. O., Schneider, I. A. H., Kautzmann, R. M. no periódico Natural Resourources Research, em 2019. Por fim, a seção 6, traz as principais conclusões obtidas pela autora e referências.

1.1 OBJETIVOS

1.1.1 Objetivo geral

Estudar a geoquímica dos resíduos de rochas vulcânicas produzidos no processo de extração e britagem de mineradoras do Distrito Mineiro do município de Nova Prata-RS, visando uma avaliação para aplicação prática destes materiais minerais como remineralizadores de solos.

1.1.2 Objetivos Específicos

1) Realizar a caracterização física e físico-química de 5 amostras de pó de rochas vulcânicas que constituem resíduos de britagem, provenientes de 4 mineradoras, localizadas no Distrito Mineiro do município de Nova Prata, no Rio Grande do Sul. Esta etapa inclui a determinação dos seguintes parâmetros: a) distribuição granulométrica; b) descrição petrográfica; c) composição química elementar e; d) composição mineralógica das partículas.

2) Avaliar a liberação de nutrientes minerais por meio de ensaios em laboratório, correlacionando as extrações de elementos contidos na rocha, ao tipo de solução lixiviante (simulando condições ácidas do solo), a granulometria do pó de rocha e a sua mineralogia.

3) Avaliar o potencial uso do subproduto como re-mineralizador do solo em culturas de aveia preta e milho.

4) Criar uma base de dados para nortear futuros estudos para caracterizar as propriedades mineralógicas e químicas visando a utilização do pó de rocha na substituição de fertilizantes altamente solúveis.

1.2 INTEGRAÇÃO DOS ARTIGOS CIENTÍFICOS

Os estudos realizados nesta tese seguem uma linha de pesquisa voltada à Tecnologia Mineral, Ambiental e Metalurgia Extrativa, para compreender os processos envolvidos na disponibilização de elementos nutrientes e potencialmente tóxicos, por meio de testes de lixiviação em soluções aquosas contendo pó de rochas vulcânicas e demonstrar suas potencialidades na fertilização e correção da acidez dos solos.

Os principais avanços deste trabalho foram:

1) Melhor entendimento dos processos geoquímicos de alteração dos minerais das rochas e liberação de nutrientes em função das soluções extratoras, da composição mineralógica e granulometria dos pós de rochas;
2) Incorporar ao conceito de agricultura ecológica a utilização de insumos minerais *in natura*, justificando cientificamente as qualidades que aporta ao solo;
3) Compreender que a utilização dos resíduos provenientes da extração e beneficiamento de rochas vulcânicas é uma alternativa adequada para resolver o problema dos subprodutos depositados fora das minas e diminuir o consumo de fertilizantes solúveis;
4) Transferência do conhecimento adquirido aos setores de mineração de rochas vulcânicas e agrícola, a partir da remineralização de solos, que é uma técnica promissora e viável, especialmente aos pequenos e médios agricultores que poderão ser beneficiados em termos de produtividade e custos mais acessíveis. Assim como, as empresas mineradoras da região de Nova Prata poderão transformar seus resíduos em produtos reduzindo de forma significativa os impactos ambientais e os custos elevados com disposições finais.

Anteriormente a este estudo, no artigo “A preliminary study of acid volcanic rocks for stonemeal application”, publicado em 2014, no periódico Environmental Nanotechnology, Monitoring & Management, foi realizada uma caracterização química e mineralógica detalhada de quatro amostras de pó de rochas provenientes das empresas Basel Indústria e Comércio de Minerais (amostra B1), Concresul Britagem (amostra C1), Sindicato da Indústria de Extração de Pedreiras de Nova Prata (amostra NP2) e Zilli Basalto e Britagem (amostra Z1), localizadas no Distrito Mineiro do município de Nova Prata, no estado do Rio Grande do Sul. Além disso, foram realizados testes de lixiviação em solução de ácido cítrico a 2% para avaliar a liberação de nutrientes pelas amostras. O objetivo do trabalho foi estimar o potencial agronômico das rochas como fertilizante do solo. As técnicas analíticas utilizadas foram: difração de raios-X (DRX), fluorescência de raios-X (FRX), espectrometria de massa com plasma indutivamente acoplado (ICP-MS) e lixiviação por extração com solução de ácido cítrico a 2%. A composição mineral determinada por DRX demonstrou que as amostras de pó de rochas possuem uma estrutura cristalina com predomínio de labradorita (73,5% para a amostra B1, 51% para a amostra C1, 52% para a amostra NP2 e 61% para a amostra Z1) e quartzo (9% para a amostra B1, 19% para a amostra C1, 15% para a amostra NP2 e 13% para a amostra Z1), augita nas amostras B1, NP1 e Z1 (6%, 12%, 13%, respectivamente), feldspato alcalino nas amostras B1 (5%) e C1 (15%), e esmectita nas amostras B1 (3%), C1 (7%) e NP2 (10%). A determinação dos óxidos por FRX das amostras apresentou valores médios de 65% de SiO_2, 13,2% de Al_2O_3, 7,1% de Fe_2O_3, 3,5% de CaO, 3,5% de K_2O e 3,1% de Na_2O. Os estudos de disponibilização de nutrientes em solução de ácido cítrico a 2% demonstraram que as amostras foram capazes de liberar macronutrientes como P (>100 mg L^{-1} por todas as amostras), K (152 mg L^{-1} pela amostra B1, 59 mg L^{-1} pela amostra C1, 104 mg L^{-1} pela amostra NP2 e 76 mg L^{-1} pela amostra Z1). As amostras também liberaram micronutrientes como Cu (8 mg l^{-1} pela amostra B1, 4 mg L^{-1} pela amostra C1, 2 mg L^{-1} pela amostra NP2 e 5 mg L^{-1} pela amostra Z1), Mn (3 mg L^{-1} pela amostra B1, 2 mg L^{-1} pela amostra C1, 6 mg L^{-1} pela amostra NP2 e l mg L^{-1} pela amostra Z1) e Zn (2 mg L^{-1} por todas as amostras), importantes para o desenvolvimento vegetal, embora em teores baixos. A capacidade de troca catiônica (CTC) e o conteúdo de argila da amostra NP2 foi significativamente superior às demais amostras. A amostra NP2 apresentou uma CTC de 11,6 cmolc dm^{-3} e um teor de argila de 51%, enquanto as amostras B1, C1 e Z1 apresentaram 8,8, 8,9 e 9.5 cmolc dm^{-3} e 12%, 6%, e 6%, respectivamente. Os elevados valores de CTC indicam que as amostras possuem capacidade de disponibilizar cátions para o solo, proporcionando assim a troca de nutrientes com o meio e confirmando seu potencial para utilização como remineralizadores de solos.

No artigo “Chemical characterization, nano-particle mineralogy and particle size distribution of basalt dust wastes” foram utilizadas as mesmas amostras de pó de rochas do artigo “A preliminary study of acid volcanic rocks for stonemeal application”. O objetivo deste trabalho foi avaliar os possíveis efeitos adversos à saúde humana e de poluição ambiental ocasionados pelas partículas ultrafinas e nanométricas que compõem as amostras de pó de rochas. Com base na caracterização geoquímica e nanomineralógica foi possível evidenciar que as amostras de pó de rochas vulcânicas apresentaram minerais suscetíveis ao intemperismo tais como labradorita, augita e feldspato alcalino, que representam entre 30 a 35% da composição mineralógica das amostras. Também foi constatada a presença de esmectita (de 1,4% a 4,7%) e barita (de 1% a 2%). Considerando o valor médio de 63% de fase amorfa para as rochas vulcânicas do Fácies Caxias, estes materiais em pó com granulometria < 500 µm, apresentariam uma tendência para se alterar em minerais secundários (argilominerais) liberando macro e micronutrientes. A análise granulométrica demonstrou que as amostras possuem uma ampla variação nos tamanhos de partículas. Nas partículas ultrafinas e nanométricas, foram identificados alguns elementos potencialmente tóxicos, que poderiam apresentar riscos de inalação à população das áreas urbanas localizadas em torno da zona de mineração de basalto. A implicação dessa observação é que o uso dessas partículas de tamanho nanométrico como fertilizante de solo poderia provocar problemas à saúde humana como doenças respiratórias, sugerindo a realização de futuros trabalhos abordando a toxicidade relacionada ao uso de pó de rochas, e com isso, avaliar efetivamente os riscos à saúde humana e de poluição ambiental.

Os estudos preliminares de caracterização química, mineralógica e potencial de liberação de macro e micronutrientes das amostras de pó de rochas apresentados no artigo do “A preliminary study of acid volcanic rocks for stonemeal application”, bem como da caracterização geoquímica e nanomineralógica apresentados no artigo “Chemical characterization, nano-particle mineralogy and particle size distribution of basalt dust wastes” motivou a seleção do material mineral da empresa Sindicato da Indústria de Extração de Pedreiras de Nova Prata, para dar continuidade aos estudos de liberação de nutrientes em diferentes meios aquosos. No artigo “A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer” foram investigadas as características mineralógicas, petrográficas e geoquímicas de uma amostra de pó de rocha vulcânica, com tamanho de partículas < 0,1 mm, proveniente da empresa Sindicato da Indústria de Extração de

Pedreiras de Nova Prata, localizada no Distrito Mineiro de Nova Prata. Além disso, foram avaliados através de testes laboratoriais de lixiviação, a liberação dos elementos nutrientes e potencialmente tóxicos. Os testes de lixiviação foram realizados em água Milli-Q; solução de ácido cítrico a 1% e 2%; e solução de ácido oxálico a 1% e 5%. Os resultados obtidos neste estudo permitiram concluir que a amostra de pó de rocha vulcânica estudada pode ser utilizada como fonte de macro e micronutrientes para o solo, pois apresenta em sua composição uma matriz amorfa vítrea facilmente intemperizável, bem como os minerais plagioclásio e piroxênio, facilmente alteráveis sob condições exógenas. Os testes de lixiviação em meios aquosos ácidos demonstraram influência na velocidade de liberação desses minerais, tornando o processo de liberação de nutrientes mais rápido. As maiores concentrações de elementos lixiviados ao longo do período experimental foram observadas quando a solução de ácido oxálico 1% foi utilizada como extrator. No entanto, os testes de liberação de nutrientes em soluções ácidas mostraram que apenas uma fração dos minerais é solúvel e que os elementos de alta toxicidade tais como As, Cd e U, entre outros, apresentaram baixa biodisponibilidade por estarem presentes na amostra em baixas concentrações. As características de desvitrificação da matriz observadas na amostra estudada tornam a rocha interessante para remineralização de solos, pela facilidade de desestabilização do vidro sob condições exógenas. Com isso, há grandes vantagens do uso agronômico de rochas vulcânicas como fertilizantes, como por exemplo: a) baixa solubilidade de nutrientes na água de Milli-Q, resultando em menores perdas por lixiviação e fixação e; b) alta solubilidade dos minerais em soluções de ácidos orgânicos de baixo peso molecular, semelhante a composição das soluções dos solos, resultando na liberação lenta, gradual e eficiente dos mesmos para as culturas. Portanto, o pó de rocha vulcânica tem um potencial promissor como fonte alternativa de fertilizante, de liberação lenta (pois diminuem as perdas de nutrientes por lixiviação), em culturas que demandem nutrientes a longo prazo, como por exemplo, culturas perenes.

O artigo “Evaluation of the potential of volcanic rock waste from southern Brazil as a natural soil fertilizer” foi desenvolvido para avaliar as propriedades químicas e mineralógicas da mesma amostra usada no artigo “A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer”, porém com tamanhos de partículas < 90 µm e < 38 µm, para os testes de lixiviação. Adicionalmente, foi utilizada uma solução extratora composta por uma mistura de ácidos orgânicos de baixo peso molecular, nos testes de lixiviação. Os estudos petrográficos utilizando microscopia ótica convencional e microscópio eletrônico de varredura permitiram verificar que a amostra é composta principalmente por piroxênio, feldspato e conteúdo variável de matriz vítrea. Os elementos majoritários detectados na amostra por FRX foram Ca, Si, Al, Fe e com menores concentrações o K e P.

Nutrientes importantes como Ca, K, Mg, P e Si foram transferidos para as soluções ácidas, indicando o potencial significativo e viabilidade desses resíduos para serem usados como remineralizadores. Destaca-se que a solução de ácido oxálico a 1% apresentou a melhor eficiência de extração. As concentrações de elementos potencialmente tóxicos também foram baixas, corroborando os resultados obtidos no artigo “A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer”. As principais vantagens agronômicas do uso de resíduos de rochas vulcânicas como fertilizante podem ser a baixa solubilidade de nutrientes na água, resultando em perdas reduzidas por lixiviação e fixação, e a liberação lenta de nutrientes importantes para o desenvolvimento das plantas. Os resultados deste estudo são de grande relevância para o setor de mineração e para a agricultura da região, porque constituem uma alternativa segura para o seu descarte e diminuir o consumo excessivo de fertilizantes solúveis.

No artigo “Evaluation of Soil Re-mineralizer from By-Product of Volcanic Rock Mining: Experimental Proof Using Black Oats and Maize Crops foi apresentado um estudo de caracterização física, petrográfica, mineralógica e química da mesma amostra usada nos artigos “A preliminary evaluation of volcanic rock powder for application in agriculture as soil a remineralizer” e “Evaluation of the potential of volcanic rock waste from southern Brazil as a natural soil fertilizer”, além de em experimento em casa de vegetação com aveia preta e milho para avaliar o potencial uso do subproduto como o re-mineralizador do solo. A amostra de subproduto foi obtida de uma pedreira no distrito de mineração de Nova Prata, no sul do Brasil. A distribuição do tamanho de partículas do subproduto e do solo foi determinada por peneiramento. A descrição petrográfica da rocha foi realizada em uma seção fina polida por microscopia ótica. As fases mineralógicas do solo e da rocha foram identificadas por DRX. A composição química do subproduto e do solo foi determinada por FRX. Espectrometria de massa com plasma indutivamente acoplado foi utilizada para determinar elementos potencialmente tóxicos, como, Cd, Hg e Pb no subproduto. A composição química adicional do subproduto e do solo foi analisada utilizando um microscópio electrônico de varredura e espectroscopia de energia dispersiva. As culturas de aveia-preta e, sequencialmente, de milho foram cultivadas em solo tratado com o subproduto em uma estufa agronômica. Cinco doses de subprodutos (0, 906, 1813, 3625 e 7251 kg ha^{-1}) foram adicionadas em vasos contendo solo, cada um com sete repetições. As

respostas aos tratamentos foram avaliadas a partir da produção de matéria seca, estado nutricional das culturas e nas mudanças das propriedades do solo, após 70 dias de cada cultivo. Os resultados mostraram que o subproduto é composto por plagioclásio, K-feldspato, quartzo, clinopiroxênio, esmectitas e minerais opacos com apatita como mineral acessório. A adição de 3625 e 7251 kg ha^{-1} de subproduto aumentou substancialmente o rendimento de matéria seca das folhas de milho. A absorção de Ca pelas folhas de milho cultivadas em solo com 7251 kg ha^{-1} de subproduto foi significativamente maior que nas outras doses, e todas as doses de subprodutos promoveram altas concentrações de Mg e Ca. As quantidades acumuladas de Ca, K, Mg e P foram suficientes para suprir as necessidades nutricionais do milho. Melhorias nas propriedades do solo, como altos níveis de Ca, K e P, e baixos níveis de saturação de Al e Al trocáveis foram observados. Os resultados do estudo sugerem que o subproduto pode ser usado como re-mineralizador do solo.

CHEMICAL CHARACTERIZATION, NANO-PARTICLE MINERALOGY AND PARTICLE SIZE DISTRIBUTION OF BASALT DUST WASTES

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2 CHEMICAL CHARACTERIZATION, NANO-PARTICLE MINERALOGY AND PARTICLE SIZE DISTRIBUTION OF BASALT DUST WASTES

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ABSTRACT

Understanding the geochemistry of basalt alteration is central to the study of agriculture systems. Various nano-minerals play an important role in the mobilization of contaminants and their subsequent uptake by plants. We present a new analytical experimental approach in combination with an integrated analytical protocol designed to study basalt alteration processes. Recently, throughout the world, ultra-fine and nano-particles derived from basalt dust wastes (BDW) during "stonemeal" soil fertilizer application have been of great concern for their possible adverse effects on human health and environmental pollution. Samples of BDW utilized were obtained from companies in the Nova Prata mining district in southern Brazil for chemical characterization and nano-mineralogy investigation, using an integrated application of advanced characterization techniques such as X-ray diffraction (XRD), High Resolution-Transmission Electron microscopy (HR-TEM)/ Energy Dispersive Spectroscopy (EDS) / (selected-area diffraction pattern) SAED, Field Emission-Scanning Electron Microscopy (FE-SEM/EDS), and granulometric distribution analysis. The investigation has revealed that BDW materials are dominated by SiO_2, Al_2O_3, and Fe_2O_3, with a complex micromineralogy including alkali feldspar, augite, barite, labradorite, hematite, heulandrite, gypsum, kaolinite, quartz, and smectite. In addition, we have identified a number of trace metals such as Cd, Cu, Cr, and Zn, that are preferentially concentrated into the finer, inhalable, dust fraction and, thus, could present a health hazard in the urban areas around the basalt mining zone. The implication of this observation is that use of these nanometric-sized particulates as soil fertilizer may present different health challenges to those of conventional fertilizers, inviting future work regarding the relative toxicities of these materials. Our investigation on the particle size distribution, nano-particle mineralogy and chemical composition in typical BDW samples highlights the need to develop cleaning procedures to minimise exposure to these natural fertilizing basalt dust wastes and is, thus, of direct relevance to both the industrial sector of basalt mining and to agriculture in the region.

Keywords: basalt dust wastes; nano-mineralogy; detailed waste geochemistry; XRD, HRTEM/EDS/SAED, and FE-SEM/EDS; environmental safety

2.1 INTRODUCTION

Alteration of basalt is a common process in geosciences and agricultural tests. However, the current scientific understanding of the kinetic laws controlling such processes is very limited. Natural silicates, oxides, sulphates, and carbonates represent important sinks for metals/metalloids in soils through different immobilisation mechanisms including sorption, surface complexation or co-precipitation. Rock waste application as agricultural fertilizer has a long history. For example, Leonardos (1976) reported centuries-old cases of the implementation of rock fragments in soil in Brazil. In recent years, many studies have been developed in recent years with the aim of applying rock reject material to soils, with positive results for productivity (DA SILVA et al., 2011; LOURENÇO, 2011; PRATES, 1998; PLEWKA et al., 2009). This application of mineral particles as soil fertilizers, also known as the stonemeal technique, can provide important macronutrients such as Ca, K, Mg, N, P, Si, and S, as well as micronutrients such as Cr, Cu, Fe, Mn, Zn, and Na, to the plant, water, soil, and interfaces of the biosphere (RAMOS et al., 2014).

In general, agricultural practices, especially in tropical regions, mostly rely on acid soils with low productivity without technology intervention. A great challenge in using basalt dust for agricultural activities is to obtain natural materials with a special ability to restore productivity. In Brazil, in the current years, increased construction and building activities have promoted an exploitation growth of basaltic, which are widely applied as ornamental rocks (NUNES et al., 2014). Toscan et al., (2007) investigated the productive processes of 110 basalt mining companies in Nova Prata, Rio Grande do Sul State, Brazil (Figure 5) and revealed the existence of 647,000m^3 of basalt waste disposed in piles along with a monthly production of 7000m^3.

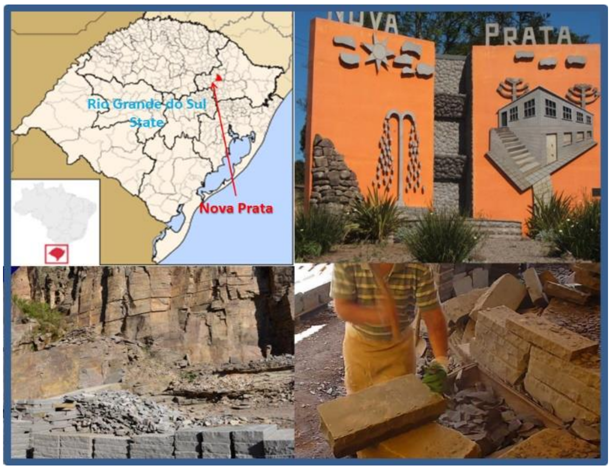

Figure 5. Location of basalt mining are where samples for this study were obtained (Nova Prata).

Later studies (KAUTZMANN, 2011; RAMOS et al., 2014) have further demonstrated the growth of this sector, estimating a generation of 17,000 tons of waste per month from 256 companies in the same region during 2011. The Basalt Dust Waste (BDW) use for stonemeal application as a fertilizer material is increasing in Brazilian agricultural production, being applied, for example, in soil amendment, cattle feeders, and soil stabilization. New or combined processes are manufacturing high grade and expensive materials for multiple specialized applications, although so far there remains little information with regard to the nanomineralogy of the basalt dusts involved, especially with regard to their utilization, handling, storage, and disposal. In an industrial context, BDW usually refers to wastes produced during basalt mining, and the BDW studied in this investigation is mainly used locally as soil fertilizers.

Basalt dusts contain several agricultural essential elements (Ca, Mg, K, P, S and Fe) and beneficial elements (Na and Si) for crops. Basalt dusts are naturally obtainable (GILLMAN et al., 2002; KLEIN, 2002) and are environmentally sound as a soil amendment. Curiosity in the efficiency of crushed basalt to amend poor soils (especially highly weathered soils) and improve crop growth has been shown by D’Hotman (1961) who reported that basalt-treated soils remarkably increased sugarcane yield in Mauritius with concomitant long residue effect.

Previous studies have been conducted on the characterization of BDW-derived ultra-fine/nanoparticles (NUNES et al., 2014; RAMOS et al., 2014). This paper contributes further information by offering a study on the micromineralogy and geochemistry of the BDW in order to provide more data on possible applications.

Nanoparticles and ultrafine particles are thought to induce more severe health impacts than larger particles (OSMOND-MCLEOND et al., 2011; GUZMAN et al., 2006). The high degree of comminution of rock dusts generated in rock crushing facilitates the exposure to minerals, especially when the rocky matrix is microcrystalline, such as in volcanic rocks which are the focus in this study. Reducing the particle size increases the exposure to individual mineral phases and the consequent action of weathering which causes mineral alteration, including clay minerals generation, and elements to become released in the dissolved phase (RAMOS et al., 2014). The rock powder produced by this process is a low cost material with decentralized production and is recommended for the remineralization of soils (GILLMAN, 1980; GILLMAN et al., 2001). This technique is considered an alternative to reduce the use of industrial fertilizers in the soil and its increasingly widespread use emphasizes the need to investigate and characterize these nanometric BDW minerals in order to predict and improve their hazards to possible human health. In this context the present work provides geochemical characterization of basalt dust wastes from four ore deposits, examining particle size distributions and nano-compound occurrences.

2.2 EXPERIMENTAL SECTION

The experiment was carried within the Nova Prata Mining District, there is a range of basic, intermediate, and acidic volcanic rocks. At the top and middle part of the plateau, acidic rocks are interspersed with basic and intermediate rocks, whereas at the base there are only basic and intermediate rocks (PRATES, 1998). Samples were obtained from Basel Industry and Trade Minerals (sample B1, latitude: 28º36’39,38”S and longitude: 51º51’33,56’W), Concresul Crushing (sample C1, latitude: 29º07’39,30”S and longitude: 51º29’37,50’W), Union of the Industry of Extraction Quarries of Nova Prata (sample NP2, latitude: 28º46’27,37”S and longitude: 51º38’16,61’W), and Zilli and Basalt Crushing (sample Z1, latitude: 28º45’09,20”S and longitude: 51º38’38,16’W). These samples allow a preliminary assessment of the potential of the material sampled in the stonemeal technique.

The BDWs correspond to the acid volcanic effusions which are generally at higher stratigraphic levels in the volcanic succession. This lithology is described by Nardy et al. (2008) as belonging to the Palmas Member within the Serra Geral Formation, which was generated by intensive volcanism during the transition between the Jurassic and Cretaceous periods, when the splitting of Gondwana caused the separation of the South American continent from Africa and formed the South Atlantic Ocean. These rocks exhibit only slight variability in composition and so display broadly homogeneous mineralogical characteristics dominated by plagioclase and pyroxene (JUCHEM et al., 2007). For this study, five samples (4 kg) of BDW were collected using a polypropylene shovel from each ore deposit and were subsequently transferred to clean polypropylene bags. These samples were then mixed, resulting in a composite sample of 20 kg that was then submitted to homogenization and subsequent quartering procedures according to standard methods for mineral particles (OLIVEIRA; AQUINO, 2007), resulting in two portions of 10 kg each. One portion (10 kg) was reprocessed by quartering, resulting in ten samples of approximately 1 kg that were stored in plastic bags and randomly selected to use in this work (stored in polypropylene containers in a dry system containing phosphorous pentoxide).

The major crystalline mineralogy of BDWs was evaluated by X-ray powder diffraction (XRD) at the Unidade de Raios X - RIAIDT of University of Santiago de Compostela (Spain). The BDWs were homogenized and compacted on the sample holder to obtain the uniform surface required for this technique (OLIVEIRA et al., 2012a; OLIVEIRA et al., 2012b). The sample was spun during the data collection in order to get the best peak profile and to minimize the preferred orientation effect. The samples were analysed with a Philips powder diffractometer fitted with a Philips “PW1710” control unit, Vertical Philips “PW1820/00” goniometer and FR590 EnrafNonius generator. This instrument was equipped with a graphite diffracted-beam monochromator and Cu-radiation source $\lambda(K\alpha1) = 1.5406Å$, operating at 40 kV and 30mA. The XRD pattern has been collected by measuring the scintillation response to Cu $K\alpha$ radiation versus the 2θ value over a 2θ range of 2-65, with a step size of 0.02° and counting time of 3s per step. The semi-quantification of the individual crystalline phase (minerals) in each sample was determined using the program Match! (©2003-2011 CRYSTAL IMPACT, Bonn, Germany).

Particle size analyzes were performed at the Soil Laboratory in the Center for Environmental Studies, University Center LaSalle (UNILASALLE), and at the Laboratory of

Mineral Processing (LAPROM), Federal University of Rio Grande do Sul (UFRGS). For the fine material (particle size less than 500 µm), a Silas laser diffraction granulometer was used.

The semi-quantitative mineralogical analysis was performed at the Laboratory of X-ray Diffraction of UFRGS, with a Siemens diffractometer, Model Bruker – AXS D5000. The data were processed using Diffrac Plus® Siemens – Bruker – AXS, version 11 software. For the electron beam methods, a FE-SEM (Zeiss Model ULTRA plus with charge compensation) and an HR-TEM (200-keV JEOL-2010F, equipped with a scanning - STEM unit) was used to characterize the extent of sintering and/or agglomeration in the BDWs containing the nanominerals to be able to identify the possible presence of hazardous elements (CERQUEIRA et al., 2012; CERQUEIRA et al., 2011). The HR-TEM and FE-SEM with EDS capabilities provide a view of the nanoparticle morphology and allow the estimation of the individual particle composition (SILVA; DABOIT, 2011). An Au-grid in the HR-TEM was utilized in order to track changes in the Mo and Cu contents caused by Mo-Cu-rich nanominerals (e.g. Fe-oxides, sulphates, and sulphides) and ultrafine particles. Information about the crystallinity and symmetry of the nanominerals and hazardous volatile elements (HVEs) of ultrafine/nanoparticles was obtained by utilizing a microbeam diffraction mode (MBD), selected-area diffraction pattern (SAED), and fast Fourier transformation (FFT) of the HR-TEM images. The *d*-spacing obtained were compared with the International Centre for Diffraction Data sheets (ICDD, 2011) (ICDD, 2011) for the inorganic compound powder diffraction file (PDF) database to identify the crystalline phases. The detection limit of the EDS (coupled with FE-SEM and HR-TEM) analyses is ~1 wt%, making it a useful method for characterization of major elements (> 1%) in the detected individual ultrafine particles only (SILVA et al., 2011e). It was not used for analysis of trace elements in the samples.

2.3 RESULTS AND DISCUSSION

The granulometric distribution of the <500µm fraction obtained by laser diffraction in the four samples is shown in Figure 6. Only the sample C1 has a different behavior with no clay fraction.

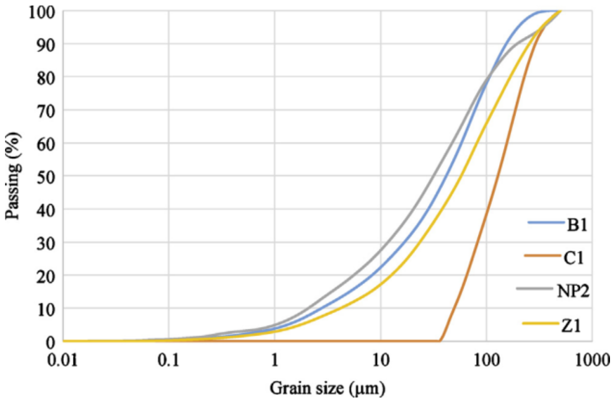

Figure 6. General granulometric distribution curves of the < 500 μm fraction obtained by laser diffraction for all studied samples.

The FE-SEM/EDS and HR-TEM/SAEDMBD/FFT/EDS studies of these samples revealed regions with a stacked, layered microcrystalline arrangement with lattice fringes ranging from 1.2 to 3.6 Å (e.g. Figure 7).

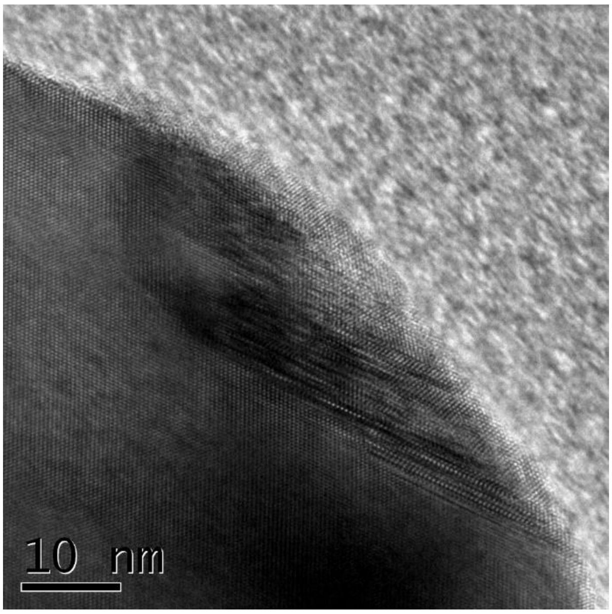

Figure 7. General HR-TEM image of polymorph silicon matter showing lattice fringes.

Thus, all XRD, FE-SEM, and HR-TEM, coupled with EDS analyses, demonstrate the presence of amorphous clays, alkali feldspar, albite/anorthite, augite, barite, clinochlore, cristobalite, illite, labradorite, laumonite, hematite, heulandrite, gypsum, kaolinite, mordenite, montmorillonite, quartz, sanidine, smectite, and X-zeolite as well as a range of metals and metalloids (e.g. Figure 8).

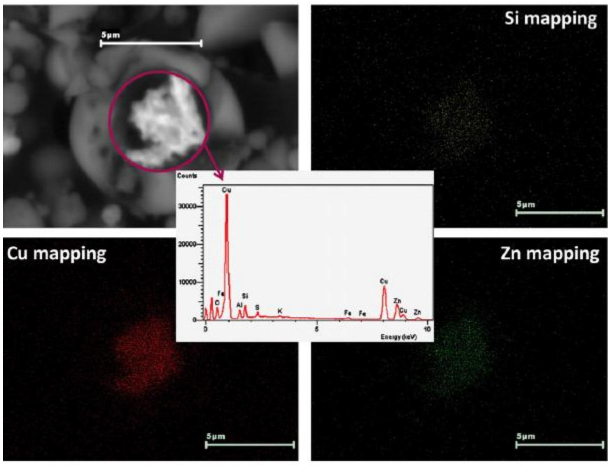

Figure 8. FE-SEM image of spherical hematite and Al–Si–O–S–Fe–K–Cu–Zn amorphous clay.

The FE-SEM/E advanced electron bean DS results present an excellent occurrence relation between P, Nd, Ce, La, and Th (element maps by EDS) suggesting that the fine particles detected in BDWs probably include the accessory phosphate mineral monazite, containing mixed amorphous/crystalline phases. A correlation also exists between Al, Si, and Fe, suggesting that amorphous aluminosilicates are present around these particles. These observations on the nano-scale mineral assemblages present in these fertilizer dusts can be utilised in the interpretation of the chemical data, particularly with relevance to substitutions occurring in the nanoparticle structures. It is now understood that the relatively high concentrations of the hazardous elements are mostly due to the abundant ultrafine and nanominerals as indicated by FE-SEM/EDS measurement. The BDW samples are therefore classified as complex heterogeneous materials composed both of silicate material and of inorganic amorphous materials associated with potentially hazardous metalliferous trace elements.

Several larger amorphous and crystalline particles (between 1-26µm in size) of Fe-oxides, especially hematite (Figure 9), occur in all BDW samples, as revealed by the XRD, FE-SEM/EDS, and HR-TEM/EDS/SAED/FFT analyses.

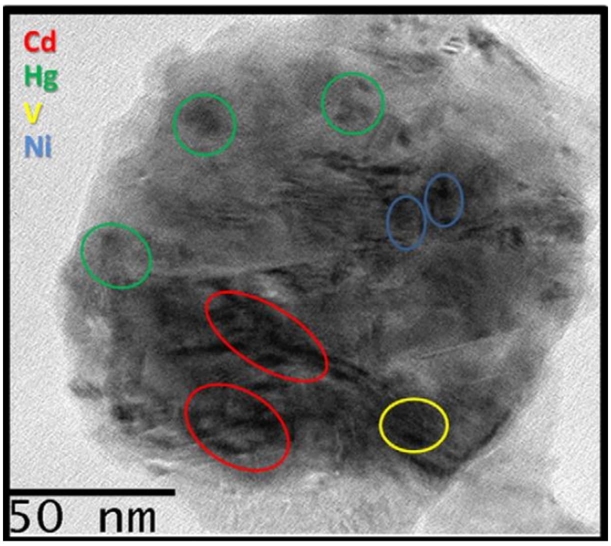

Figure 9. Bright-field HR-TEM image of nanohematite agglomerates detected by SAED and EDS. Complex interaction between spherical hematite containing hazardous elements (Cd, Hg, Ni, and V) and amorphous Al–Si-nanominerals.

Advanced environmental studies have recognized the importance of iron oxide and hydroxides to metal sorption and the fate of transportation (SILVA et al., 2011b; SILVA et al., 2011d; SILVA et al., 2011c), but only recently has it been shown that the Fe-hydroxide mineral structure, stability, and reactivity may change as a function of particle size (HOFMANN et al., 2005). Amorphous phases and ultra-fine/nano-minerals with Fe-Al nano- (hydr) oxides in ultrafine/nanoparticles might act as major absorption sites for hazardous elements. Traditionally, investigators have compared element sorption edges on different mineral samples without accounting for the differences in specific surface area within the reaction vessels (PONNURANGAM et al., 2012).

The BDW ultra-fine/nanoparticles, as presently observed, may form various strong aggregate types. Forces at the mineral-water interface may drive aggregation, particularly at ionic strengths high enough to cause collapse of the double layer, and it has been shown that the mechanism of aggregation (pH, ionic strength, drying, and freezing) of nanoparticles can affect the sorption, retention, and speciation of elements (GILBERT et al., 2009). These processes may also remove the reactive surface area from contact with a metal sorbate (BARTON et al., 2011), and they have been linked to slow metal adsorption kinetics involving nano-particulate Fe nano-(hydr) oxyhydoxides (HOFMANN et al., 2005). In general, they can also greatly affect nanoparticle mobility through porous media (GUZMAN et al., 2006), thus affecting the mobility of absorbed hazardous elements present with the BDW samples.

2.4 CONCLUSIONS

A multifaceted approach presented here and the combination of mineralogical investigations and geochemical data with respect to different basalt conditions are essential to investigate the role of ultra-fine and nano-minerals application in soils. The present work combines mineralogical techniques such as XRD, HR-TEM/EDS/SAED, and FE-SEM/EDS to better understand the behaviour of BDW atmospheric matter produced during basalt mining process. The rock dusts currently being tested as viable alternatives to replacing nutrients in cultivated soils have complex compositions with a range of different particle sizes and micromineralogies. These ultra-fine/nano-fertilizers have a high surface area to volume ratio and their surface properties will presumably be more effective at a lower dose, offering a potential advantage over conventional fertilizer. However, we identify within these materials a number of metalliferous trace elements, some of which could present inhalation hazards to urban areas around the basalt mining zone. The implication of this observation is that use of these nanometric-sized particulates as soil fertilizer may present different health challenges to those of conventional fertilizers, inviting future work regarding the relative toxicities of these materials in order to conduct a realistic assessment of the human health and environmental pollution risks from BDWs. Our investigation on the particle size distribution, nanoparticle mineralogy and, chemical composition of typical BDW samples highlights the need to develop cleaning procedures to minimise exposure to these natural fertilizing basalt dust wastes and is of direct relevance to both the industrial sector of basalt mining and to agriculture in the region.

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A PRELIMINARY EVALUATION OF VOLCANIC ROCK POWDER FOR APPLICATION IN AGRICULTURE AS A SOIL REMINERALIZER

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3 A PRELIMINARY EVALUATION OF VOLCANIC ROCK POWDER FOR APPLICATION IN AGRICULTURE AS SOIL A REMINERALIZER

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ABSTRACT

Mineralogical and geochemical characteristics of volcanic rock residue, from a crushing plant in the Nova Prata Mining District, State of Rio Grande do Sul (RS), Brazil, in this work named rock powder, were investigated in view of its potential application as soil ammendment in agriculture. About 52,400 m^3 of mining waste are generated annually in the city of Nova Prata without a proper disposal. The nutrients potentially available to plants were evaluated through leaching laboratory tests. Nutrient leaching tests were performed in Milli-Q water; citric acid solution 1% and 2% (AC); and oxalic acid solution 1% and 5% (AO). The bulk and leachable contents of 57 elements were determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Mining waste were made up by CaO, K_2O, SiO_2, Al_2O_3, Fe_2O_3, and P_2O_5. The analysis by X-ray diffraction (XRD) showed the major occurence of quartz, anorthite, cristobalite, sanidine, and augite. The water leachable concentrations of all elements studied were lower than 1.0 mg/kg, indicating their low solubility. Leaching tests in acidic media yield larger leachable fractions for all elements being studied are in the leachate of the AO 1%.

Keywords: volcanic rock, mining waste, leaching, nutrient availability, particle characterization, adding value to the residue

3.1 INTRODUCTION

Brazil has an important role in the world mineral industry. However, as regards agro-minerals, minerals used in agriculture, the country has not been able to meet the internal needs, making it dependent on the import of some minerals. Brazil is the fourth largest consumer of fertilizers in the world but is responsible for only 2% of world production of fertilizers (IBRAM, 2012). The country imports 91% of potassium and 51% of phosphate required, both essential for the fertilizer industry (IBRAM, 2012).

As Brazil is one the leading agricultural producers in the world and has been showing a growing demand in recent years, the use of fertilizers has intensified with the purpose of increasing productivity. A consequence of this is the trade deficit in the sector of industrial minerals, due to the large volume of imports of phosphate, potassic, and sulphuric fertilizers (OLIVEIRA; FERREIRA, 2007). The main phosphate national reserve is located in the municipality of Tapira in the State of Minas Gerais, Brazil with approximately 1 Gt of ore (SOUZA; CARDOSO, 2008). In Brazil, the potassium fertilizer production restricted to mine/mill complex of Taquari-Vassouras, in Sergipe, leased to the Companhia Vale, which produced 383 kt of K_2O in 2008 (MME, 2009). The potassium produced in Brazil is almost entirely used as fertilizer, around 95%, with 90% in the form of potassium chloride (OLIVEIRA; FERREIRA, 2007).

One of the main factors justifying the use of volcanic rock powder in agriculture refers to the possibility of reducing the use of chemical fertilizers. Studies report that the economy in the cost of production can reach up to 50% with the use of this technique (THEODORO, 2000).

Most Brazilian regions have reserves of volcanic rock, rich in elements such as phosphorus, calcium, and magnesium. The effects generated by fertilization using rock powder may extend by up to four or five consecutive years because of the slow release of nutrients (THEODORO, 2000). With that, the study and development of new fertilizers have grown in recent years and the use of rock powder in agriculture (stonemeal) has presented advantages, mainly to costs, transformation of waste in products, and market expansion for new products of quarries (LOUREIRO et al., 2009). The application of rock powder for remineralizing of soil is related to its mineral characteristics and its interaction with the environment in which it will be applied, in order to improve the conditions of soil fertility (THEODORO, 2000).

Around 52400 m^3/a of waste of mining are generated in the city of Nova Prata. However, only a fraction of this waste is intended for the production of gravel and the rest remains in the quarry without a proper disposition (TOSCAN et al., 2007). In this region, only one gravel mining company sells the powder in particle size fraction <0.1-mm.

The volcanic rock is composed mainly of SiO_2, Al_2O_3, Fe_2O_3, MnO, MgO, Na_2O, K_2O, and CaO (RAMOS et al., 2014; NUNES et al., 2014).

Given that Brazil is one of the largest suppliers of food in the world, the study of volcanic rock powder as a potential fertilizer with respect to the content and release of nutrients and to the economics and market viability is still required to provide the development of sustainability policies for the mining activity and food production. Thus, the main objectives of this study are: 1) characterize a residue of volcanic rock from the city of Nova Prata, RS; 2) evaluate the leaching tests of rock powder, through laboratory simulations, its potential to provide macro and micro-nutrients that contribute to soil fertility; 3) support future studies of rock powder used in the replacement of chemical fertilizers.

Brazil is also one of the few countries in the world with the potential to expand its agricultural production, whether by increased productivity, or the expansion of cultivable area (SCOLARI, 2006). With this, the present study may contribute, not only to meet the growing intern of its population, but also for a greater food supply in the world context. Additionally, the Brazilian Government is stimulating the search for alternative routes for the production of fertilizers.

3.2 MATERIAL, METHODS AND ANALYTICAL PROCEDURES

3.2.1 Study area

In the mining district located in Nova Prata, Rio Grande do Sul (Figure 1), there are basic, intermediate, and acidic igneous rocks. At the top of the plateau, acidic rocks are interspersed with basic and intermediate rocks. At the base of the plateau, there are only basic and intermediate rocks (PRATES et al., 1998). A large (20kg) mining waste sample was obtained from the Sindicato da Indústria de Extração de Pedreiras de Nova Prata (latitude: 28º46’27,37” S and longitude: 51º38’16,61’ W).

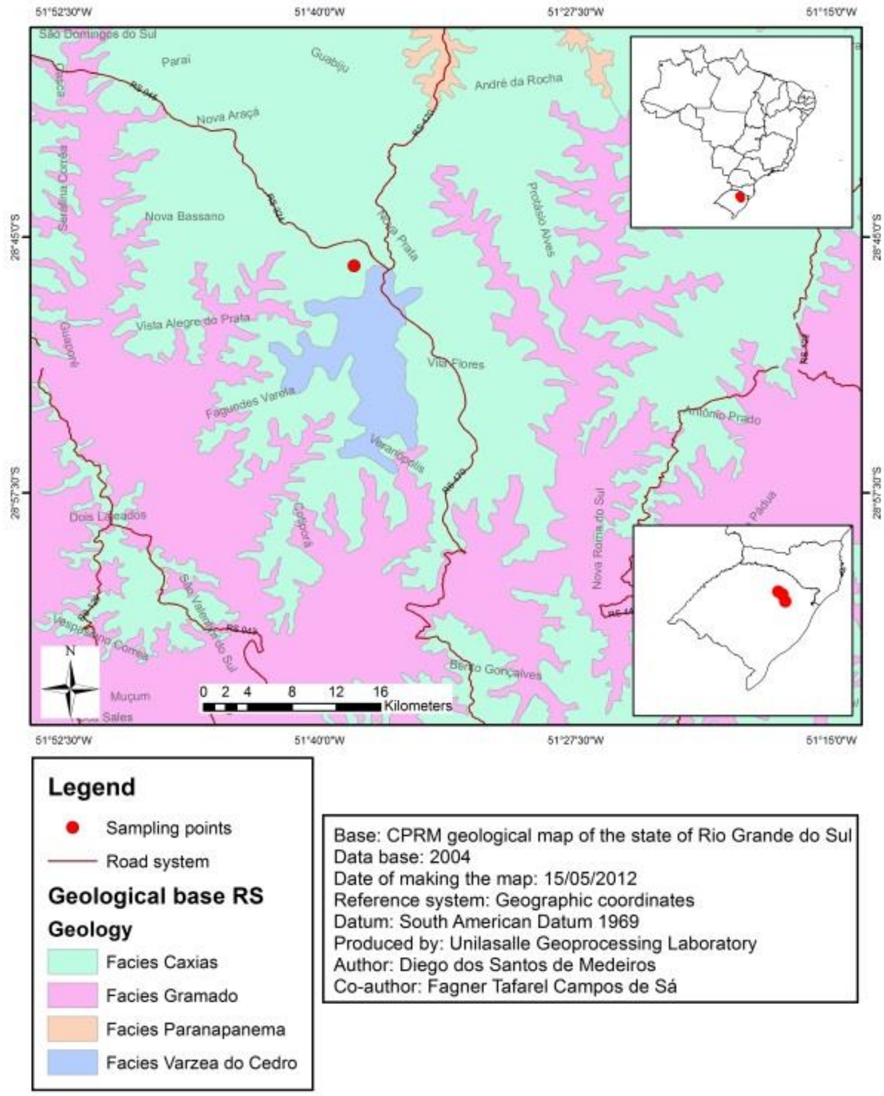


Figure1. Location and sampling point of rock powder in the city of Nova Prata.

The residue of volcanic rock belongs to the Caxias facies, and corresponds to the volcanic lava flows, which are acid in the upper position of the volcanic eruption, in general. This lithology was described by Nardy et al. (2008) as belonging to the Palmas Group of Serra Geral Formation, which was generated by intense volcanism during the transition between the Jurassic and Cretaceous periods, where the division of Gondwana and the separation of the South American continent from Africa formed the South Atlantic Ocean. These rocks have only a slight variation in composition and a continuity of mineralogical characteristics (JUCHEM et al., 2007).

For this study five random samples (each 4 kg) of volcanic rock powder were collected from each ore deposit using a polypropylene shovel and were subsequently transferred to clean polypropylene bags. These samples were then mixed, resulting in a primary sample of 20 kg that was then submitted to homogenization and subsequent quartering procedures according to standard methods for mineral particles (OLIVEIRA; AQUINO, 2007), resulting in two parts of 10kg each. One portion (10 kg) was reprocessed by quartering, resulting in ten samples of approximately 1kg that were stored in plastic bags and randomly selected to use in this work.

3.2.2 Mineralogy

The mineral composition of the mining waste major crystalline mineralogy of volcanic rock powder was evaluated by X-ray powder diffraction (XRD) at the Unidade de Raios X - RIAIDT of University of Santiago de Compostela (Spain). The sample was homogenized and compacted on the sample holder to obtain a uniform surface, required for this technique (OLIVEIRA et al., 2012a, 2012b). The sample was spun during the data collection in order to get the best peak profile and to minimize the preferred orientation effect. The sample was analysed with a Philips powder diffractometer fitted with a Philips “PW1710” control unit, Vertical Philips “PW1820/00” goniometer and FR590 EnrafNonius generator. The instrument was equipped with a graphite diffracted-beam monochromator and Cu-radiation source $\lambda(K\alpha 1) = 1.5406Å$, operating at 40 kV and 30mA. The XRD pattern has been collected by measuring the scintillation response to Cu Kα radiation versus the 2Θ value over a 2Θ range of 2-65, with a step size of 0.02° and counting time of 3s per step. The semi-quantification of the individual crystalline phase (minerals) of sample was determined using the program Match! (©2003-2011 CRYSTAL IMPACT, Bonn, Germany).

Field emission scanning electron microscope (FE-SEM) and high-resolution transmission electron microscope (HR-TEM) allow the direct (real space) visualization of minerals. The morphology, structure, and chemical composition of minerals were investigated using a FE-SEM Zeiss Model ULTRA (with charge compensation for all applications on conductive as well as non-conductive samples). The FE-SEM was equipped with an energy-dispersive X-ray spectrometer (EDS). The working distance of the FE-SEM/EDS was 5-10-mm, beam voltage 5-20.0 kV, aperture 6, and micron spot size 5 or 5.5. The mineral identifications were made on the basis of morphology and grain composition using both secondary electron and back-scattered electron modes. EDS spectra were recorded in FE-SEM and images mode and then quantified using ES Vision software that uses the thin-foil method to convert X-ray counts of each element into atomic or weight percentages.

Petrographic analyzes were performed in transmitted light microscope, Nikon, model Eclipse - 50iPOL with five objectives with correction to infinity, with total magnification of 25; 40; 100; 200; and 400 times.

3.2.3 Chemical characterization and mobility of the elements

The Si concentration was determined by fusion with $LiBO_2$ followed by analysis of X-ray fluorescence spectrometer on a Philips model PW1480. The rock dust sample was acid digested following a two-step digestion method (QUEROL et al. 1997); this consisted of a HNO_3 hot extract followed by $HF:HNO_3:HClO_4$ acid digestion of the residue. The resulting solution was then analysed at the Institute of Environmental Assessment and Water Research (Spain) by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major and selected trace elements and by inductively coupled plasma mass spectrometry (ICP-MS) for additional trace elements.

Leaching tests of the elements present in the sample were performed in Milli-Q water and five acidic solutions in particle size range <0.1-mm. Concentrations of major elements and trace elements in the leachate were determined by ICP-MS and ICP-AES.

In order to study the leaching of elements, the compliance leaching test EN 12457-2 (EN 2002) was applied at the Institute of Environmental Assessment and Water Research (Spain). This is a single batch leaching test performed at a liquid to solid ratio (L/S) of 10 L/kg with 24 h of agitation time and deionised water as leachant. In all cases, analyses were performed in duplicate. Major, minor, and trace element concentrations in solid sample and leachates were determined by means of ICP-MS and ICP-AES, respectively.

3.2.4 Leaching tests

The leaching tests are used to determine or evaluate the chemical stability of the waste when in contact with aqueous solutions, thus verifying the degree of mobilization of its nutrients. Thus, this assay seeks to reproduce in the laboratory the phenomena of drag, dilution, and desorption occurring by passing water through a waste when disposed in the environment. Such a test may represent several years of natural phenomena leaching (ARROIO, 1984). The leaching tests with acidic solutions are meant to reproduce the soil environment during the assimilation of nutrients by plant roots.

In evaluating the leachability of the material, a comparison is made between the concentration of the nutrient in the leachate and the crude residue. These values indicate the portion of waste released to the environment. The leaching test is influenced by the temperature, the type of leaching solution of the residue / leaching ratio of the number of extractions, the specific surface area of the waste, and the degree of agitation used in the assay (CHAMIE, 1994). Assays leaching of nutrients present in the sample were performed in Milli-Q water and five acidic solutions in particle size range <0.1-mm. The pH of each leachate was also measured (with a pH meter DM-2P Digimed) to trace the relationship between this parameter and leachables elements. All analyzes were performed in duplicate. The development of this research was based on six leaching methods (Table 1).

Table 1. Composition of the solutions extractors, processes and methodologies used in the leaching of nutrients.

Extractor	Extracting solution	Conc. (mol L^{-1})	Amount of sample (g)	Amount of solution (mL)	Agitation (rpm)	Period of agitation (min)	Methodology
1	Milli-Q water		1	10	60	1440	EN 12457-2 (2002)
2	AC ($C_6H_8O_7$)	0.02	5	500	40	30	MAPA – Brasil (2007)
3	AC ($C_6H_8O_7$)	0.02	5	100	40	1440	Adapted of MAPA – Brasil (2007)
4	AC ($C_6H_8O_7$)	0.01	5	50	300	1440	Silva (2009)
5	AO ($C_2H_2O_4.2H_2O$)	0.05	5	50	300	1440	Adapted of Silva (2009)
6	AO ($C_2H_2O_4.2H_2O$)	0.01	5	100	300	1440	Silva (2009)

According to Castilhos and Meurer, (2001), studies where been conducted for quantify the nutrient release rates of mineral sources for the nutrition of plants. In these studies, ion-exchange resins were used, saline solutions at sodium tetraphenylborate dilute, and low molecular weight organic acids such as citric and oxalic acids. These acids can facilitate rock weathering of minerals through formation on metalorganic complexes and are naturally produced by plants in the rhizosphere (root zone). Given this, these acids were used in this study as solutions extractors.

Although a mineral may have a high content of nutrients and, consequently, it can be considered as alternative fertilizer in potential, these nutrients may not be fully available to the extractors. Therefore, the extractors will define the element "available" that is a partial indication (or proportion) of the amount that the plant could absorb. In this way, one can deem it necessary to employ some sort of structural modification of this mineral in order to make the nutrient more accessible to the extraction process.

According to Bigham et al. (2001), some organisms are able to promote weathering in rocks through the secretion of low molecular weight organic acids. Oxalic acid, for example, is an agent for the efficient extraction of octahedral cations of rocks by combining protonic attack and complexation reactions (GIRGIN; OBUT, 2002).

3.3 RESULTS AND DISCUSSIONS

3.3.1 Mineralogy

The results of the semiquantitative analysis of the minerals of the sample by X-ray diffraction are given in Table 2 and Figure 2A.

Table 2. Semiquantitative mineralogical characterization by X-ray Diffraction.

Mineral phase	(%)
Quartz	15
Anorthite	54
Sanidine	19
Cristobalite	1
Augite	10

According to the these, the crystalline mineral assemblage is made of 54% anorthite, a Ca-plagioclase, feldspar with low resistance to weathering (ALLEONI; MELO, 2009). Therefore, it can release nutrients more easily to the environment. Sanidine contains high proportion of K. This mineral presents average resistance to weathering (ALLEONI; MELO, 2009). Augite, which composes 10% of the sample, a Fe-Mg-pyroxene, can release Si, Mg, Fe, and Ca and form new minerals (SONG; HUANG, 1988). Furthermore, the mining waste contains an undetermined proportion of glassy, no X-ray detectable mass that may supply also a number of elements to the soil.

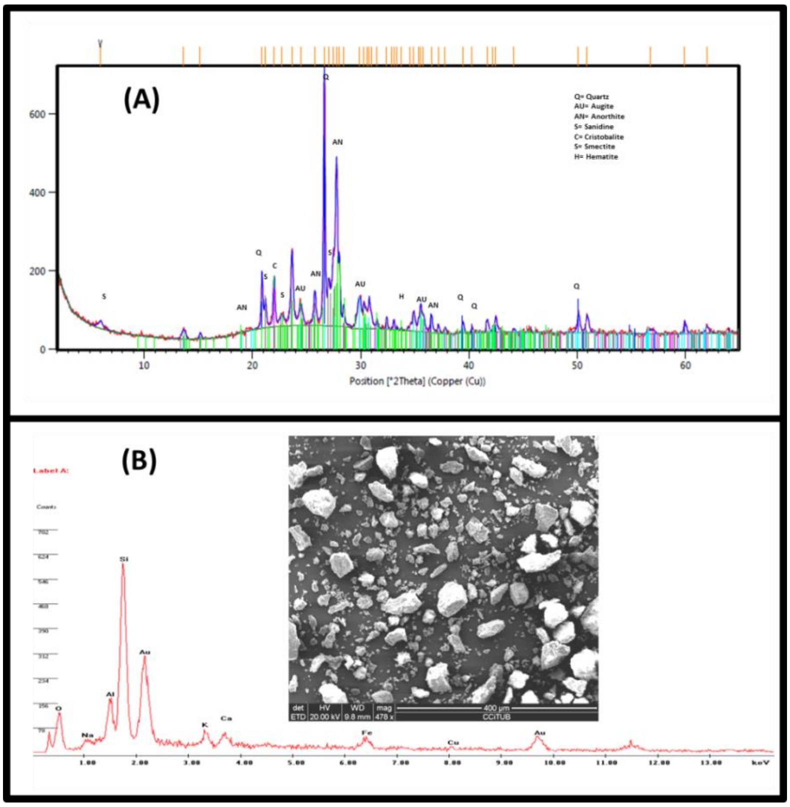


Figure 2 (A) – Diffractogram of X-rays from the sample of rock powder detailed in Table 2, (B) Elements detected by FE-SEM/EDS in the studied rock powder.

The analysis by FE-SEM/EDS proved to be a satisfactory technique that can be used for chemical characterization of volcanic rock dust sample, containing Al, Si, K, Ca, Fe, Cu, and Na most of the particles that were evaluated and later analysed with EDS (Figure 2B). The sample shows the irregular and angular morphology of particles (Figure 2B).

Petrographic results demonstrated that the rock consists predominantly of microphencryst of plagioclase (anorthite), which occur as spherulitic aggregates, and smaller amounts of alkali feldspar (saninide) and pyroxene (augite), which represent approximately 35% of the mineral phases present in the sample. Many of the microphenocryst of plagioclase anorthite and alkali feldspar have stains of oxidation along of microfractures. The microphenocrysts of pyroxene (likely clinopyroxene (augite)) were very oxidized and replaced with opaque minerals, also occurring in a small fragments (Figure 3A and 3B). Some pyroxene crystals are more preserved, but the small size of the grains does not permit the determination of the optical properties to determine the existence of two pyroxenes.

Opaque minerals likely comprise titanomagnetite, which occur as microphencryst and aggregated with skeletal shapes, often replacing the pyroxene. Apatites occur with relative abundance, constituting an accessory mineral phase.

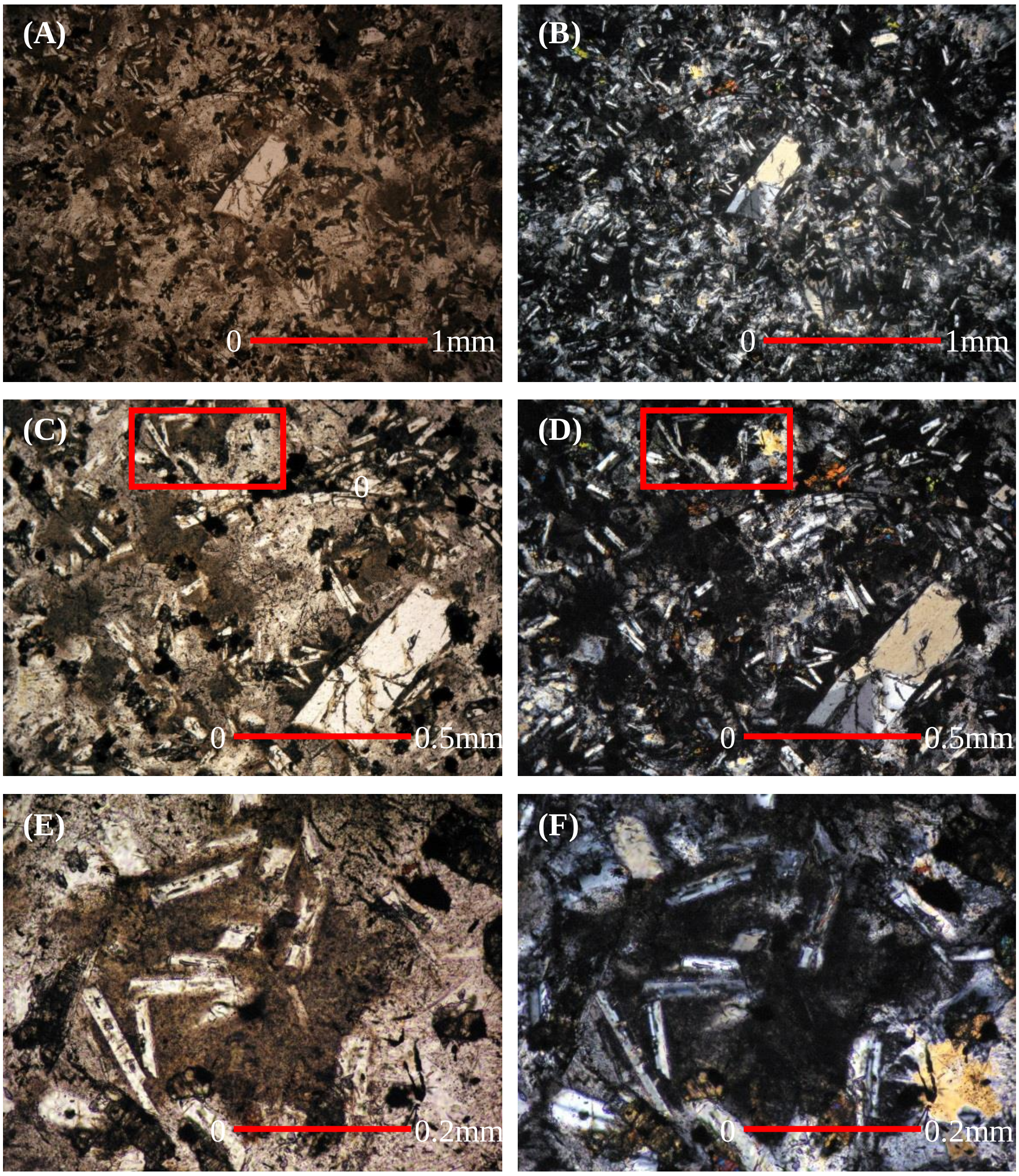


Figure 3. A and B: Phenocrysts of plagioclase in microcrystalline array composed of crystallites of plagioclase and pyroxene in spherulitic intergrowth (Natural Light (LN) and polarized light (PL)/ increase of 25 x/graphic scale 1.0 mm); C and D: showing in detail the previous photomicrography the aggregates with spherulitic texture in the array (LN and LP/increase of 40 x/graphic scale 0.5 mm); E and F: detail of the area bounded in red (LN and LP/ increase of 100 x /graphic scale 0.2 mm), characterizing the occurrence of crystallites of plagioclase in association with mafic minerals and incipient micrographic texture.

3.3.2 Chemical characterization and mobility of the elements

Besides the SiO_2 that accounts for 64.8% of the whole rock, the main elements that make up the rock powder sample are shown in Table 3. According to these results, the Si comes from the quartz, anorthite, cristobalite, sanidine, and augite, detected in the sample by mineralogical analyses, but also for the amorphus glassy matrix.

Aluminum is the second most abundant element in the sample (Table 3). Studies by Kautzmann et al. (2011) and Nunes (2012) showed that basalt rock powder samples from the same region did not provide Al to the environment. This fact is important since Al^{+3} is toxic to plants and inhibits the growth and development of roots because it changes the adsorption of water and nutrients (MALAVOLTA, 2006). At pH values greater than 5.8, practically the entire Al appears as insoluble $Al(OH)_3$ therefore, non-toxic to plants (FAQUIN, 2005).

The presence of opaque minerals, probably titanomagnetite may be related to high content of iron and titanium. Iron is insoluble in aqueous medium, at pH >4 which is fundamental, because the excess iron can cause growth problems in plants and the necrosis in leaves (MALAVOLTA, 2006).

Both sodium, and potassium appeared in the sample with levels close to 0.6-1.5% of its composition probably due to the presence of sanidine.

Other inorganic chemicals elements analyzed represent less than 1.5% of the total composition of the sample. Of note was the abundance of elements such as Ca, P, and S, which with the weathering via hydrolysis are easily available to the soil (ALLEONI; MELO, 2009), thus providing macro and micronutrients essencial for plant growth. The results of chemical composition by ICP-MS, and ICP-AES, EDS (Figure 2B) confirm that the sample under study is coming from minerals typical of volcanic rocks but specially for the amorphous glassy matrix.

Therefore, the methodology used has proved to be effective for analyses of rock powder with applicability in agriculture.

Table 3. Chemical composition of major elements and trace elements of rock powder.

Element	mg/kg	Element	mg/kg	Element	mg/kg	Element	mg/kg
Al	43769	V	84	Mo	1	Ho	2
Ca	16536	Cr	7	Pb	19	Er	4
Fe	28398	Co	14	Sn	5	Dy	7
K	16054	Ni	3	Nb	44	Yb	4
Mg	5047	Cu	66	Cs	7	Th	13
Na	14029	Zn	116	Ba	647	Hf	6
P	691	Ga	21	La	42	Ta	3
S	449	Ge	1	Ce	81	W	1
Mn	863	As	3	Pr	12	Tl	1
Li	17	Tb	1	Nd	35	Zr	243
Be	3	Rb	116	Sm	8	U	4
B	31	Sr	170	Eu	2		
Sc	19	Y	45	Gd	8		

ICP-MS analysis verifies that the concentrations of potentially toxic elements such as As, Pb, and Li, among others, do not represent environmental risk (Table 3).

3.3.3 Leaching tests

The concentrations of the fractions of the elements leached during standardized test of the European Union (12457-2, 2000) and other methodologies along with pH are expressed in Tables 4. The latter was a factor of great importance in geochemical mobility of the elements present in the sample of rock powder. Because, while the sample at pH = 7.55 have low nutrient release, in acids solution (that are present in the rhizosphere), the mobility of nutrients present in the sample increases considerably (Table 4).

Table 4. pH, concentration of elements in leachate rock powder and nutrient release potential of rock powder through the solutions extractors (percent).

pH	7.55		2,89		2,89		3,04		2,99		1,91	
Nutrients	Extractor 1		Extractor 2		Extractor 3		Extractor 4		Extractor 5		Extractor 6	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Al	<1	0	651	2	602	1	700	2	717	2	4078	9
Ca	1	0	751	5	1132	13	1631	10	129	1	2690	16
Fe	<1	0	1119	4	947	3	1118	4	1796	6	9725	34
K	<1	0	320	2	201	1	177	1	135	1	506	3
Mg	<1	0	294	6	272	5	303	6	302	6	1541	30
Na	<1	0	403	3	202	1	232	2	130	1	632	4
P	0	0	592	85	527	76	243	35	555	80	644	93
S	<1	0	28	6	13	3	8	2	8	2	4	1
Si	<1	0	449	0	415	0	475	0	414	0	2341	0
Mn	0	0	178	21	222	26	236	27	160	18	603	70
Li	0	0	<1	1	<1	1	<1	2	<1	2.0	2	14
Be	0	0	<1	7	<1	6	<1	8	<1	6	<1	23
B	0	0	1	4	1	3	1	4	1	2	2	8
Sc	0	0	<1	3	<1	4	1	5	<1	2	1	7
V	0	0	2	3	1	2	2	2	3	3	13	16
Cr	0	0	3	50	2	25	2	30	1	17	4	67
Co	0	0	2	11	2	13	2	15	2	12	7	49
Ni	0	0	<1	24	<1	22	<1	26	<1	20	2	76
Cu	0	0	8	12	7	11	8	12	7	11	34	52
Zn	0	0	14	12	9	8	9	8	8	7	27	23
Ga	0	0	<1	2	<1	2	<1	2	<1	2	2	8
Ge	0	0	0	0	0	0	0	3	<0.1	2	<1	5
As	0	0	1	42	1	29	<1	23	<1	22	2	68
Rb	0	0	<1	<1	<1	<1	<1	<1	<1	<1	<1	<1
Sr	0	0	7	4	6	3	6	3	2	1	9	5
Y	0	0	6	13	6	14	6	13	<1	<1	<1	<1
Zr	0	0	8	3	5	3	9	4	7	3	25	10
Nb	0	0	1	2	<1	2	<1	2	2	5	13	29
Mo	0	0	<1	60	<1	15	<1	20	<1	9	<1	45
Sn	0	0	<1	5	<1	4	<1	3	<1	8	1	20
Ba	0	0	29	5	28	4	28	4	22	3	76	12
La	0	0	4	10	5	12	4	10	<1	<1	<1	<1
Ce	0	0	16	19	17	21	16	20	<1	<1	<1	<1
Nd	0	0	8	23	8	24	7	21	<1	<1	<1	<1
Hf	0	0	<1	9	<1	8	<1	9	<1	8	2	28
Ta	0	0	<1	11	<1	6	<1	8	1	43	3	83
W	0	0	<1	36	<1	33	<1	37	<1	41	<1	54
Pb	0	0	4	24	3	15	2	8	<1	1	<1	3
Th	0	0	<1	6	2	12	2	16	<1	1	<1	1
U	0	0	<1	6	<1	5	<1	6	<1	2	<1	16

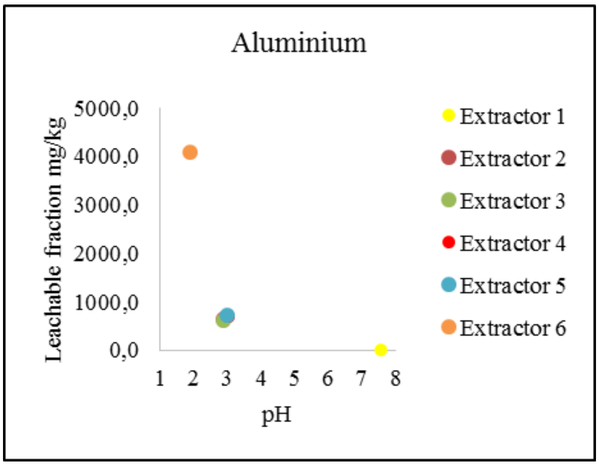
Typically, the fertilizers are applied directly into the soil near the plant roots (the rhizosphere). Specifically, in this region, there is natural production of citric and oxalic acids (ERNANI et al., 2007). Therefore, the present study shows that this practice also applies using powder of rock, causing it to reduce the cost of agriculture and agrochemical consumption.

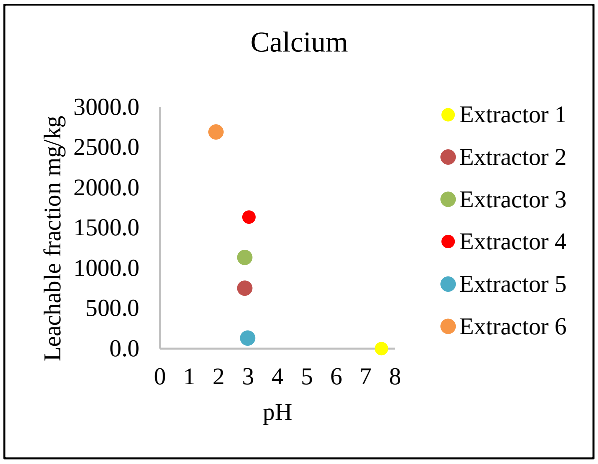
Chemical elements considered essential for the plants and, therefore, primary macronutrients are N, P, and K; secondary macronutrients-Ca, Mg, and S; and micronutrients Al, B, Co, Cu, Cl, Fe, Ni, Mn, Mo, and Zn (ARNON; STOUT, 1939). Concentrations of nutrients present in leachate of rock powder are presented in Table 4. Therefore, it can easily demonstrate that the lower the pH value (Figure 4), the greater mobility of the elements present in the rock powder and, with it, greater bioavailability. Specially, these elements associated to the amorphous phase can be more easily solubilized given that this amorphous component can be more weathered by acidic solutions than the crystalline minerals.

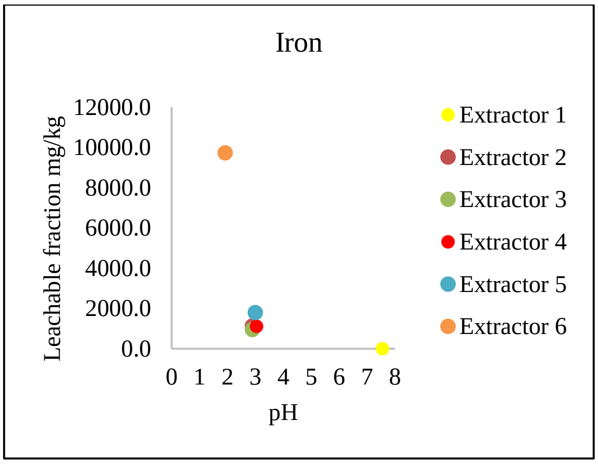
It is important to note that elements of high toxicity such As, Cd, and U, among others, have low bioavailability by being present in the sample at low concentrations. This reinforces the implementation of such material in food production, after all, even in extremely acid pH there was no high fraction leachable.

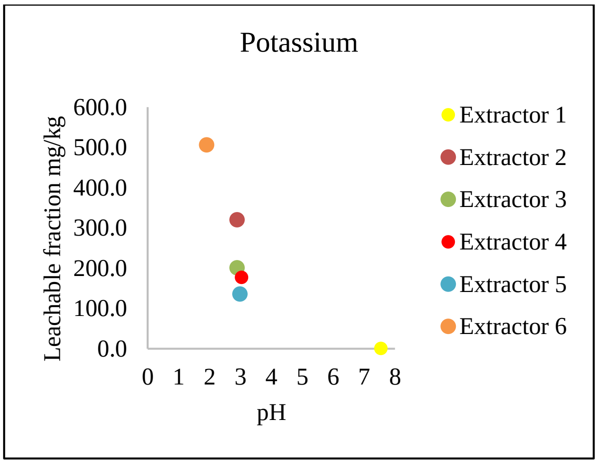
Aluminum, Fe, Ca, Si, Mg, Na, Mn, and K are the most mobile elements in the leaching tests (Figure 4), because they were detected in higher concentrations in the chemical composition of the sample (Table 3).

The acidics extractors solutions of the number 2 until 5, obtained similar concentrations, both for major elements as trace elements (Table 4). Table 4 shows that the concentrations of major elements and trace elements were the most abundant in the leachate of extractor 6 (extremely acid extractor). These elements can be easily explained given that the sample contains considerable proportions of aluminosilicates glass matrix (of low resistance to weathering) which when, proved during the leaching test, were attacked by oxalic acid releasing their nutrients. Additionally, the high acidity conditions of extraction solution favours the amendment of the rock species that may contain macro and micronutrients, thus contributing to the increase of the concentration resulting in the dissolution of the leaching test. Additionally, it became clear that the mobility of all elements was dependent on pH.


Aluminium
Leachable fraction mg/kg
5000,0
4000,0
3000,0
2000,0
1000,0
0,0
1 2 3 4 5 6 7 8
pH
Extractor 1
Extractor 2
Extractor 3
Extractor 4
Extractor 5
Extractor 6


Calcium
Leachable fraction mg/kg
3000.0
2500.0
2000.0
1500.0
1000.0
500.0
0.0
0 1 2 3 4 5 6 7 8
pH
Extractor 1
Extractor 2
Extractor 3
Extractor 4
Extractor 5
Extractor 6


Iron
Leachable fraction mg/kg
12000.0
10000.0
8000.0
6000.0
4000.0
2000.0
0.0
0 1 2 3 4 5 6 7 8
pH
Extractor 1
Extractor 2
Extractor 3
Extractor 4
Extractor 5
Extractor 6


Potassium
Leachable fraction mg/kg
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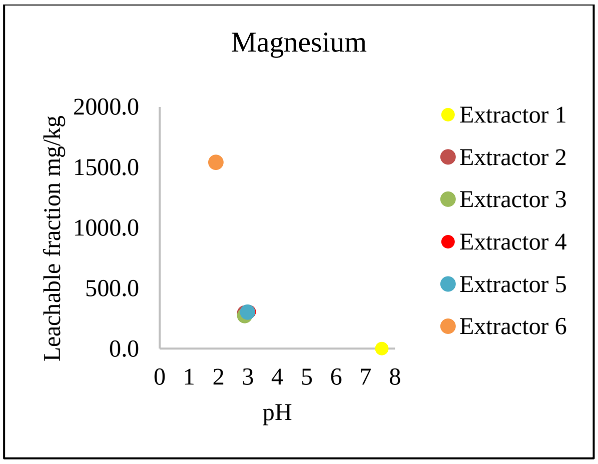
500.0
400.0
300.0
200.0
100.0
0.0
0 1 2 3 4 5 6 7 8
pH
Extractor 1
Extractor 2
Extractor 3
Extractor 4
Extractor 5
Extractor 6


Magnesium
Leachable fraction mg/kg
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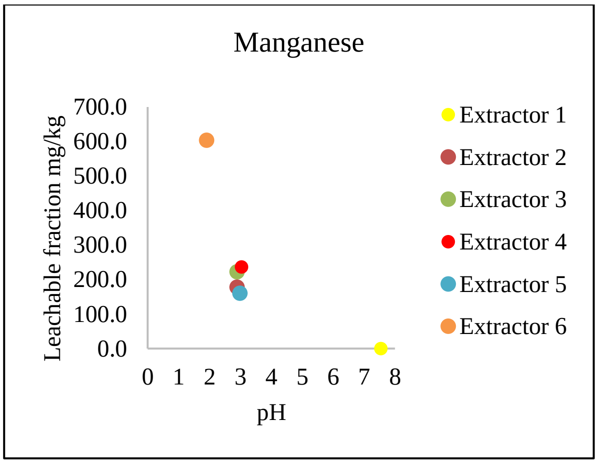
1500.0
1000.0
500.0
0.0
0 1 2 3 4 5 6 7 8
pH
Extractor 1
Extractor 2
Extractor 3
Extractor 4
Extractor 5
Extractor 6


Manganese
Leachable fraction mg/kg
700.0
600.0
500.0
400.0
300.0
200.0
100.0
0.0
0 1 2 3 4 5 6 7 8
pH
Extractor 1
Extractor 2
Extractor 3
Extractor 4
Extractor 5
Extractor 6

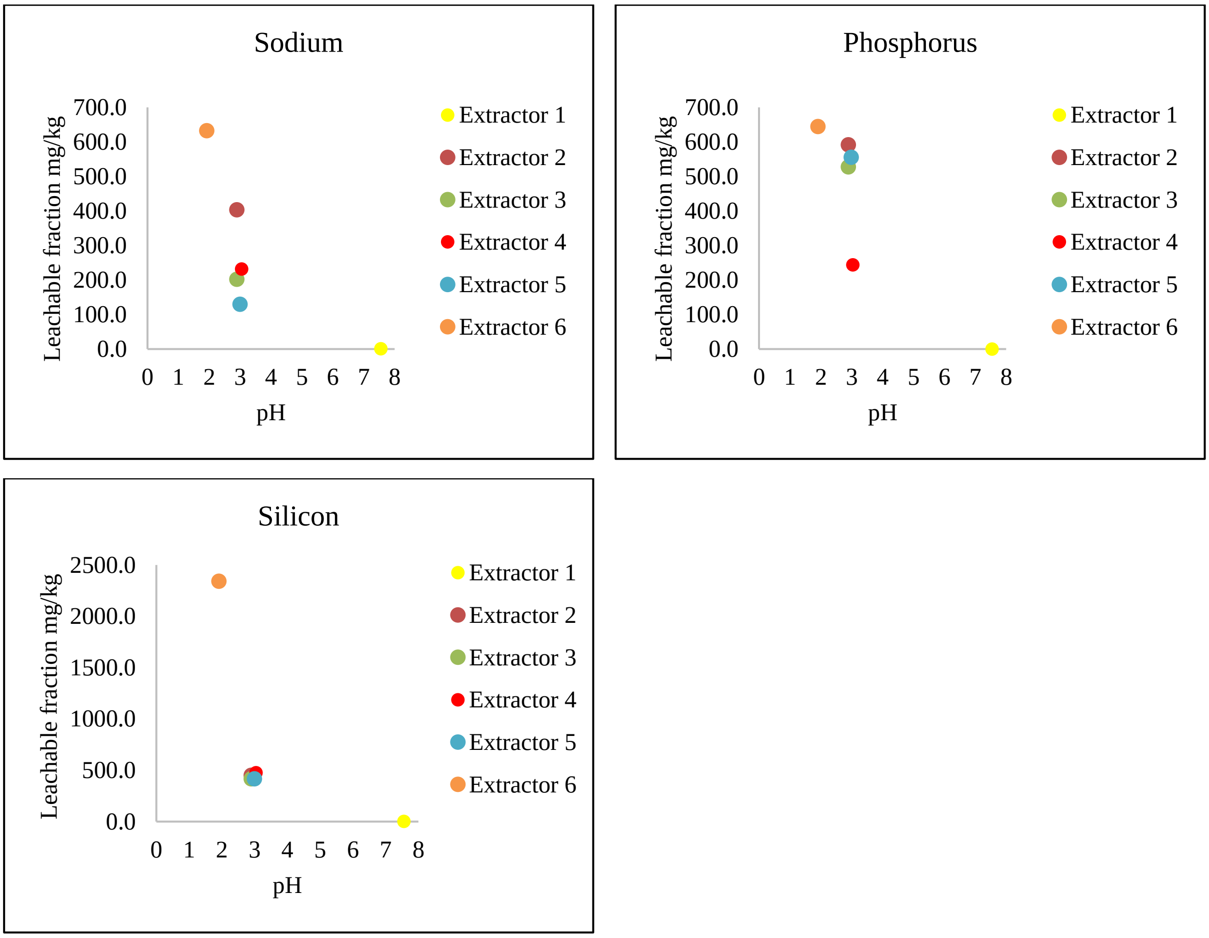


Figure 4. pH values and extractable proportions for different elements.

Despite the sample contain high concentrations of Al in its composition (Table 3), the leachable fraction of this element was 4,077 mg/kg (6 extractor), which corresponds to a potential release of 9.3%. This element undergoes weathering in acidic soil, releasing the aluminium to the environment, which can precipitate in the form of aluminum hydroxide (ALLEONI; MELO, 2009) that is practically insoluble in water. This can be confirmed with the data presented in Table 4, which presents a concentration of 0.2 mg/kg of water-soluble aluminium. However, the application of rock powder on the soil would not be impaired by the release of toxic elements for plants.

Calcium is slightly soluble in water, but its solubility in acidic solutions increased, presenting variable concentrations (751.5 mg/kg, 1,132.4 mg/kg, 1,630.7 mg/kg, and 129.3 mg/kg) in the leachate of the extractors solutions (2-5), respectively. However the extractor 6 presents a higher concentration (2,690.6 mg/kg) than the other extractors. The pH influence on mobility of this element, because calcium concentrations increased in the leachate with higher acidity.

The data in Table 4 shows that the sample provided a 9,725 concentration mg/kg (486.27 mg/L) of Fe in leachate from 6 extractor, representing a potential release of 34.2%. Iron is highly immobile at pH greater than 4.5 and its release increases with decreasing pH (SILVA et al., 2011). However, according to Sposito (1989), the ideal level of this nutrient in the soil must be in the range of 25,000 to 40,000 mg L^{-1}. This demonstrates that although the sample has a high concentration of this micronutrient in its composition, the availability for the soil will be low.

Potassium levels (135.5-506.2 mg/kg), Mg (272.5-1,541.3 mg/kg), Na (129.9 – 631.8 mg/kg), P (243,3 – 644.4 mg/kg) and Mn (160.2 - 603.2 mg/kg) leachate (Figure 4) leached an extractable proportion similar to other elements, even if they are less abundant, but of similar geochemical mobility, as expressed the quantification in Tables 3 and 4.

Phosphorous presented a high mobility in all leaching tests, mainly in the 6 extractor leachate, where practically the entire amount of P was released (93.3%) (Figure 4). In leachate of extractors (2-5), the concentration of Si was similar (448.8 mg/kg, 415.6 mg/kg, 475.2mg/kg, and 414.5 mg/kg). In the leachate of the 6 extractor, their mobility was approximately five times greater (2,341 mg/kg) than in other leachates, which indicates that, if necessary, the rock powder can be tested together with other wastes in order to increase the mobility of this macronutrient in case cultivation requires the element to be bioavailable.

3.4 CONCLUSIONS

According to the results obtained in this study, it is concluded that the volcanic rock powder can be used as a source of macro and micro-nutrients to the soil, because it presents in its composition a relevant proportion of easily weathered glassy amorphous matrix as well as many silicate minerals such as plagioclase, pyroxene, and iron-magnesium minerals easily amendable. Leaching tests in an acidic medium demonstrated an influence on the release speed of these minerals, making the process faster and, consequently, the release of the elements/nutrients to the soil. The best extraction efficiencies were observed when the solution of oxalic acid 1% (6 extractor) was used as an extractor. However, the tests of nutrient release in acid solutions showed that only a fraction of the minerals are soluble. The characteristics of devitrification observed in the sample studied make interesting rock for jobs in stonemeal, by the ease of destabilization of glass in exogenous conditions. The weathering of this glassy matrix with the weathering of feldspars and pyroxenes, in addition to the clay which fill fractures and venules and that also occur in the array may be indicating a process of hydrothermal alteration, raising the potential for destabilization (replacement and/or transformation) of these mineral phases, with consequent increase of the cations release potential that can contribute to soil remineralization in the region. With that, great there are advantages of agronomic use of volcanic rocks as fertilizer, as, for example:

- Insolubility of nutrients in water, resulting in smaller losses by leaching and fixation;
- Solubility of the nutrients in solution of weak acid, as existing in soil solutions, resulting in slow and efficient release of same for the cultures.

However, it can be concluded that the dust of volcanic rock has a promising potential as alternative fertilizer application of slow release in cultures that require nutrients in the long run, as for example, perennial crops.

Additionally, future studies will be carried out by mixing with volcanic rock powder and other materials such as sludge from the dairy and sweets industries, aiming at modifications in the structure of the rock powder and largest release of nutrients in smaller time interval.

ACKNOWLEDGMENTS

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EVALUATION OF THE POTENTIAL OF VOLCANIC ROCK WASTE FROM SOUTHERN BRAZIL AS A NATURAL SOIL FERTILIZER

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4 EVALUATION OF THE POTENTIAL OF VOLCANIC ROCK WASTE FROM SOUTHERN BRAZIL AS A NATURAL SOIL FERTILIZER

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ABSTRACT

This study was developed to evaluate the chemical and mineralogical properties of acid volcanic rock waste from mining activities by measuring the availability of macronutrients and micronutrients in Milli-Q water, and in acidic solutions to evaluate the potential use of this type of waste as natural soil fertilizers. The sample used in this work was obtained from a company of the mining district of Nova Prata, Rio Grande do Sul State, southern Brazil. Petrographic studies using conventional optical microscopy and scanning electron microscope allowed to define the mineral composition of in powder wastes as being comprised mainly by pyroxene, feldspar, and variable contents of amorphous glass in matrix. The primary oxides detected in the samples by X-ray Fluorescence were calcium oxide, silicon dioxide, aluminium oxide, iron oxide, and with concentration minor potassium oxide, and phosphorus oxide. Several important nutrients were transferred into the acidic solutions, indicating the significant potential and feasibility of these wastes to be effectively used as natural fertilizers. This study is of great relevance to the sector of mining and to agriculture in the region because it can create an alternative disposal treatment for tailings, and improve the environmental sustainability of local farms, thereby avoiding excessive chemical fertilizer consumption.

Keywords: Volcanic rock powders; Mining waste; Safe environmental; Natural soil fertilizers

4.1 INTRODUCTION

In recent years several researches have been conducted to mitigate the different environmental impacts related to agricultural activities. In particular, the use of chemical fertilizers consisting of nitrogen, phosphorus and potassium, namely NPK, has drawn significant attention due to the adverse environmental impacts caused by the excessive application of these products. The fertilizer in excess is carried by rainwater from the soil surface to other water resources, causing pollution, algae proliferation and the eutrophication of aquatic ecosystems (HODGES; CROZIER, 1996; ALMEIDA et al., 2006; SANTUCCI, 2012). The studies of Knapik (2005), Theodoro and Leonardos (2006), Nunes (2012) have intensified the use of rock powder as a soil fertilizer or pH corrective as alternatives to decrease the dependence of Brasil on imported raw materials, and minimize environmental impacts (FYFE et al., 2006).

The fertilization of soils with volcanic rock powder, also know as a stonemeal technique, can provide a large range of macronutrients such as nitrogen, phosphorus, potassium, calcium, magnesium and sulfur and micronutrients such as iron, manganese, copper, zinc and sodium, to the suitable plant growth. Application of rock powders for soil fertilization is directly related to the composition and amount of minerals phases, and is also dependent of the weathering conditions, including temperature, rainfal amount, organic matter production in soils in order to increase the potential conditions to solubilize inorganic chemical compounds improving soil fertility (THEODORO; LEONARDOS, 2006; LOUREIRO et al., 2009). Volcanic rock powder minerals are source of nutrients for plant growth during long periods and promotes an increasing in cation exchange soil capability due to formation of a series of clay minerals during the process of weathering mineral alteration (MELAMED et al., 2005).

Due to the increased construction and building activities was promoted an increase in the exploration of volcanic rock, which are widely applied as ornamental rock. While this development in the mineral sector is relevant, the generation of waste has also increased, causing detrimental environmental problems that must be addressed.

According to Toscan et al. (2007) in Nova Prata Rio Grande do Sul, Brazil, were generated large piles of waste by mining activity of volcanic rock, with approximately 647,000 m^3 in 2005, and a monthly production of 7,000 m^3. Additionally, Kautzmann (2011) showed the growth of the mining sector and estimated production of 17,000 tons of waste for the year 2011.

Several authors (VILLIERS, 1947; EVANS, 1947; GILLMAN, 1980; HENSEL, 1989; MOTTA; FEIDEN, 1992; HINSINGER et al., 2001; THEODORO; LEONARDOS, 2006; VAN STRAATEN, 2002; NUNES 2012) have shown that the addition of crushed rock to agricultural soil dates back to antiquity.

Volcanic rock powder is among the major mineral fertilizers studied, researched and discussed in existing literature (KNAPIK, 2005; NUNES et al., 2014; SANTUCCI, 2012). The interest in this mineral, in Brazil, is because volcanic rock processing generates a significant amount of rock powder waste, which is composed of important mineral elements that can be used for plant metabolism. These minerals are emitted in dust form from comminution operations or discarded in the solid/solid separation in screening units and thus constitute an adverse environmental impact for the mining sector.

Villiers (1947) after a long series of field experiments recommended the use of powdered basaltic rocks for rejuvenation of depleted soils of humid regions in the Congo, that showed a considerable increase in production of sugar cane with increasing crop production after four cuts. Evans (1947) demonstrated an increase of 33.7% and 56.7% in dry matter production with cultivation of oats in pots, also applying powder basaltic rocks. Gillman (1980) correlated the raise of soil pH with increasing application of crushed basalt in highly weathered soils. Finer ground material and longer incubation times enhanced this effect. Also, Julius Hensel (1989) advocated the use of rock powders as an alternative to reduce the use of chemical fertilizers in agriculturable lands to improve soil quality. Motta and Feiden (1992) determined that application of basalt powder was enough to raise the level of available phosphorus, behaving as a corrective fertilizer for soils. Hinsinger et al. (2001) reported the use of crushed silicate rocks or parent rocks rich in primary minerals could be potential nutrient sources for soil fertility. Gillman et al. (2002) also demonstrated correlation among the application of crushed basalt on highly weathered low pH soils, showing reduction in the acidity of soils.

Theodoro and Leonardos (2006) reported an increase in plant production, reaching up to 50% of total with application of “stonemeal” technique. The release of nutrients from the crystal lattice of the minerals is mainly a consequence of the action of organic acids produced by plants and microorganisms in the soil (MORAES, 2014). Regions with natural acidic soils have high potential for the successful application of rock powder as a fertilizer soil supplier.

Experiments using volcanic rock powders (2.7 to 3.0 wt% K_2O) and KCl industrial fertilizer (60, 120 e 240 kg ha^{-1}), were applied to millet agriculture (SOUZA et al., 2010). In that research, the agronomic efficiency of the volcanic rock powders was close to 40% for each 240 kg ha^{-1}. Considering Brazil to be one of the largest suppliers of agriculture commodities in the world, and its greater potential to expand cultivable soils (SCOLARI, 2006), detailed studies of volcanic rock powders as soil fertilizers may contribute with the definition of new routes and processes to supply demand of chemical fertilizers.

Through this study it was possible evidence that global mining impacts can be minimized with the total utilization of the exploited resource, the recycling of the generated byproducts and innovative usage of the environmentally impacted areas. In this context, the study of the mining wastes as potential fertilizers is a practice that can be developed to further contribute to sustainability. The use of natural fertilizers is relevant for the development of more sustainable farming and mining activities, thus providing several advantages to a significant portion of our society.

This study evaluated a mineralogical and chemical characterization of volcanic rock powders from mining industry of the Nova Prata region, Rio Grande do Sul State, Brazil, examining the potential of available nutrients to evaluate their use as a soil natural fertilizer.

4.2 MATERIAL, METHODS AND ANALYTICAL PROCEDURES

4.2.1 Volcanic rock powder samples

In the Nova Prata region, the geological setting consists of phanerozoic volcanic rock sequencies of the Serra Geral Formation, comprising mainly volcanic rocks of basic, intermediate and acid composition. At the bottom of the sequencies dominated by basic-intermediate volcanic rocks, and at the top dominated intermediate-acid composition (PRATES et al., 1998). It is relevant emphasize that these rocks are primarily composed of plagioclase and pyroxenes and are from the same volcanic eruptions and therefore show similar composition in the wide extension of the ore deposits (NARDY et al, 2008).

The studied samples belong to the upper sequencie of the Serra Geral Formation denominated Caxias facies of the Palmas Group (NARDY et al., 2008). Therefore, the studied samples comprise acid volcanic rock powders from rock-cut mining for industry, located in the Nova Prata mining district, southern Brazil (DATUM SAD´69 28º46’27.37” S / 51º38’16.61” W). Rock-milled powders passing through ASTM Series #170 (90 µm) and #400 (38 µm) sieves were supplied by the Union of the Mining Industry of the Nova Prata district.

4.2.2 Petrographic and mineralogical analysis

The mineralogical and petrographic studies were developed using thin sections and volcanic rock powders. Petrographic analysis were performed using transmitted light microscope, (Nikon, Eclipse - 50iPOL with five objectives, from 5x to 100x across the entire field of view). The mineralogical composition of the samples was evaluated by X-ray powder diffraction (XRD) at the Unidade de Raios X - RIAIDT of the University Santiago de Compostela (Spain). The samples were analyzed with a Philips powder diffractometer fitted with a Philips "PW1710" control unit, vertical Philips "PW1820/00" goniometer and FR590 Enraf Nonius generator. The instrument was equipped with a graphite diffracted-beam monochromator, and Cu-radiation source λ (Kα1) = 1.5406Å, operating at 40 kV and 30mA. The XRD pattern has been collected by measuring the scintillation response to Cu Kα radiation versus the 2Θ value over a 2 Θ range of 2-65, with a step size of 0.02° and counting time of 3s per step. The semi-quantification of the individual crystalline phase (minerals) of sample was determined using the program Match! (©2003-2011 CRYSTAL IMPACT, Bonn, Germany). Field emission scanning electron microscope (FE-SEM Zeiss ULTRA) with charge compensation was used for all applications on conductive as well as non-conductive samples. The working distance of the FE-SEM was 5-10 mm, beam voltage 5-20.0 kV, aperture 6, and micron spot size 5 or 5.5.

4.2.3 Chemical characterization of volcanic rock powders

Major elements concentrations were determined by fusion with LiBO2 followed by X-ray fluorescence (XRF) analysis on a spectrometer Philips (PW1480).

The rock powder samples were digested in acidic solutions following a digestion method proposed by Querol et al. (1997); this consisted of a HNO_3 hot extract followed by $HF:HNO_3:HClO_4$. The resulting solutions were analyzed at the Institute of Environmental Assessment and Water Research (Spain) by inductively coupled plasma atomic emission spectrometry (ICP-AES) for major elements, and by inductively coupled plasma mass spectrometry (ICP-MS) for trace elements.

4.2.4 Availability of macronutrients and micronutrients of volcanic rock powders

Leaching tests with acidic solutions, and Milli-Q water were done under laboratory conditions trying to reproduce the soil environment during the assimilation of nutrients by plant roots. The leaching tests were applied to determine and evaluate the chemical stability of the waste when in contact with aqueous solutions, thus verifying the degree of mobilization of its nutrients. Thus, this assay seeks to reproduce in the laboratory the phenomena of drag, dilution, and desorption occurring by passing water through a waste when disposed in the environment. Such a test may represent several years of natural phenomena leaching (KRISHNA, 2013).

The availability studies of macronutrients and micronutrients were performed in laboratory conditions with six different acidic solutions, and Milli-Q water, the extraction methodologies are shown in Table 5. The particles size of volcanic rock samples used were <90 µm, and <38 µm.

Table 5. Methods used in the availability experiments of macronutrients and micronutrients of volcanic rock waste.

Extractor	Extraction solutions	Conc. (mol L^{-1})	Sample Qty (g)	Qty solution (ml)	Agitation (rpm)	Period of agitation (min)	Method
1	Milli-Q water		1	10	60	1440	EN 12457-2, European Committee for Standardization, 2002
2	Citric Acid	0.02	5	500	40	30	MAPA– Brasil, (2007)
3	Citric Acid	0.02	5	100	40	1440	Adapted from MAPA– Brasil, (2007)
4	Citric Acid	0.01	5	50	300	1440	Silva, (2009)
5	Oxalic Acid	0.05	5	50	300	1440	Adapted from Silva, (2009)
6	Oxalic Acid	0.01	5	100	300	1440	Silva, (2009)
7	Rhizosphere Organic acids 43 % acetic acid; 31 % citric acid; 21 % latic acid, 5 % oxalic acid	 1.00 0.72 0.49 0.12	25	100	40	360	Pires et al., (2004)

Concentrations of major and trace elements presents in the extraction solutions (leachates) were determined by ICP-MS and ICP-AES. The analysis were applied in duplicate.

The pH of each leachate was also measured (with a pH meter DM-2P Digimed) to trace the relationships between this parameter and leaching elements.

4.3 RESULTS AND DISCUSSIONS

4.3.1 Petrographic and mineralogical analysis

The main mineral phases identified through conventional optical microscopy and SEM in the samples were clinopyroxene (augite) ± Ca-plagioclase ± K-feldspar (sanidine/orthoclase) phenocrysts (30-35%), quartz ± apatite (5%), and other accessory minerals (Ti-magnetite ± ilmenite). Glomeroporphyritic, spherulitic, and hypocrystalline are the dominant textures identified in thin sections. The hypocrystalline vitrophyric matrix (50-60%) presents devitrified sites with local holocrystalline texture defined by the mineral association feldspar ± pyroxene (augite) ± opaque minerals. Many of Ca-plagioclase and sanidine feldspars microphenocrysts contain oxidation paths joint to microfractures indicating secondary mineral phases. Pyroxene microphenocrysts (augite) are generally replaced by Fe-Ti oxides. Small pyroxene grains occur disseminated on the matrix (Figures. 10A-B). The small size pyroxene grains do not allow definition of the optical properties, and their chemical composition are not been classified. Oxide minerals likely comprise titanomagnetite and ilmenite, which occur as microphenocrysts and aggregates with skeletal shapes, often a product of pyroxene alteration. Apatite comprises an accessory mineral phase.

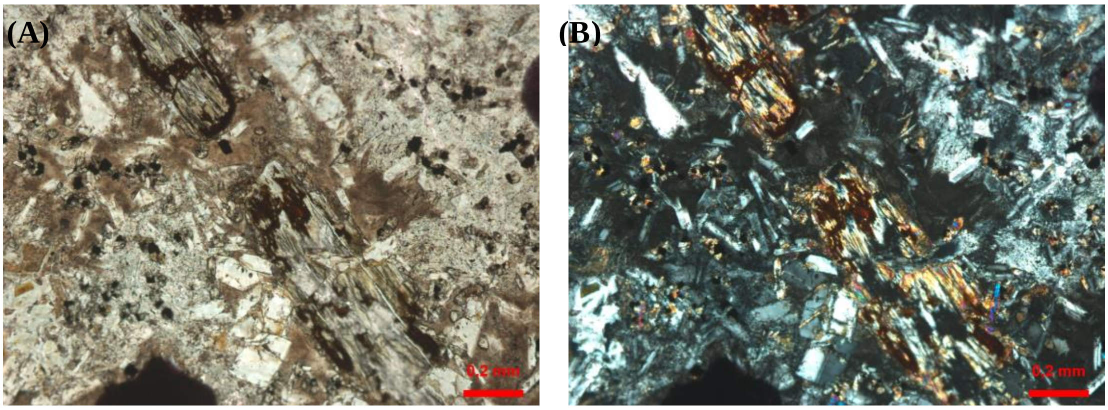

Figure 10. A and B: Phenocrysts of plagioclase in microcrystalline array composed of crystallites of plagioclase and pyroxene in spherulitic intergrowth (Natural Light (LN) and polarized light (PL)/ increase of 10 x/graphic scale 0.2 mm) characterizing the occurrence of crystallites of plagioclase in association with mafic minerals and incipient micrographic texture.

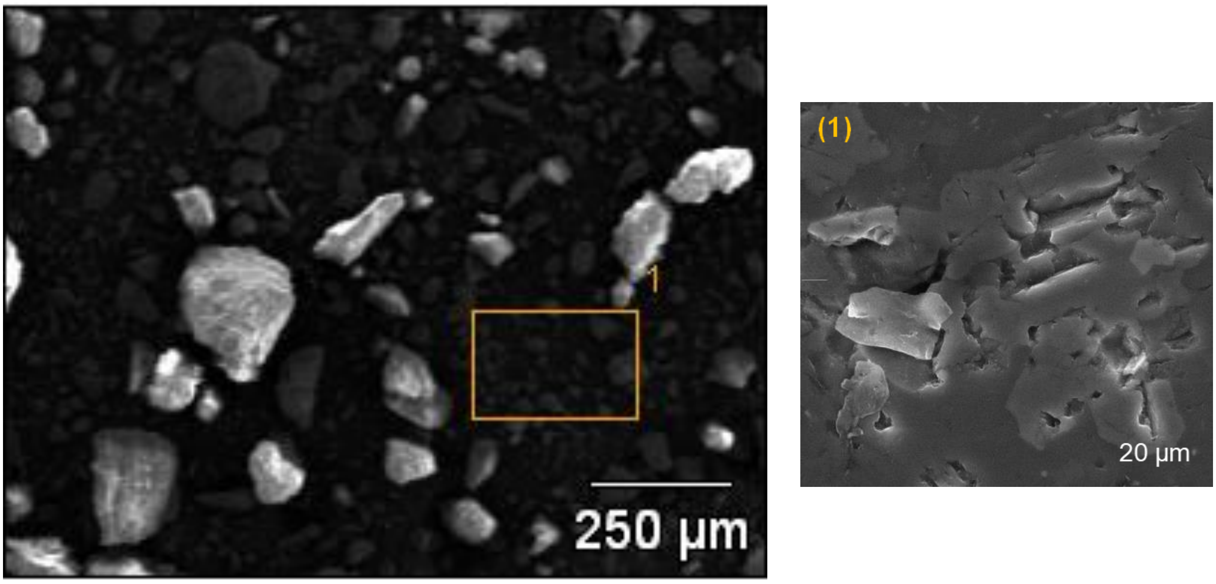

Figure 11. Dominant textures identified by SEM in the volcanic rock waste; (1): In detail, glomeroporphyritic, spherulitic, and hypocrystalline as textures.

SEM allowed to verify the texture of the mineral phases, and define mineral compositions, helping to characterize the chemical elements (nutrients) (Figure 11). Semi-quantitative X-ray diffraction analyzis showed the occurrence of Ca-feldspar (59%), sanidine (15%), quartz (10 %), augite (9%), cristobalite (6%), and an undetermined proportion of glassy material in the matrix (Figure 12).

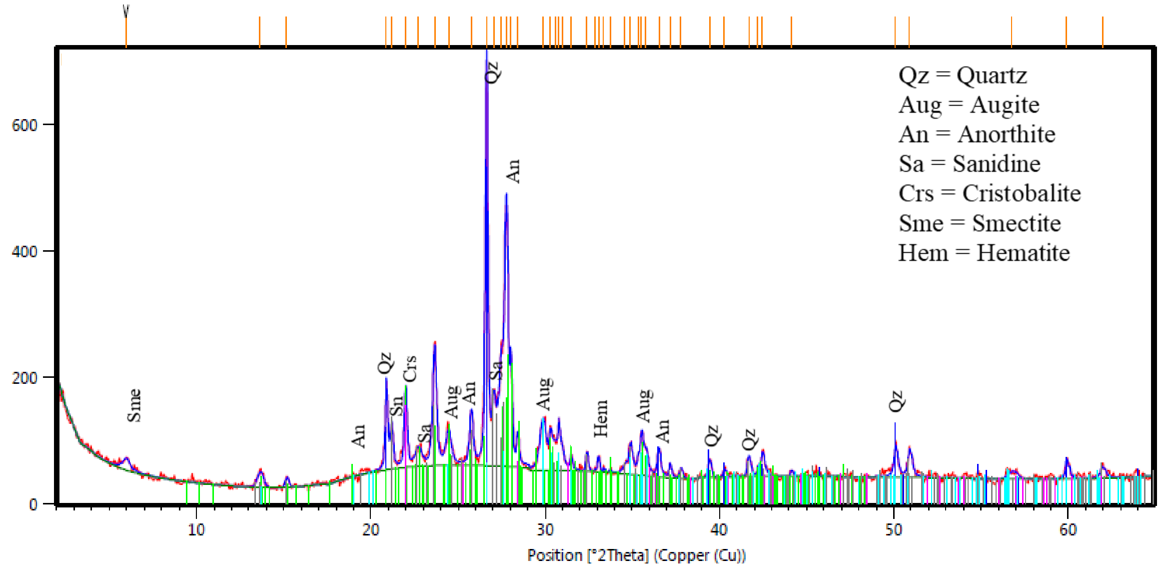

Figure 12. Diffractogram of X-rays of the volcanic rock waste.

The results concur with the studies of Knapik (2005) who showed an augite concentration of 10%, and 15% of quartz in basalt waste samples used in stonemeal studies. The glassy material is quite susceptible to weathering (Eggleton, 1986; Allen and Hajek, 1989), making it an important source of macro and micronutrients, with effective nutrient release from rock powder under weathering actions. The presence of all these mineral that are susceptible to weathering is a good indication that the wastes have the ability to release macronutrients and micronutrients into the soil.

4.3.2 Chemical characterization of volcanic rock powders

The results obtained by X-ray Fluorescence demonstrated that the main elements in the rock powder samples are Si (64.8%), Ca (3.56%), and minor Mg (1.27%). Na and K vary from 0.6% to 1.5%. Other inorganic chemicals elements analyzed incuding P and S represent less than 1.5% of the total composition of the sample. These results agree with those found by Theodoro and Leonardos (2006), who studied the characterization of similar rock powder and their application as natural fertilizers.

Additional elements as Ca could be supplied from pyroxene and feldspars alteration, and K from K-feldspar. Plagioclase and orthoclase are important sources of Ca, and K in soils, and orthoclase may be the largest reservoir of K (HUANG, 1989). The results of analysis by

ICP-MS, and ICP-AES demonstrates that the volcanic rock samples were characterized by a series of macronutrients and micronutrients described in existing literature (ARNON; STOUT, 1939; SONG; HUANG, 1988), and the low concentrations of potentially toxic elements such as As, Pb, Cd, and Li, among others, do not represent environmental risk (Table 6). These facts have proved that these volcanic rock powder will be effectives for applicability in agriculture.

Table 6. Chemical composition of macronutrients and micronutrients of volcanic rock waste.

Nutrients	mg kg^{-1}	Element	mg kg^{-1}	Element	mg kg^{-1}	Element	mg kg^{-1}
Al	43769	V	84	Mo	1	Ho	2
Ca	16536	Cr	7	Pb	19	Er	4
Fe	28398	Co	14	Sn	5	Dy	7
K	16054	Ni	3	Nb	44	Yb	4
Mg	5047	Cu	66	Cs	7	Th	13
Na	14029	Zn	116	Ba	647	Hf	6
P	691	Ga	21	La	42	Ta	3
S	449	Ge	1	Ce	81	W	1
Mn	863	As	3	Pr	12	Tl	1
Li	17	Tb	1	Nd	35	Zr	243
Be	3	Rb	116	Sm	8	U	4
B	31	Sr	170	Eu	2		
Sc	19	Y	45	Gd	8		

4.3.3 Availability of macronutrients and micronutrients of volcanic rock powder

The results of studies on the availability of macronutrients and micronutrients showed a suitable potential for the application of volcanic rock waste as a natural fertilizer. These rocks wastes released several nutrients from the solid structure to the aqueous solutions as shown in Table 7.

Table 7. pH and levels of macro and micronutrients available in extractor solutions (mg kg^{-1}).

Extractor	1		2		3		4		5		6		7	
pH	7.55		2.89		2.89		3.04		2.99		1.91		2.55	
Particle size	<90 µm	<38 µm	<90 µm	<38 µm	<90 µm	<38 µm	<90 µm	<38 µm	<90 µm	<38 µm	<90 µm	<38 µm	<90 µm	<38 µm
Al	<1	<1	541	762	546	659	632	766	698	737	3805	4350	759	820
Ca	1	1	394	1109	2018	2246	1482	1779	1124	1135	2575	2806	1373	1426
Fe	<1	<1	897	1342	846	1048	962	1275	1682	1911	8498	10953	1336	1440
K	<1	<1	256	385	185	217	169	186	132	139	476	537	153	170
Mg	<1	<1	247	341	245	300	277	330	297	307	1427	1655	332	341
Na	1	1	276	331	148	255	221	243	123	137	609	655	176	192
P	<1	<1	318	348	312	342	227	260	254	256	559	661	235	256
Si	1	1	433	464	424	407	424	526	338	491	2057	2625	442	475
Mn	0	0	159	198	198	247	209	264	157	163	539	668	225	229
Li	0	0	0	0	0	0	0	0	0	0	2	3	0	0
Be	0	0	0	0	0	0	0	0	0	0	1	1	0	0
B	0	0	1	1	1	1	1	2	1	1	2	3	1	1
Sc	0	0	0	1	1	1	1	1	0	0	1	2	1	1
V	0	0	2	3	1	2	2	2	2	3	12	15	2	2
Cr	0	0	3	4	2	2	2	2	1	1	5	4	2	2
Co	0	0	1	2	2	2	2	2	2	2	7	7	2	2
Ni	0	0	0	1	0	1	1	1	0	1	2	2	1	1
Cu	0	0	8	12	7	8	7	8	7	8	34	34	9	8
Zn	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ga	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ge	0	0	0	0	0	0	0	0	0	0	0	0	0	0
As	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Rb	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sr	0	0	1	1	1	1	1	1	0	0	1	1	1	1
Y	0	0	1	1	1	1	1	1	0	0	0	0	1	1
Zr	0	0	1	1	1	1	1	1	1	1	2	3	1	1
Nb	0	0	0	0	0	0	0	0	0	0	1	1	0	0
Mo	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Sn	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ba	0	0	3	3	2	3	3	3	2	2	8	8	3	3
La	0	0	0	0	0	1	0	1	0	0	0	0	1	1
Ce	0	0	2	2	2	2	1	2	0	0	0	0	2	2
Nd	0	0	1	1	1	1	1	1	0	0	0	0	1	1
Hf	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Ta	0	0	0	0	0	0	0	0	0	0	0	0	0	0
W	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Pb	0	0	0	1	0	1	0	0	0	0	0	0	0	0
Th	0	0	0	0	0	0	0	0	0	0	0	0	0	0
U	0	0	0	0	0	0	0	0	0	0	0	0	0	0

It is relevant to emphasize that the smaller the pH value, the greater the availability of nutrients becomes. In additional, the leaching elements concentrations are higher in samples with particle sizes smaller than 38 µm, and in extractor solution with 1% oxalic acid – extractor 6 (Table 7). These results agree with studies of Blum et al. (1989), who compared the dissolution of basalt at different grains sizes (<200 µm and <2000 µm) in 1% citric acid solution and found that nutrient release was greatest for the <2000 µm fraction.

This study showed considerable concentrations of Fe, Ca, Al, P, Si, Mg, Na, and K in all acidic solutions, therefore in Milli-Q water the availability for all nutrients was insignificant. The results showed that, specially the phosphorus, was available in high concentrations, above 90% of rock total composition (Table 6) in extractor 6 (Table 7). In general, the availability of P found in this study supports the application of volcanic rock powder as a natural soil fertilizer.

The available Potassium concentrations were also high (132 - 537 mg kg^{-1}) for all extractor solutions. Therefore, the availability of potassiun obtained in this study indicates that this nutrient may be of great potential in aiding several processes of plant growth through fertilization with volcanic rock waste.

Magnesium (245 - 1,655 mg kg^{-1}), Na (123 – 655 mg kg^{-1}), P (227 – 661 mg kg^{-1}) and Mn (157 - 668 mg kg^{-1}) levels showed a similar extractable proportion in all extractor solutions, even less abundant, as expressed in Table 7.

The extractor solutions 2-5 and 7 have showed similar concentrations of all nutrients. Therefore, in extractor solution 6 the Si availability was around five-times greater than in the other extraction solutions (Table 7). According to Gillman et al. (2002) the application of volcanic rock powders is able to raise Si in soils above the critical levels, but field trials are necessary to accurate assess of the criteria.

It is relevant to note that elements of high toxicity such As, Cd, and Pb, among others, have low availability (Table 7) by being present in the sample at low concentrations (Table 6). This reinforces the implementation of such material in food production, after all, even in extremely acid pH there was no high fraction leaching of these elements.

High aluminum concentration (4,350 mg kg^{-1}) was found in extractor solution 6, particle size <38 µm, but corresponding to a low potential release, of 10% approximately of total rock composition. The interpretation for this behavior could be the presence of high content of aluminosilicate glassy matrix (with low resistance to weathering processes). Aluminum released during dissolution in soils above pH 5 is generally precipitated as secondary aluminosilicates (LINDSAY, 1979). Thus, aluminum toxicity from dissolution of silicate rock powders is not expected (HARLEY; GILKES, 2000).

Calcium is slightly soluble in water (HARLEY; GILKES, 2000). Its solubility increases in acidic solutions showing variable concentrations in the leachates, although extractor 6 presents higher concentrations than the other extractors.

The leachate obtained from extractor 6 provides 10.95 mg kg^{-1} (547.67 mg L^{-1}) of Fe, representing a potential release of 38.5% (Table 7). Fe is immobile at pH higher than 4.5, and its release increases with decreasing pH (SILVA et al., 2011). According Sposito (1989), the level of this nutrient in the soil should range from 25,000 to 40,000 mg L^{-1}. This demonstrates that, although the sample has a high concentration of iron in its composition, the availability for the soil will be low.

The results in Table 7 show availability for micronutrients such as B, and Cu that appear in low concentrations as beneficial for plant nutrition. In addition, some of the nutrients studied may be available as a function of time, allowing for a gradual weathering of the rock powder maintaining nutrition in the soil.

4.4 CONCLUSIONS

According to the results obtained in this study, it is concluded that the volcanic rock can be used as a source of macronutrients and micronutrients to the soil, as it has in its composition several silicate minerals such as pyroxene, plagioclase and easily alterable ferromagnesian by weathering. The crystalline texture of volcanic rock is glassy. This fact turns this type of rock suitable for stonemeal due to the easy glass destabilization in exogenous conditions. The oxidation of feldspar and pyroxene, in addition to clay minerals that fill fractures and veinlets, and also occur in the matrix, it may indicate a hydrothermal process, bringing the destabilizing potential (replacement and/or processing) of these mineral phases, with consequent increase in the potential release of cations such as Ca, Fe, K, Mg, Na, P and Si, among others that may contribute to soil fertilization. Nutrient release experiments in acidic solutions conducted in the laboratory showed that the oxalic acid solution 1% (extractor 6) had the best extraction efficiency. Iron, Ca, Al, P, Si, Mg, Na, and K were the main nutrients available in the acidic solutions. The agronomic advantages of using volcanic rocks waste as a fertilizer may be the insolubility of nutrients in water, resulting in reduced losses by leaching and fixation, and the solubility of nutrient solution of weak acids such as exists in the soil solution, resulting in slow and efficient release of important nutrients for plant development. The volcanic rock, beyond their potential for use as natural fertilizer the soil, can reduce the environmental impacts of conventional agriculture and give appropriate destination to the waste produced in mining areas.

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EVALUATION OF SOIL RE-MINERALIZER FROM BY-PRODUCT OF VOLCANIC ROCK MINING: EXPERIMENTAL PROOF USING BLACK OATS AND MAIZE CROPS

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5 EVALUATION OF SOIL RE-MINERALIZER FROM BY-PRODUCT OF VOLCANIC ROCK MINING: EXPERIMENTAL PROOF USING BLACK OATS AND MAIZE CROPS

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ABSTRACT

This study was focused on physical, petrographical, mineralogical, and chemical characterization of a volcanic-rock mining by-product (dacite rock), as well as on greenhouse experiment with black oats and maize crops to evaluate the potential use of the by-product as soil re-mineralizer. The by-product sample was obtained from a quarry in the Nova Prata mining district in southern Brazil. The particle size distribution of the by-product and soil was determined by sieving. Dacite rock petrographic description was performed on a polished thin section by optical microscopy. The soil and dacite rock mineralogical phases were identified by X-ray diffraction. The by-product and soil chemical composition was determined by X-ray fluorescence. Inductively coupled plasma mass spectrometry was performed to determine potentially toxic elements, As, Cd, Hg and Pb in by-product. Additional chemical compositions of the by-product and soil were analyzed using a scanning electron microscope equipped with an energy dispersive X-ray detector. Black oats and, sequentially maize, crops were cultivated in a typical Hapludox soil treated with the by-product in a greenhouse. Five by-product doses (0, 906, 1813, 3625, and 7251 kg ha^{-1}) were added into pots containing soil, each with seven replications. Responses to treatments were evaluated from dry matter production, nutritional status of the crops, and in the changes in soil properties after 70 days of each cultivation. The results showed that the by-product is composed of plagioclase, K-feldspar, quartz, clinopyroxene, smectites, and opaque minerals with apatite as accessory mineral. The addition of 3625 and 7251 kg ha^{-1} doses of the by-product substantially increased the dry matter yield in maize leaves. The Ca uptake by maize leaves cultivated in soil with 7251 kg ha^{-1} dose of the by-product was significantly higher in soil with other doses, and all by-product doses promoted high concentrations of Mg and Ca. The accumulated amounts of Ca, K, Mg and P indicated that they were enough to supply maize nutritional needs. Improvements in soil properties, such as high levels of Ca, K and P and low levels of exchangeable Al and Al saturation were observed. The results of the study suggest that the by-product can be used as soil re-mineralizer. The dacite rock by-product studied here has potential to be an environmental solution to soil fertilization problem because it does not require chemical processing and can be used as it is mined.

Keywords: volcanic rock by-product, soil re-mineralization, agronomic efficiency, sustainable agriculture.

5.1 INTRODUCTION

Most tropical soils are acidic and have low fertility (Melfi et al. 1999; Rabel et al. 2018). However, to reduce ecological and economic damage from modern and intensive agriculture in external inputs, especially in highly soluble fertilizers, many alternative measures have been carried out (Ferrari et al. 2018). One of the measures that has been taken was to restore leached or degraded soils by adding rock mining by-products, which would yield the elements lost through leaching (Ramos et al. 2017). With regard to the use of ground rock as fertilizer, several experiments and data have shown that a wide variety of materials, with low environmental impact, can be used as alternative fertilizer for soils (Escosteguy and Klamt 1998, Kronberg et al. 1976; Leonardos et al. 1976; Gillman et al. 2001; Nunes et al. 2014).

Mining is mineral resource extraction, which induces environmental impacts on both the mined and nearby areas (Sánchez-Peña et al. 2018). In general, the by-products of rock mining are discarded in landfills or disposed of in the environment without any treatment processes (Machado et al. 2014). Thus, the application of by-products of volcanic rock mining as soil re-mineralizer can minimize the environmental impact caused by agricultural and mining activity and, hence, provide a wide range of nutrients that result in the improved quality of food and an environmentally safe technique (Ramos et al. 2015). Near agricultural production centres in the State of Rio Grande do Sul (RS) and Santa Catarina (SC), there is a wide distribution of volcanic rock deposits. Therefore, it is of great relevance to conduct research on the agronomic performance of these rocks, especially for plants demanding Si and K (Bergmann et al. 2017).

In the rock aggregate mining sector, fine crushed powders are by-products intended for uses such as asphalt filler. However, such by-products can create environmental problems when the demand is lower than production. In this case, their application in agriculture should be considered as an alternate to re-mineralize nutrient-depleted soils. Mineralogical and chemical characterization and an evaluation of their agronomic performance is required for evaluating the environmental risk of this material (Korchagin et al. 2018). Basalt by-products from quarries in South Brazil are well known as a soil re-mineralizer (Nunes et al. 2014), but dacite has not yet been utilized. The use of crushed rocks (mining by-products) as soil re-mineralizer is a long-standing practice to improve soil properties and increase crops productivity. It is also associated with the reduction of production costs, since re-mineralizers are cheap compared to soluble fertilizers (Silva 2016; Manning and Theodoro 2018).

In 2013, Brazilian law nº 12890/2013 included soil re-mineralizers as an input category for agriculture. Soil re-mineralizers are all mineral materials that have undergone only size reduction and size classification by mechanical processes and that change the soil fertility indices by addition of macro- and micro-nutrients for crops and improve the physical or physicochemical properties or the biological activity of soils. In Brazil, soil re-mineralizers have been developed, and Brazilian federal law (Brazil 2013) allows these to be used for crop nutrition, with specifications clearly defined by Normative Instruction (IN) nº 5 of the Ministry of Agriculture, Livestock and Supply (Brazil 2016). This approach provides a model that all countries to explore local geological sources and reduce the use on of high solubility fertilizers (Manning and Theodoro 2018).

Several rock powders such as basalt, phonolite, phlogopite, and granite, among others, have been studied to evaluate its potential use as fertilizer (van Straaten 2007). Dacite rock has different chemical and mineral compositions compared to the rocks cited above because of hydrothermal alteration (Meunier et al. 1988; Rosenstengel and Hartmann 2012). No geochemical/mineralogical study has been conducted to date to assess dacite rock by-product for application as re-mineralizer in tropical soil. Information from such study is fundamental for ensuring safe and efficient use of this by-product as soil re-mineralizer. Dacite rock not only contains primary minerals, but also clay minerals and accessory minerals that contain nutrients for plants (e.g., phosphorus, potassium) and may increase soil cation exchange capacity. To be considered and marketed as soil re-mineralizers, dacite rock by-product must meet the specific criteria established by the Ministry of Agriculture, Livestock and Supply (MAPA) (Brazil 2016).

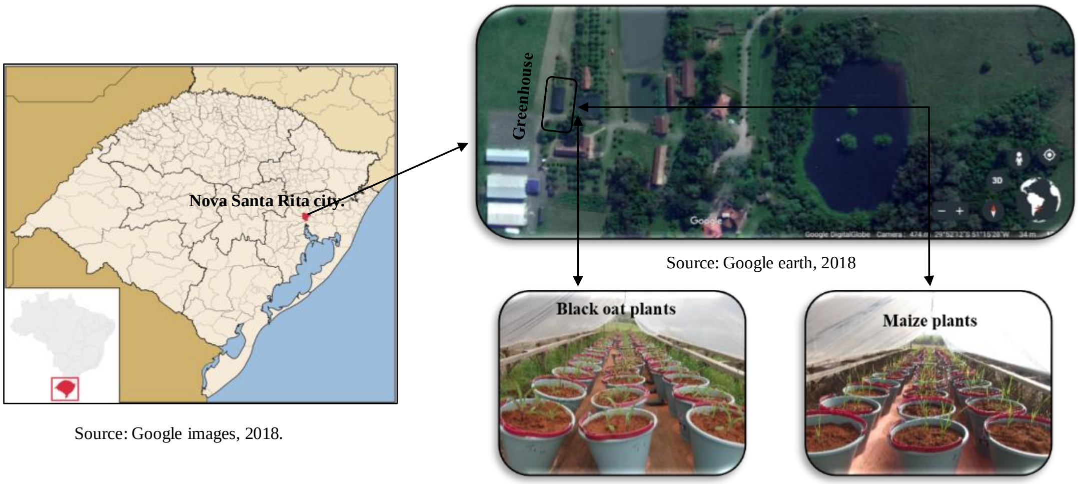
The objective of this study was to evaluate the potential use of the by-product produced from volcanic rock mining in the fertilization of the tropical soil, in the nutrition of the black oats and the maize crops, in a greenhouse located in Nova Santa Rita city, Rio Grande do Sul state, Brazil, and finally to serve as the basis for several countries that produce these types of rock aggregate by-product. The crops considered were selected because they are widely cultivated in Brazil. Another crop that shows great potential for the application of the dacite rock by-product would be soybean, which is considered as the largest consumer of fertilizers in Brazil. This study presents a viable sustainable alternative that could replace soluble fertilizers adding value to the investigated rock by-product.

5.2 MATERIAL AND METHODS

5.2.1 Soil, By-product, and Seeds Samples

Soil was sampled in June 2013 from several locations in the experimental site, in the Nova Santa Rita city (29°52'12" S; 51°15'28" W, South American Datum 1969), before re-mineralization treatments application. Soil samples were collected at depths of 0 to 20 cm (A horizon) to evaluate the soil fertility, mineralogy, and particle size distribution. For soil classification, samples were collected at depths of 20 to 40 cm (Bw horizon).

Soil of 1300 kg was collected at depths of 0 to 20 cm for the greenhouse experiment. This material was air-dried, homogenized, sieved at 4 mm mesh, and then finally quartered. For fertility analysis, an amount of approximately 500 g of soil was used. The experimental overview is shown in Figure 1.



Source: Google earth, 2018

Source: Google images, 2018.

Fig. 1 Experimental overview.

Twenty kg of by-product powder for particle size classification and chemical characterization and 1 kg of bedrock for petrographic description and chemical composition by scanning electron microscope were used in this investigation. The samples were obtained from the quarry Sindicato da Indústria de Extração de Pedreiras de Nova Prata in Southern Brazil (28º 46'27,37" S; 51º 38'16,61' W, South American Datum 1969). The distance between the quarry and the experimental site is 172.6 km.

For the cultivation of black oats and maize, seeds of black oats (Campo Bello - Controlled by the State Commission of Seeds and Seedlings - CESM/RS) and maize (cultivar HIB ITAP 700 - Seed ISA 509) were purchased in a local store.

5.2.2 Soil and By-product Particle Size Distribution

The particle size distribution of soil and by-product powder was determined according to the methodology for Brazilian norm, NBR-7181 (ABNT 1984). This methodology is relevant because the smaller the size of the mineral particles, the greater will be the surface area exposed to weathering, favoring the alteration of the material (Priyono and Gilkes 2008). For this analysis, 120 g of each sample were oven dried for 24 h at 105 ºC. The samples were then split into different particles sizes using sieves of different apertures (ASTM 4 - 4.8 mm, ASTM 7 - 2.8 mm, ASTM 10 - 2.0 mm, ASTM 20 - 0.84 mm, and ASTM 50 - 0.3 mm). The sieves were stacked on a mechanical shaker (Produtest®) for 15 minutes. After this, the particles retained per size were weighed on a semi-analytical scale (Gehaka ®, BG 1000, accuracy of ±

0.01 g). The percentages of particles sizes were determined from weights materials passing through each mesh size.

5.2.3 Analytical Procedures

5.2.3.1 By-product Petrography

Thin-section petrographic observations were made to identify the dacite mineral phases. The samples were analyzed on a Nikon Eclipse 50iPOL optical microscope (OM) under natural (NL) and polarized reflected light (PL).

5.2.3.2 By-product and Soil Mineralogy

X-ray diffraction (XRD) technique was employed to characterize the mineralogical composition of the by-product and soil samples using a Philips X-ray diffractometer, model X'Pert MPD, equipped with a curved graphite monochromator and fixed copper anode, operating at 40 kV and 40 mA. The angle range analyzed was from 5 to 75º. The step size used was 5º / 1s. Cu Kα radiation (1.54184 Å), Kα1 (1.54056 Å), Kα2 (1.54439 Å) and Kβ (1.39222 Å). The mineral identification from XRD data was done using the X'pert High Score Software.

5.2.3.3 By-product and Soil Chemical Composition

Chemical analyses of the by-product and soil were performed in triplicate, after manual milling using a porcelain mortar and pestle to obtain particles less than 0.074 mm. Chemical composition in percentage weight of oxides was determined by X-ray fluorescence (XRF) using a Panalytical brand MagiX equipment (DY1583) after digestion of 2 g of the sample by total fusion in automatic machine with lithium tetraborate (Silva et al. 2011).

The by-product sample was digested with four acids ($HCl:HNO_3:HF:HClO_4$) in a microwave for 1 h (Querol et al. 1997) to determine a potentially toxic elements (PTEs), As, Cd, Hg, and Pb composition. The analysis was performed at the Institute of Environmental Assessment and Water Research (Spain) by inductively coupled plasma-mass spectroscopy (ICP-MS).

Soil fertility was determined according to Tedesco et al. (1995), before application of the treatments and after harvesting of black oats and maize crops. This analysis included P and K (Mehlich 1), Ca, Al, and Mg (KCl 1 mol l^{-1}), and pH in water (1:1).

The micromorphology, texture, and chemical composition of the by-product were investigated on a polished thin section. The soil sample was adhered to stub using carbon tape. Then, the materials were gold-coated using a sputter coating device (BAL-TEC, SCD 005) for 3 min at 30 mA. The analyses were performed using a Zeiss EVO MA10 scanning electron microscope equipped with an energy-dispersive X-ray spectrometer (EDS). The mineral identifications were made using a back-scattered electron mode to produce images displaying high resolution.

5.2.4 Location and site preparation

The experimental site was in a greenhouse located in Nova Santa Rita city in the state of Rio Grande do Sul, Brazil. The work started in June 2013. The re-mineralization treatments were defined based on fertilization practices used in the region according to the Brazilian Society of Soil Science (SBCS 2004). Most of the tropical soils are acid and have low fertility, with very low P and K contents (Rabel et al. 2018). For this reason, the treatments were dimensioned from the K (62 mg l^{-1}) concentration in the experimental soil and on the K_2O concentration of by-product. This because 3.31 % K_2O concentration in the by-product is higher than that of MgO (2.27 %), and P_2O_5 (0.26 %).

Before planting, limestone, triple superphosphate (TSP), and by-product doses were thoroughly mixed in the soil. The re-mineralization treatments are show in Table 1.

Table 1. Doses of limestone, TSP and by-product and equivalents doses in K_2O, CaO, MgO and P_2O_5 applied in greenhouse treatments.

Treatments	Limestone[*]	TSP[**]	By-product	K_2O	CaO	MgO	P_2O_5
	(kg ha^{-1})						
T1	3,030	238	0	0	0	0	0
T2	3,030	238	906	30	32	21	2
T3	3,030	238	1,813	60	65	41	5
T4	3,030	238	3,625	120	129	82	9
T5	3,030	238	7,251	240	258	165	19

[*]Dolomitic limestone with total neutralization relative power (TNRP) of 72%; [**]Triple superphosphate (TSP).

5.2.5 Experimental design

The experiment was carried out using a randomized block design with five treatments replicated seven times, and each experimental unit consisted of three pots. Generally, in greenhouse experiments, containers are small (usually with a capacity of around 10 kg of soil), which do not allow the development of plants until the physiological maturation stage of the cultivated species (usually more than 110 cycle days, depending of the species). Thus, black oats were produced in the first 70 days and in sequence maize crops were also cultivated for 70 days. For this, nine seeds of black oats were planted on the drilled pots in the background, which contained 10 dm^3 of soil with treatments, and only three plants were grown for 70 days. Plants were harvested, washed with de-ionized water, and separated into leaves, stems, and roots. The material was dried at 40 °C until weight stabilization, weighed, and then finally milled. According to Jones et al. (1991), after digestion in concentrated H_2SO_4 and H_2O_2 at 390 °C, concentrations of Ca, K, Mg, and P in the leaves were determined using an atomic absorption spectrophotometer. According to Tedesco et al. (1995), for soil fertility analysis, approximately 500 cm^3 of soil was collected from each treatment.

Thereafter, the remaining soil samples (approximately 9.5 dm^3) were homogenized and passed through a 4 mm mesh sieve and repotted. Then, in the same soil samples, nine seeds of maize were planted, and only three plants were cultivated for 70 days. Plant and soil samples were processed as described above for black oats.

The least significant difference (LSD) test was used to examine the results. Regression models were used to analyze the effects of treatments on dry matter production and nutrient accumulation in plant leaves. To determine the relationship between the mean accumulated concentrations of nutrients in the leaves and the averages of dry matter yield of black oats and maize crops at 5 % probability, the Pearson's linear correlation was applied using the t-test. The BioEstat Statistics software (free distribution copy), version 5.3, was used to run all tests.

5.3 RESULTS AND DISCUSSION

5.3.1 By-product and Soil Particle Size Distribution

The particle size distribution of the by-product and soil, obtained by sieving, is shown in Tables 2 and 3, respectively.

Table 2. Particle size distribution of the by-product sample.

Sieve aperture (mm)	By-product (%)
4.8	100
2.8	100
2.0	100
0.84	81.2
0.3	56.8

The size distribution analysis showed that 100 % of the particles of the by-product measure less than 2 m. This result meets the granulometric guarantee established by IN nº 5 (Brazil 2016). The lower size distribution in the by-product may increase nutrients release. This interpretation was proven by the investigations of Priyono and Gilkes (2008), who studied the dissolution kinetics of silicate rock with particles size below 0.25 mm and 0.15 mm in an organic acid solution. These authors showed that the rate of cations dissolution increase with finer particle size.

The soil was classified as a typical Hapludox (HSoil), according to the United States Department of Agriculture soil classification (USDA 1999), with 21 % of clay in A horizon and 13 % in Bw horizon. The soil particle size results (Table 3) confirm that the soil is a typical

Hapludox. Briefly, the soil is composed of medium K (62 mg dm^{-3}), low P (6.2 mg dm^{-3}) and Al (0.3 cmolc dm^{-3}) concentrations. Soil has 6.9 cmolc dm^{-3} cation exchange capacity (CEC) with pH_{H2O} of 5.2, Ca and Mg concentrations of 2.6 and 0.7 cmolc dm^{-3}, respectively, 50 % base saturation (V), and 7.8 % of Al saturation indicator (m).

Table 3. Particle size distribution of the soil sample collected at depths of 0-20 cm.

Size fraction	Sieve aperture (mm)	Soil (%)
Course sand	2 – 4.8	3
Fine sand	0.05 – 0.42	5
Silt	0.005 – 0.05	16
Clay	< 0.005	76

5.3.2 By-product Petrography

Optical microscope observations revealed that the dacite has an acid composition, featuring a micro-crystalline to glassy matrix (amorphous) with porphyritic to micro-porphyritic texture of granulation less than 0.25 mm (Fig. 2a, b). Phenocrysts, micro-phenocrysts (less than 10 % of the volume of the rock) and a significant number of vesicles were observed (Fig. 2a, b). Plagioclase micro-phenocrysts appear isolated and comprise 67 % of the volume of the rock with grains size of 0.5-1.5 mm (Fig. 2c). The micro-phenocrysts of clinopyroxene are less than 1.8 mm length (Fig. 2d, e). The minerals identified in the matrix were plagioclase (albite), clinopyroxene (augite), quartz, and opaque (hematite) minerals with apatite as accessory mineral. The quartz is colorless and anhedral, with diameter less than 0.35 mm, and occupies interstitial spaces (Fig. 2d). Apatite crystals have needle shapes of grains less than 0.15 mm (Fig. 2f).

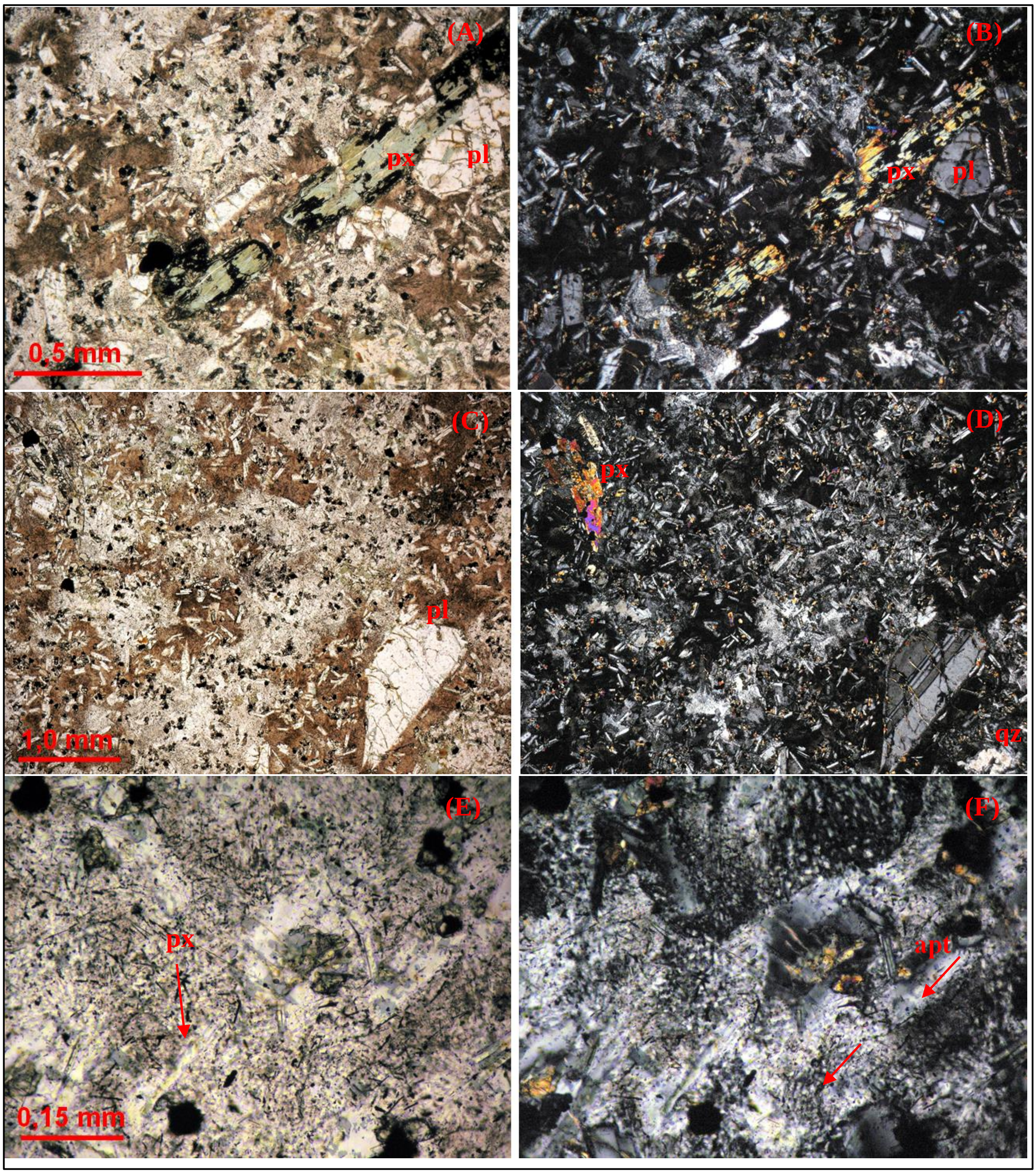


Fig. 2 Photomicrographs of dacite rock. (A) and (B) plagioclase (pl) and clinopyroxene (px) phenocrysts under NL and PL; (C) plagioclase (pl) phenocrysts under NL; (D) clinopyroxene (px) microphenocryst and quartz (qz) under PL; (E) clinopyroxene (px) phenocryst under NL; (F) apatite (apt) crystals under PL.

5.3.3 By-product and Soil Mineralogy

The presence of montmorillonite, saponite, and hematite (Fig. 3) shows that the by-product has been altered by a hydrothermal agent. Hydrothermal alteration of volcanic rock produces high proportions of amorphous material, which presents low mineralogical stability when exposed to exogenous conditions (Ridley 2012). This makes the rock interesting for use in soil re-mineralization (Ramos et al. 2017). The by-product contains an undetermined proportion of glassy mass, undetectable by X-ray diffraction analysis, which may supply macro-nutrients such as Ca, K and Mg to soil (Deer et al. 2013). The weathering of the glassy matrix, together with the weathering of sanidine, albite and augite, in addition to clay minerals that fill the vesicles and occur in the rock matrix, indicates hydrothermal alteration. This process changes the mineral phases, increasing the cations release potential, which may contribute to the soil re-mineralization (Korchagin et al. 2019). The dominant minerals observed in the by-product were plagioclase albite and pyroxene augite (Fig. 3) are the most common volcanic rock-forming minerals (Deer et al. 2013).

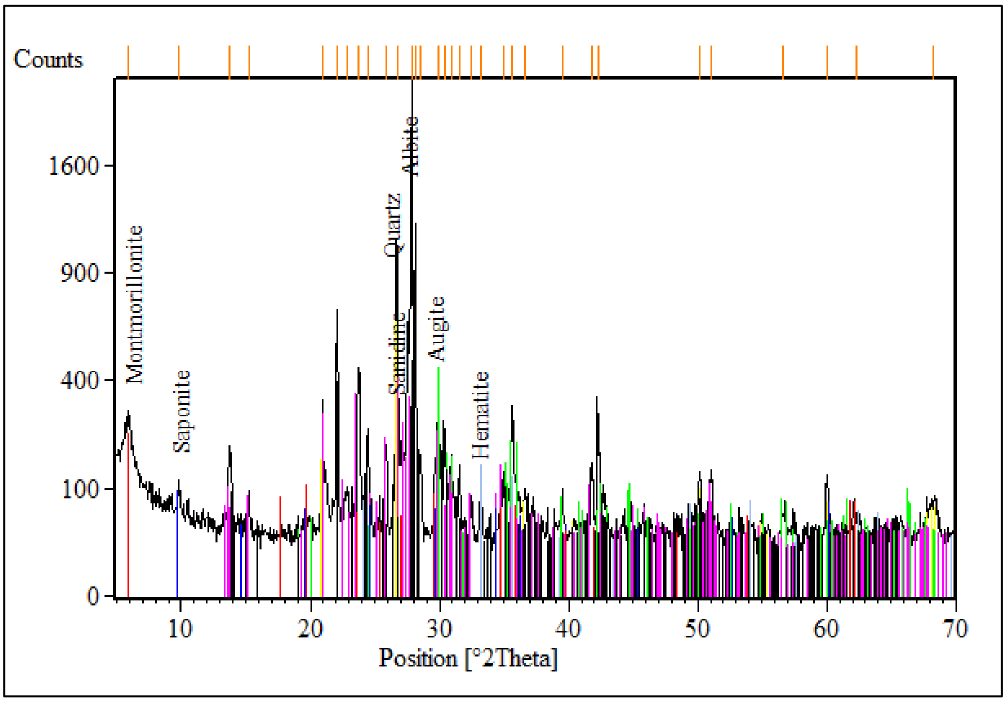


Fig. 3 X-ray diffractogram of by-product sample.

X-ray diffraction and SEM/EDS analysis show the occurrence of sanidine in the by-product (Fig. 3 and 4a). This mineral belongs to the group of K-feldspars, and when added to soil can release its elements more easily due to the action of weathering (Manning et al. 2017). K-feldspar is an important source of K to the soils and may be the largest reservoir of K (Ciceri et al. 2017). The presence of smectites (montmorillonite and saponite) as clay minerals in the by-product was observed in Figure 3. Smectites have a relevance in soils due to their high cation exchange capacity (Huggett 2015).

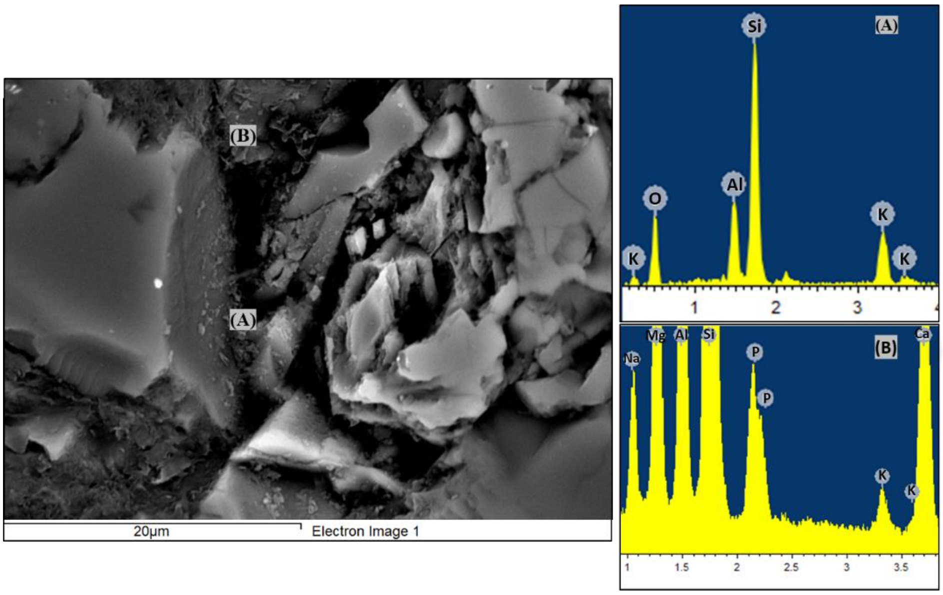


Fig. 4 SEM/EDS of (A) sanidine and (B) apatite detected in the by-product sample.

Apatite is a widespread accessory phosphate mineral that occurs in almost all igneous rocks and is known to be partially resistant to weathering (Piccoli and Candela, 2002). This suggest slow dissolution and P release. This interpretation is contradictory to studies of Ramos et al. (2015), which showed recovery up to 93 % of the P in leaching tests using dacitic rock powder from the same region of this study. The presence of apatite is a good indication that by-product can release P to the soils. Figure 5 shows the appearance and composition of the mineral particles of HSoil. The soil consists predominantly of quartz, kaolinite, and goethite.

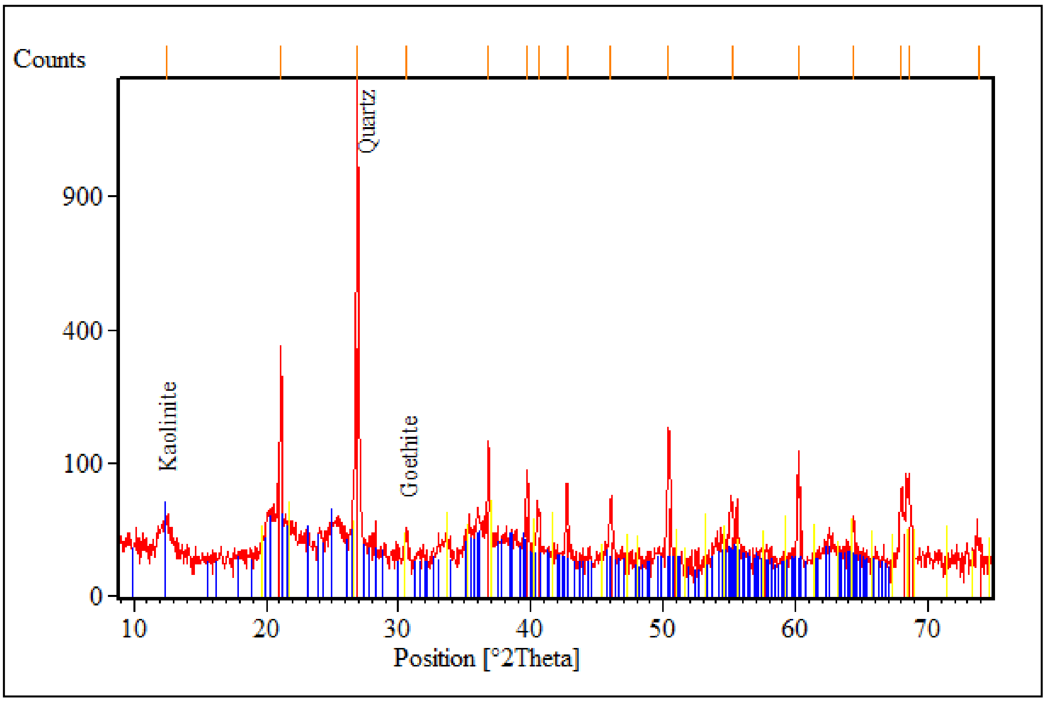


Fig. 5 X-ray diffractogram of soil sample collected at depths of 0-20 cm.

5.3.4 By-product and Soil Chemical Composition

The data in Table 4 indicate the predominant presence of Si, Al, Fe, and Ti oxides in decreasing order, and, in smaller proportions, oxides of Mg, Mn, P, Ca, K, and Na in the Hsoil sample.

Table 4. Chemical composition in percentage weight of oxides in the by-product and soil samples.

Oxides	By-product	HSoil
	(%)	
SiO_2	64.8	75.2
TiO_2	0.86	1.49
Al_2O_3	13.8	9.76
Fe_2O_3	6.06	6.12
MnO	0.13	0.1
MgO	2.27	<0.1
CaO	3.56	0.15
Na_2O	3.13	0.11
K_2O	3.31	0.27
P_2O_5	0.26	0.11
LOI*	1.35	6.57
Total	99.53	99.88

* Loss on ignition

The by-product contains different chemical elements, expressed as oxides (Table 4). These results concur with those obtained by Nunes et al. (2014), who characterized four similar rocks and their application as a soil re-mineralizer. The results of XRD (Fig. 5) and XRF, with respect to Al, Si, Fe, and Ti oxides, support the presence of quartz, kaolinite and goethite (Fig. 6a, b, c).

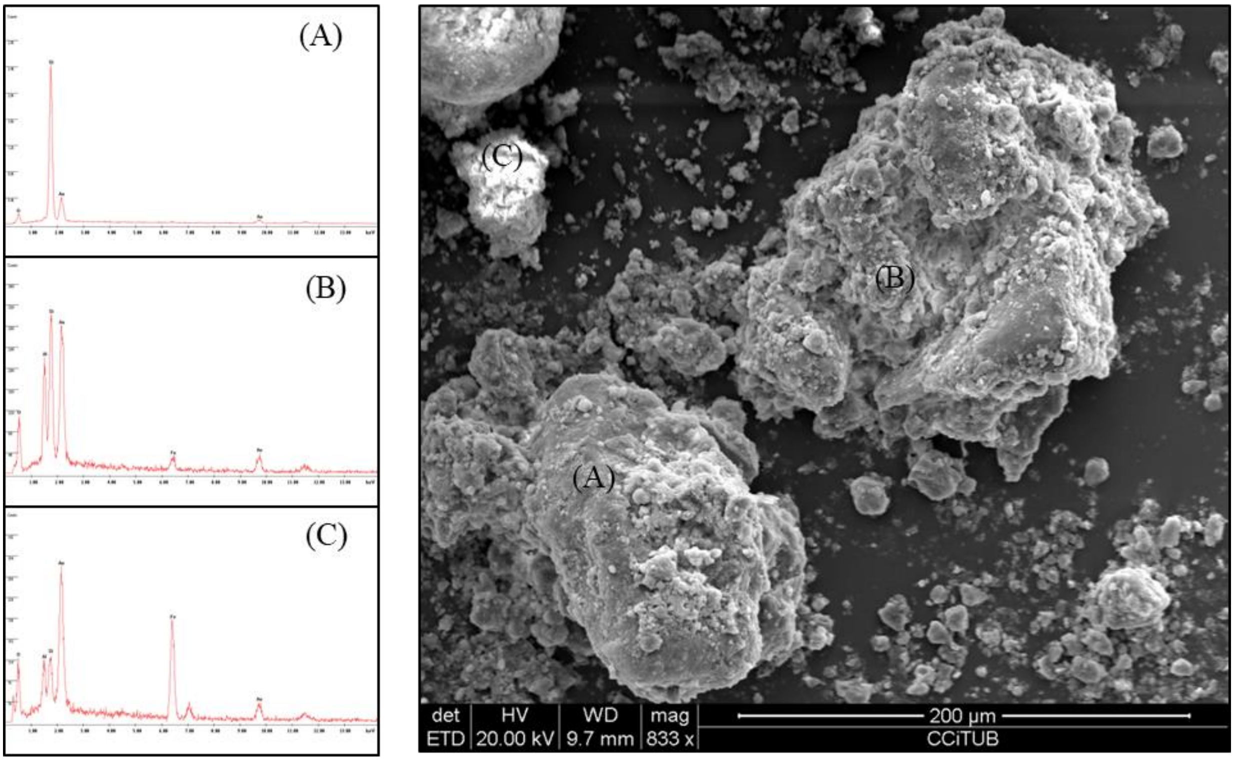


Fig. 6 SEM/EDS of (A) quartz, (B) kaolinite and (C) goethite detected in soil sample collected at depths of 0-20 cm.

In terms of chemical composition expressed as major and minor elements, it can be stated that the studied rock is dacite (Streckeisen 1976). In terms of potential (based on content) for the macro-nutrient K, the by-product could be indicated as a soil re-mineralizer according to the Brazilian IN nº 5 (Brazil 2016). The by-product presents the sum of chemical compounds (CaO + MgO + K_2O) higher than 9 % and K_2O content higher than 1 %, in compliance with the Brazilian IN nº 5 (Brazil 2016). According to Ramos et al. (2017), most of Brazilian volcanic rocks contain a sum of chemical compounds which K_2O content higher than the values established by Brazilian IN nº 5. From these results, the criteria for a re-mineralizer are satisfied by the by-product studied here. This is a positive characteristic that represents good potential for agricultural use, especially in nutrient-poor soil such as HSoil (Table 4).

The average phosphorus concentration of the Earth's upper crust is approximately 0.1 % P_2O_5 (Cordell and White 2011). According Table 4, the P_2O_5 content of the by-product is almost three-times above the crustal average. This result may be attributed to the occurrence of apatite in the by-product, because this mineral was identified by OM (Fig. 2f) and by SEM/EDS (Fig. 4b). This finding concurs with Ptáček (2016) that the apatite is the most abundant phosphate mineral, which accounts for more than 95% of all phosphorus in the Earth's crust and is found as an accessory mineral in volcanic rocks.

According to data presented in Table 4, the by-product is characterized by primary macro-nutrients such as K and P. Phosphorus and K are important nutrients to obtain high productivity in several crops; for example, in tropical soils (Carvalho et al. 2018). Calcium and Mg appear as secondary macro-nutrients. According to Gilliham et al. (2011), calcium serves vital physiological functions in plants. Magnesium is involved in chlorophyll pigments, in photosynthesis, and aids in phosphate metabolism, plant respiration and the activation of many enzyme systems (Guo et al. 2016). Sodium is a common constituent in plants, but it is not an essential element, although for some plants, such as sugar beet, it is an important element to achieve high yields (Nieves-Cordones et al. 2016). The high Al content in the by-products is not concerning because Al precipitates in environments with pH above 5 and will not be available for soil solution and consequently for plants (Ramos et al. 2017). This is environmentally relevant because it supports the sustainable agricultural use of the by-products and hardly causes Al toxicity to plants. High content of Na in tissues is critical to ionic toxicity in plants, because, besides interfering with the proper homeostasis of K, Na reduces the availability, translocation, and mobilization of Ca to the growing regions, which affects vegetative growth and production (Cabot et al. 2014). Silicon is a micro-nutrient considered beneficial (Haynes 2014) but not essential to plants. This nutrient is extremely important for the development and crops protection (Keeping 2017; Beerling et al. 2018).

The maximum limits of PTEs in soil re-mineralizers allowed by Brazilian normative instruction are As (15 ppm), Cd (10 ppm), Hg (0.1 ppm), and Pb (200 ppm) (Brazil 2016). The results of analysis by ICP-MS demonstrates that the by-product sample has low concentrations of PTEs As (3 ppm), Cd (<0.01 ppm), Hg (<0.01 ppm), and Pb (19 ppm), which do not represent an environmental risk.

5.3.5 Agronomic Performance of the By-product

5.3.5.1 Soil composition

Figure 7 shows that, after of the soil treatments, soil fertility attributes such as base saturation (V), Al saturation (m), Al concentration, and CEC, varied significantly when analyzed 140 days after maize crops were harvested. The application of all by-product doses (treatments T2-T5) significantly reduced the soil Al levels after 140 days. This result conforms to the observations of Ramos et al. (2017), which also supported the agricultural use of the volcanic mining by-products. Aluminium is toxic to plants, acidifies soil, and causes nutritional deficiency. The reduction of Al levels in soils with treatments T2-T5 is extremely important because most agricultural plant species do not achieve maximum production potential when produced on highly acid soils (Sade et al. 2016; Barbosa et al. 2017). Although the by-product has high levels of Al_2O_3 (13.8 %), the toxicity by its dissolution is not considered to be an environmental concern. Aluminium released during dissolution in soils with pH above 5 is generally precipitated as secondary aluminosilicates or as oxides and hydroxides (Faquin 1982; Lindsay 1979).

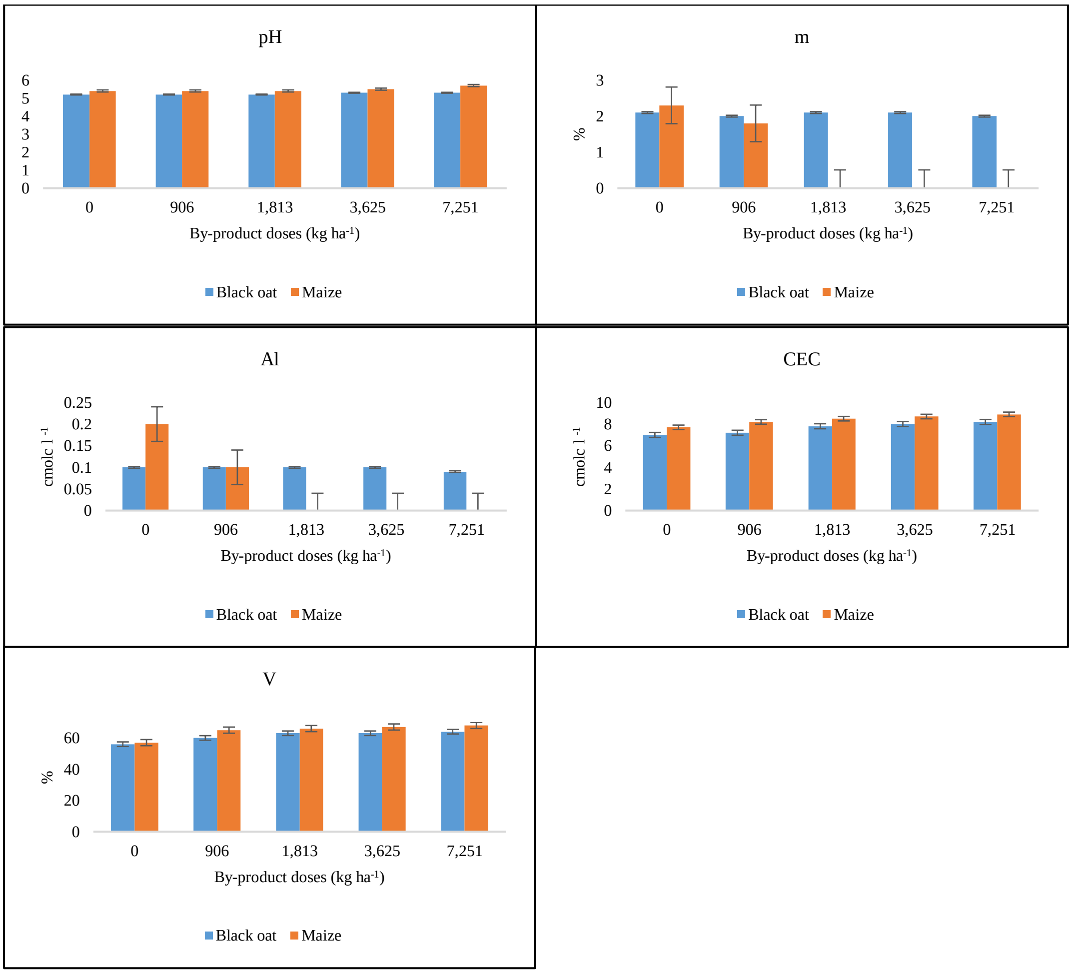


Fig. 7 Fertility attributes of soils with different treatments of the by-product. Vertical bars (I) represent the standard error from seven replications.

As illustrated in Figure 7, the pH of the soils was not increased significantly ($p = 0.3394$). The highest pH value was found in treatment T5, which was measured at the end of maize cultivation. However, the pH value was significantly higher ($p = 0.0053$) in treatment T5 as compared to the treatment T1 that received only limestone (at 3.03 t ha^{-1}) and triple superphosphate 0.238 t ha^{-1} after maize cultivation. According to Fageria (1998), it is necessary to apply approximately 12 t ha^{-1} of limestone in order to increase the pH value of the HSoil to 6.0.

The results presented in Figure 7 proved that the by-product studied has potential for increasing the soil pH because it acted as correctives of acidity in the short term (140 days). The results conform to those of Dumitru et al. (1999) whereby the application of rock dust slowly increases soil pH. One of the factors that considerably restrict the productivity of different crops in various parts of the world, including Brazil, is soil acidity. For the incorporation of these soils into the productive process, the use of materials that have the potential to increase pH is indispensable (Fageria 2009). The soil-plant system is dynamic, and it is difficult to define the optimal pH for several annual crops. According to Fageria et al. (1998), most crops can produce well in soil with pH of around 6 (Fageria et al. 1998).

With increase in the by-product doses, the CEC of the soils also increased; thus, indicating the interaction of this effect with the period of the experiment (Figure 7). Especially after maize cultivation, the tested doses provided a linear increase in CEC. However, the increases in CEC obtained in soils did not to reach 16.2 cmolc dm^{-3}, which is the minimum considered adequate by SBCS (2004).

Before treatment T1 of the HSoil, the Al saturation indicator (m) was 7.8 %. This decreased to 2.0 % after black oats cultivation (Fig. 7), which could possibly be due to the application of limestone. However, the values were significantly lower, between 1.8 % and 0 % after maize cultivation in the treatments T2 to T5, respectively. This shows that the decrease in the Al saturation indicator was caused by increased by-product doses.

The data in Figure 8 show that the by-product application did not significantly change the concentrations of Ca, K, Mg, and P in the soil after 70 days of black oat cultivation ($p > 0.05$). However, a significant ($p < 0.05$) increase in the availability of Ca, K and P in the soil was observed after maize cultivation (140 days). Though the Mg did not increase significantly, its contents reached high levels in the soils for all the treatments. Soils with Ca contents between 2.1 and 4.0 cmolc l^{-1} and Mg contents between 0.6 and 1.0 cmolc l^{-1} are considered satisfactory according to SBCS (2004). The Ca and Mg contents reached above satisfactory levels. This result can be attributed primarily to the presence of albite and augite minerals in by-product, which were able to release Ca and Mg when added to the soils. In addition, the Ca and Mg contents were well below the levels added via by-product, which showed that these materials have the potential for the immediate release of these nutrients.

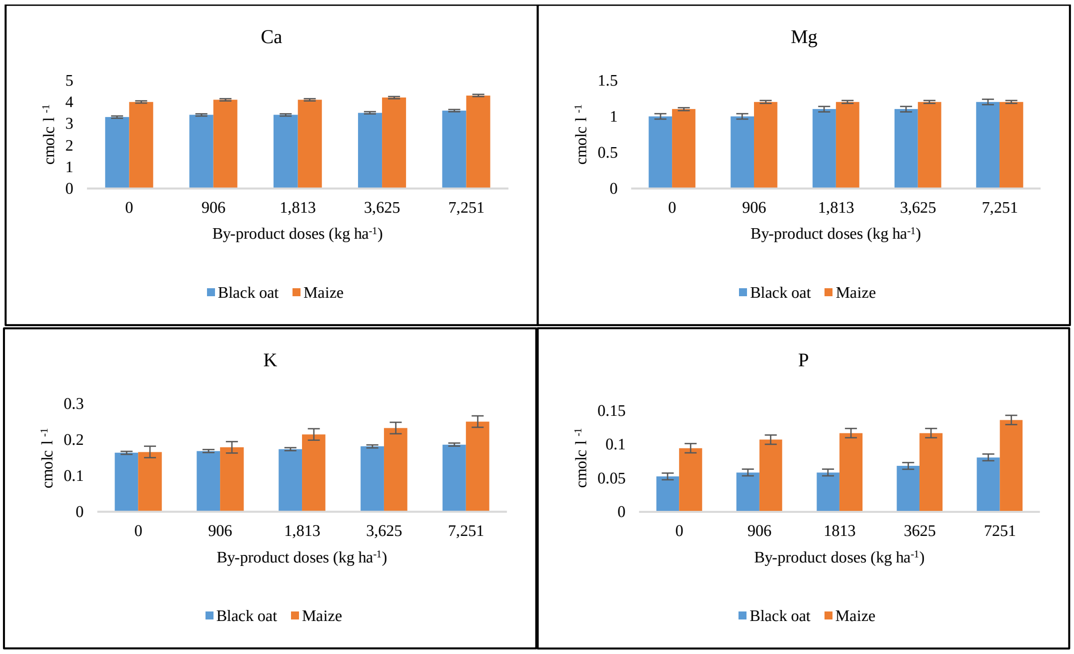


Fig. 8 Available nutrients in soils with different treatments of the by-product. Vertical bars (I) represent the standard error from seven replications.

Generally, tropical soils have low available K concentration (Zhang et al. 2017), but it is not so low as P. After P, K is the second most consumed nutrient in Brazilian agriculture (Coelho and França 1995; Nowaki et al. 2017). In this study, the available K concentrations were observed to be high (91 and 98 mg l^{-1}; SBCS 2004), which correspond to 0.23 and 0.25 cmolc l^{-1} in the treatments T4 and T5, respectively, after maize cultivation. This can be explained by the presence of sanidine mineral in the by-product, which was detected via XRD and SEM/EDS analyses (Fig. 3 and 4a) and is directly associated with the release of K. This result is very important and unusual in the existing literature. As an example, we can cite the study of Bakken et al. (2000), who investigated the release of K by crushed rocks and mining tailings by cultivating ryegrass for six months. The authors showed that K was sparsely available to plants, regardless of rock doses. Santos et al. (2016) determined the release of K in soils by the verdete rock with 77 g kg^{-1} of K and verified that soil K levels were decreased after grass, maize, and eucalyptus plantations. In soils treated with doses up to 50 t ha^{-1} of ground basalt, the low release of K was also observed by Motta and Feiden (1992). In the present study, the availability of K obtained, indicated that the dacite powder has potential for soil re-mineralization.

Typically, tropical soils have low concentrations of available P and high potential for the “fixation” of P applied by using soluble fertilizers. This factor rated P, along with N, as one of the most limiting nutrients in crop production in Brazil (Fageria 2009). The pH value of soil, as an isolated factor, is the most important factor that affects the availability of P in soil, which promoted the greater availability of P in the soil solution with pH of 5.7 (Fig. 7), and consequently it showed higher uptake by maize plants cultivated in treatment T5 (Fig. 9).

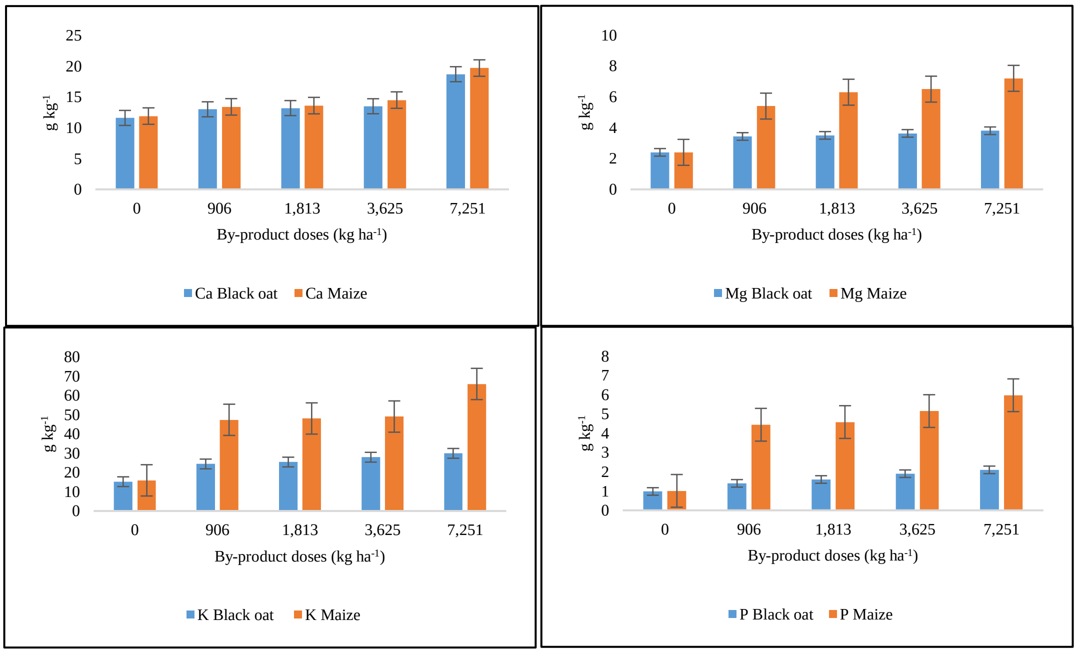


Fig. 9 Nutrient concentration in leaves of black oats and maize crops grown in soils with different treatments of the by-product. Vertical bars (I) represent the standard error from seven replications.

A gradual increase in the available P in soils with the by-product dose increase (Fig. 8) showed that such a source may be considered good as a useful fertilizer. According to SBCS (2004), these doses were enough to alter the level of P in the soils, because P concentration without by-product (treatment T1) was low (5.40 mg dm^{-3} corresponding to 0.052 cmolc l^{-1}) and the P concentration became average (11.0–14.0 mg dm^{-3} corresponding to 0.1-0.13 cmolc l^{-1}) after maize cultivation.

The results obtained in this study conform to those of Theodoro et al. (2010) that rocks can provide nutrients that are important for crops. Considering the fact that the experimental time was only 70 days for each crop, the by-product of this study presented notable reactivity in soils of treatments T3-T4.

5.3.5.2 Growth and Nutrient Uptake by Black Oats and Maize Crops

The growth and Ca, K, Mg, and P uptake by black oats and maize leaves were significantly affected by the by-product doses (Fig. 9). The reference values for black oats and maize leaves contents, according to Pauletti (2004), are show in Table 5. These results indicate that these nutrients were released rapidly from the by-product, suggesting that the by-product had an immediate effect of release nutrients onto soil.

Table 5. Reference values of Ca, K, Mg, and P contents for dry matter of black oats and maize leaves.

Crops	Ca	K	Mg	P
		g kg^{-1}		
Black oats	2.5 - 5	15 - 30	1.5 - 5	2 - 5
Maize	2 - 8	17 - 35	2 - 5	2 - 4

According to Figure 9, the K concentration in treatment T1 was below the critical value in maize leaves (15.9 g kg^{-1}), and in leaves of black oats it was at the limit of critical value (15.2 g kg^{-1}). It was possible, as evidenced in Figure 9, that with increasing by-product dose, the K content of leaves of both crops increased linearly. In treatments T2-T5 the levels of K in black oats leaves were within the appropriate range, whereas K in maize leaves was well above the range (Table 5).

The K contents in the foliar tissues of black oats cultivated in treatment T5 was two-times greater than in treatment T1. In maize leaves, it was four-times greater than treatment T1. Curi et al. (2005), stated that the release of K in soils by K-feldspars can supply the K demand of plants for some cycles. During these vegetative cycles, monitoring should be done so that the plants do not present deficiency of this nutrient.

For P, behavior similar to K was observed. The concentration of P in treatment T1 was below the critical value in maize leaves (1.01 g kg^{-1}) and in black oats (0.98 g kg^{-1}) (Fig. 9). With the increase of the application of by-product, the concentrations of P in the leaves also increased linearly (Fig. 9). In treatment T5, the P content in black oats leaves reached the appropriate range whereas in maize leaves was well above of appropriate range (Table 5). This behavior agrees with the finding of Ros et al. (2017) that P exhibits great mobility in young maize plants.

As can be observed from Figure 9, the treatments T2-T5 had the highest concentrations of P and Mg after maize harvesting. Phosphorus is significantly influenced by the synergistic concentration of Mg in the soil (Ribes et al. 2012). Foliar Ca content of black oats and maize crops presented a linear effect as a function of by-product doses and was approximately 1.6-

times higher in treatment T5 than in treatment T1 for both crops. This may have occurred because Ca was added to the soil via limestone in treatment T1 but in treatment T5 was released via weathering of the albite and augite present in by-product. These minerals were detected by XRD (Fig. 3).

As illustrated in Figure 9, it was observed that the Mg contents in black oats leaves were not significant in relation to the by-product doses. In contrast, Mg levels were significantly increased in maize leaves, probably due to limestone in treatments T1 and T2. In treatments T3–T5, such increase in Mg can be attributed to the weathering of the augite mineral present in the by-product.

The dry matter production of black oats increased linearly (Fig.10), but statistically there was no significant difference ($p = 0.246$). A quadratic response in the dry matter production of maize was observed, with statistically significant difference ($p = 0.010$) between treatments, which according to the regression model indicated efficient maximum values at 5000 kg ha^{-1} (Fig. 10). The dry matter yield of black oats obtained in this study showed increases of 11 % and 19 % in treatments T4 and T5, respectively. Evans (1947) used 247 and 497 t ha^{-1} of basalt powder and obtained increases of 33.7 % and 56.7 % in dry matter production with potted oats. If the same doses suggested by Evans (1947) were applied in the present study, the increases would be 754 % and 1311 %.

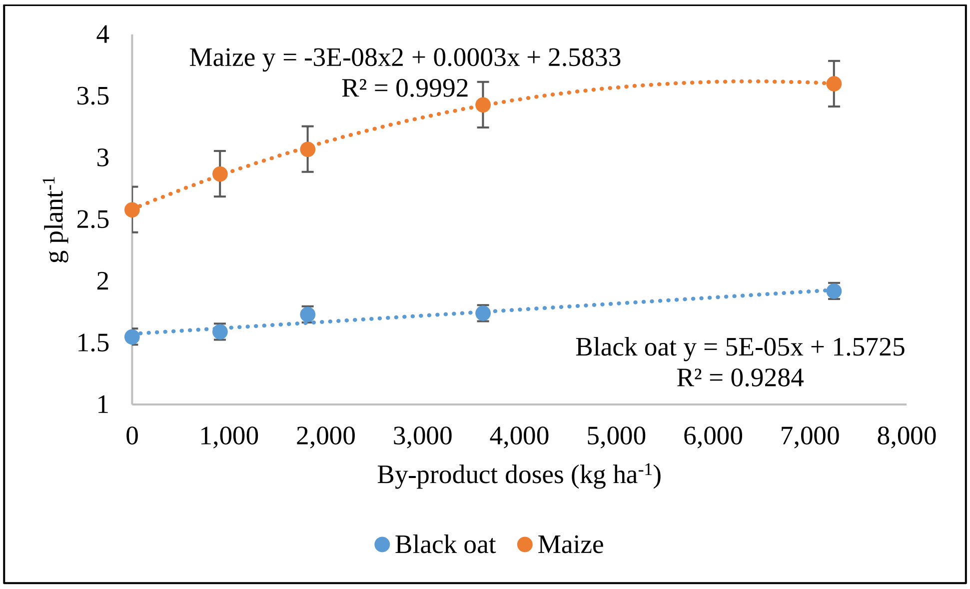


Fig. 10 Regression plot describing the effect of waste rates on dry matter production of black oats and maize grown in soils with different treatments of the by-product. Vertical bars (I) represent the standard error from seven replications.

The above results agree to those obtained by Theodoro and Leonardos (2006), who concluded that the use of the rock powder increased the production of maize, rice, cassava, sugar cane, vegetables, and fruits compared to soluble fertilization.

5.3.5.3 Nutrients Accumulation by Black Oats and Maize Crops

A linear increase in the accumulation of Ca and K in the leaves of both crops as a function of the addition rates of the by-product are presented in Figure 11. In black oats leaves, the same results were observed for Mg and P. According to the regression model, a quadratic response was observed for Mg and P accumulation in maize leaves, which indicates maximum efficiency at 5416 kg ha^{-1} and 5800, respectively (Fig. 11).

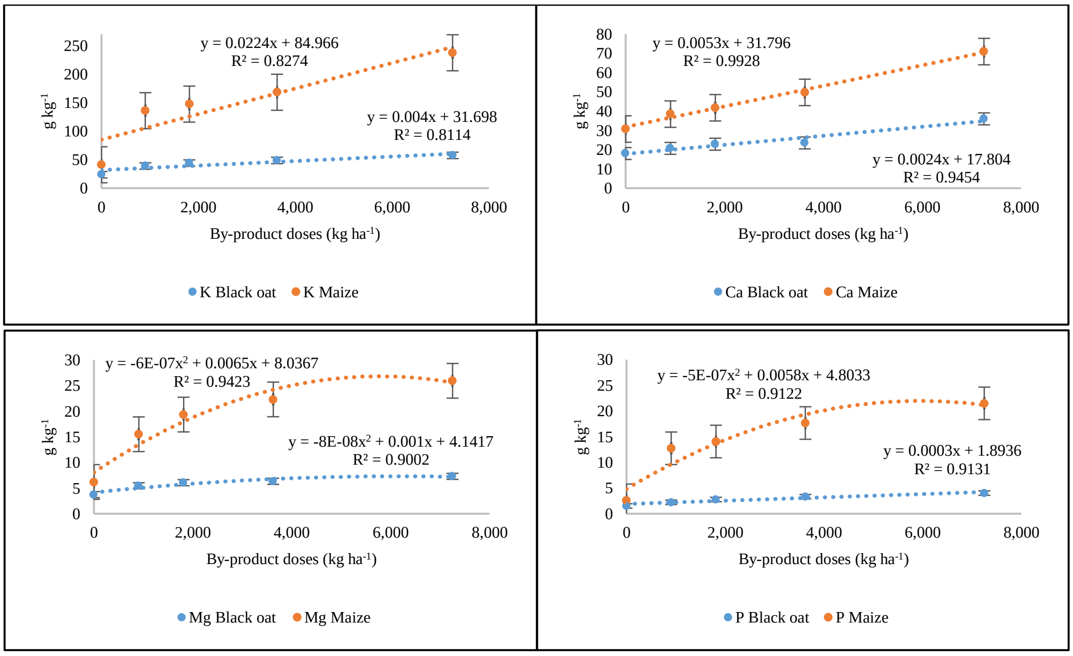


Fig. 11 Regression plots describing the effect of waste rates on Ca, K, Mg, and P cumulative absorption in leaves of black oats and maize grown in soils with different treatments of the by-product. Vertical bars (I) represent the standard error from seven replications.

Treatment T5 presented a significantly higher value ($p < 0.01$) than the other treatments for the accumulation of K by maize leaves (Fig. 11). This was possibly because the leaves were collected at 70 days, which coincides with the recommended time for leaf sampling (SBCS 2004). This result suggests that the plants absorbed the amount of K required for their complete development.

Most of the linear correlation coefficients between the mineral nutrition elements of black oats and maize crops were found by the t-test to be significant with 95 % confidence

(Table 6). As observed in Table 6 for black oats and maize crops, the positive correlations of P with K and Ca indicate that the greater P content in plant is the better the root system growth of the plants is thus allowing the plant to explore a larger volume of the soil (Malavolta et al. 1997). It was observed that K correlated positively with Ca, and the synergistic effect between K and Ca was evidenced in maize leaves due to the high correlation between them.

Table 6. Pearson correlation matrix for nutrient concentrations accumulated in black oats and maize leaves and mean dry matter yield data.

	Ca black oats	Ca maize	K black oats	K maize	Mg black oats	Mg maize	P black oats	P maize
K black oats	0.8595	-	-	-	-	-	-	-
K maize	-	0.9301*	-	-	-	-	-	-
Mg black oats	0.8459	-	0.9974*	-	-	-	-	-
Mg maize	-	0.8776	-	0.9764*	-	-	-	
P black oats	0.897*	-	0.9819*	-	0.9685*	-	-	-
P maize	-	0.8838*	-	0.9868*	-	0.9931*	-	-
Dry matter black oats	0.9487*	-	0.927*	-	0.9163*	-	0.9656*	-
Dry matter maize	-	0.9259*	-	0.9413*	-	0.9656*	-	0.9557*

* Significant correlation at the 5% probability level by the t test.

Considering the presented results, we can infer that the application of the by-product was satisfactory because it positively altered the soil fertility attributes and it met the demand for Ca, K, Mg, and P by maize crops and black oats plants in a short term. All parameters evaluated in this study met the requirements established by IN nº 5 (Brazil 2016). These results suggest that this technique can and should be adopted at a global level, especially in countries that have rock mining activity. It is important to note that several studies have shown that other rock types, such as metasedimentary rocks (e.g., verdete; Santos et al. 2016), plutonic rocks (e.g., nepheline syenite; Nascimento, 2004), and metamorphic rocks (e.g., shale; Silveira et al. 2010), are composed of minerals that are rich in nutrients, particularly K.

5.4 CONCLUSIONS

This work evaluated the ability of a by-product of volcanic rock mining to positively alter the agronomic properties of the soil and the development and productivity of black oats and maize plants. The purpose was achieved by using the optical microscopy, XRD, XRF, SEM/EDS, and ICP-MS for determining the petrographic, mineralogical, and chemical composition of the by-product.

The safe use of the by-product evaluated here requires an evaluation of the PTEs composition, to ensure the quality of the inputs added to the soil, which will result in better food nutritional quality and environmental protection. The by-product contains macro-nutrients such as Ca, K, Mg, and P, besides low PTEs concentrations, which do not represent environmental risk, indicating good potential to be used as soil re-mineralizer. This study demonstrated that the by-product positively influenced the nutrition and development of black oats and maize grown in treatments T3-T5. These results suggest that this by-product could replace soluble fertilizers. In addition, it does require chemical processing and can be used *in natura*.

The increase in pH of soil treated with 7251 kg ha^{-1} of the by-product was considered significant when compared to the treatment with zero-dose of the by-product. In treatments T3–T5, relevant reductions in exchangeable Al and Al saturation were observed, which show the residual effect due to large reserves of Ca and Mg that were slowly released by the by-product. The application of by-product doses in treatments T3-T5 increased the plant growth, reduced Al toxicity in the soil, and amplified the levels of P, Ca, and Mg in the soil and the levels of Ca and Mg in plants. The application of the by-product studied here is a sustainable technology for soil re-mineralization. The use of this by-product in agriculture may be suitable for solving the problem of by-products deposited outside the mines and decrease the consumption of soluble fertilizers.

To confirm the use feasibility of volcanic rock mining by-products in agriculture, it will be necessary to carry out experiments in field conditions. For this, it is suggested that the experiments are monitored for at least two years, with summer and winter crops. Special attention should be given to experimental sites, to obtain a correct control of the variations of soil types, fertility levels and conditions of excess and/or lack of humidity. Generally, experimental plots in the field have variable dimensions but a suitable size can be 5.0 x 5.0 m (25 m^2), which allows the useful area to provide adequate amount of grains or phytomass for the nutritional evaluations in leaves and grains. Evaluations of the response variables should consist of soil analysis, leaf tissue analysis, shoot dry mass and production/productivity. Soil analyses can only be done at the end of the last successive crop, but it is preferable that they are carried out at the end of the cycle of each crop.

ACKNOWLEDGMENTS

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6 CONCLUSÕES

De acordo com os resultados obtidos neste estudo, conclui-se que o pó de rocha vulcânica pode ser empregado como fonte de macro e micronutrientes para o solo, pois apresenta na sua composição vários minerais silicatados, como piroxênios, plagioclásios e minerais ferromagnesianos facilmente alteráveis. Os ensaios de lixiviação em meio ácido demonstraram ter acelerado a liberação dos elementos/nutrientes para a solução extratora. As melhores eficiências de extração foram observadas quando a solução de ácido oxálico a 1% foi utilizada como agente extrator. No entanto, os ensaios de liberação de nutrientes em soluções ácidas mostraram que somente uma fraçãodos minerais encontrou-se na forma solúvel.

As características de desenvolvimento lento e espontâneo da textura cristalina das rochas as tornam interessantes para emprego como remineralizares, pela facilidade de desestabilização em condições exógenas. A oxidação dos feldspatos e piroxênios, além dos argilominerais que preenchem fraturas e vênulas e que também ocorrem na matriz, indicam o potencial de desestabilização (substituição e/ou transformação) destas fases minerais, com consequente aumento do potencial de liberação de cátions, que podem contribuir para a remineralização dos solos. Com isso, grandes são as vantagens agronômicas da utilização de resíduos de rochas vulcânicas como fertilizantes, como por exemplo: a) baixa solubilidade dos nutrientes em água, resultando em menores perdas por lixiviação e fixação e; b) alta solubilidade dos minerais em solução de ácidos fracos, como existente nas soluções do solo, resultando em liberação lenta e eficiente dos mesmos para os vegetais.

Pode-se concluir que o pó de rocha vulcânica *in natura* possui um potencial promissor de aplicação como fertilizante alternativo de liberação imediata para culturas de aveia preta e milho. As quantidades acumuladas de Ca, K, Mg e P foram suficientes para suprir as necessidades nutricionais do milho. Melhorias nas propriedades do solo, como altos níveis de Ca, K e P, e baixos níveis de saturação de Al e Al trocáveis foram observados. Os resultados do estudo sugerem que o subproduto pode ser usado como re-mineralizador do solo.

O estudo sobre a aplicação de pó de rocha ou remineralizadores, ainda merece esforços e pesquisa para o conhecimento dos mecanismos de disponibilidade dos nutrientes e suas características tecnológicas.

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