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MINERALOGICAL CHANGES OF CLAY SIZED PHLOGOPITE AND MUSCOVITE AS AFFECTED BY ORGANIC MATTER AMENDMENT IN RHIZOSPHERE

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Abstract: Weathering of K-bearing minerals is the major source of potassium in soils which is of special importance under K deficient conditions. Many studies have been carried out on the effect of plant types and microorganisms on the transformation of micaeous minerals and their potassium release. However, there is no information on the effect of organic matter on mineralogical changes in micaceous minerals. The objective of this study was to investigate the effect of organic matter on transformation of muscovite (a dioctahedral mica) and phlogopite (a trioctahedral mica) in the rhizosphere of alfalfa. A pot experiment was carried out in a completely randomized design with factorial combination and three replicates. The growth medium was a mixture of quartz sand, micaceous mineral (muscovite or phlogopite) and organic matter (0, 0.5 and 1 %). During 120 days of cultivation, plants were irrigated with either complete or K-free nutrient solution and distilled water as needed. At the end of cultivation, plants were harvested and their K uptake was measured by flame photometer following the dry ash extraction. Also, the mica particles and their weathering products in each pot were separated from the quartz sand and their clay fraction analyzed using x-ray diffraction (XRD). The results showed a significant increase of total K uptake occurred in pots containing trioctahedral mica (phlogopite) and organic matter as compared to those with no organic matter amendment, under both nutrient solution treatments. XRD data clearly showed transformation of phlogopite under both nutrient solution treatments, but no XRD detectable transformation of muscovite was recognized. Organic matter amendment seems to have created considerable mineralogical changes in clay sized phlogopite. Root activities and organic matter decomposition appear to have increased the acidity of rhizosphere which, in turn, facilitated the K release from trioctahedral mica (phlogopite) and induced the transformation of phlogopite to vermiculite and a minor quantity of smectite and chlorite. In conclusion, the effect of organic matter on mineralogical changes greatly depends on the type of micaceous mineral.

Key Words: Potassium release, Phlogopite, Muscovite, Organic matter, Vermiculite, Smectite, Chlorite

1. INTRODUCTION

Soil potassium (K) is often divided into four forms: soluble, exchangeable, non-exchangeable and structural or mineral (Sparks, 1987).The amount of non-exchangeable K is greatly affected by the content and type of clay minerals present in soil (Jalali, 2007). When soluble and exchangeable K fractions reach low levels as a result of K uptake by crops (McLean and Watson, 1985) non-exchangeable K from the interlayer of mainly illite or mica is released into the soil solution (Tributh et al., 1987). Mineralogical changes in micaceous minerals have been reported after cropping and fertilization (Hinsinger et al., 1992; Norouzi and Khademi, 2009; Robert and Berthelin, 1986; Velde and Peck, 2002). Hinsinger et al. (1992, 1993) demonstrated that in the rhizosphere of rape and ryegrass, trioctahedral mica (phlogopite), as the sole source of K, rapidly weathered and vermiculitized after root-induced release of interlayer K. Some soil microorganisms are able to solubilize unavailable forms of K-bearing minerals by excreting organic acids which either directly dissolve K-bearing minerals or chelate silicon ions to bring K into solution (Barker et al., 1998; Barzegar et al., 2002). Dissolved organic compounds have been found to play an extremely important role in weathering processes in forest soils (Pohlman and McColl, 1988). Khademi and Arocena (2008) indicated that OM led to the formation of a greater quantity of kaolinite from the transformation of palygorskite and sepiolite in the rhizosphere of alfalfa, barley and canola. The role of organic compounds in the weathering of K-bearing minerals has been established using pure minerals and specific organic acids such as oxalic and citric acids (Song and Huang, 1988). However, there is no information on the effect of natural OM on the weathering of K-bearing minerals.

The objectives of this study were: (1) to investigate the effect of OM on the transformation of phlogopite and muscovite in the alfalfa rhizosphere, and (2) to examine the influence of OM on potassium uptake from phlogopite and muscovite by alfalfa.

2. MATERIAL AND METHODS

This research was carried out as a pot experiment using pure minerals under greenhouse conditions. Detailed information on growth media, their preparation and different treatments is given below.

2.1. Growth media

A trioctahedral (phlogopite) and a dioctahedral (muscovite) mica, from Hamadan Province, Iran, were chosen as the source of K for plants. Mica samples were ground and sieved and the <60 μm size fraction was collected for the experiment. Hamadan quartz sand sized greater than 52 μm was used as the plant growth medium. It consisted of almost pure SiO_2 (97.53%) and was free of clay minerals and other substances (Norouzi and Khademi, 2009). The quartz sand was washed with 0.2 N HCl, repeatedly rinsed with distilled water until the supernatant solution was chloride-free, oven-dried at 105 ˚C and used in the pot experiment. The chemical composition of the reference minerals and quartz sand are reported in Norouzi and Khademi (2009). Cocopeat, a commercial peat made of coconut residues, was used as the OM amendment after washing with tap water on a 1 mm sieve to remove the likely mineral particles. The peat was saturated with NH_4^+ using 1 N NH_4Cl solution, washed with distilled water, oven-dried at 60 °C, and then ground to <60 mesh size prior to usage in the experiment. The cocopeat contained an extremely low amount of K (0.00025%) and, therefore, did not contribute significantly to plant K uptake.

2.2. Pot experiment

The experiment was conducted in a greenhouse for 120 days. Each pot contained 600 g of the growth medium. The experimental design was a completely randomized 3×3×2 factorial with 18 treatments and 3 replications. The treatments were combinations of 3 growth media, 3 levels of OM addition and 2 kinds of nutrient solutions.Growth media included quartz sand (control), quartz sand + phlogopite and quartz sand + muscovite. To supply equal quantities of K (0.35% K_2O), 21 g of muscovite or 22.6 g of phlogopite was added to each pot. The three levels of OM treatment were O_0 (0%, control), O_1 (0.5%) and O_2 (1%). The two types of nutrient solution were K-free (-K) and complete (+K) nutrient solutions prepared according to Stegner (2002).Before sowing alfalfa (Medicago sativa L.) seeds, the growth media were incubated for 30 days at the near field capacity moisture level and at room temperature to initiate the decomposition of OM. Microbial organisms contained in 10 ml field soil extract (including 49 mg/l K) were added to each pot. During the cultivation, plants were irrigated with either the complete or the K-free nutrient solution and distilled water as needed.

2.3. Laboratory analyses

Plants harvested at the end of cultivation were washed with distilled water and dried at 70 °C for 48 h. Biomass was weighed and ashed at 550 °C for 4 h. Each ash sample was dissolved in 10 ml of 2 N HCl and its K concentration was measured by a flame photometer. Total K uptake in each pot was the sum of K uptake in shoot and root.

At the end of the experiment, the particles of mica and its likely weathering products surrounding the roots in each pot were separated from the quartz sand by washing them on a 60 µm sieve and their OM content was removed using 30% H_2O_2. Finally, the clay fraction was separated using a centrifuge.The mineralogy of the clay fraction was determined by X-ray diffraction (XRD) before and after the pot experiment. Oriented slides were prepared for both K- and Mg-saturated samples. The Mg-saturated slides were solvated with ethylene glycol (Eg) or Glycerol (Gly) while the K-saturated samples were heated at 550 °C. Oriented plates were analyzed by a D8 X-ray diffractometer (Bruker AXS, USA) using Co-Kα radiation (λ=0.17903 nm) generated at 40 kV and 20 mA. The XRD peak intensity ratios were used as an index to quantitatively evaluate any mineralogical changes to phlogopite and muscovite.

3. RESULTS AND DISCUSSION

3.1. Characteristics of growth medium components

The chemical compositions of micaceous minerals and quartz sand indicated the relatively high purity of the reference minerals used in the experiment (Norouzi and Khademi, 2009). The XRD patterns of the Mg-saturated phlogopite (before the experiment) showed a 1.4 nm peak as impurity, but with a very low intensity (Figure 1a). This peak was attributed to vermiculite. The muscovite sample was almost pure (Figure 1b).

3.2. Potassium uptake

The addition of OM (O_1 and O_2) increased K uptake by alfalfa in different growth media under the complete nutrient solution (Figure 2). Under the K-free condition, however, only in combination with trioctahedral mica (phlogopite) could OM increase the K uptake by alfalfa. Potassium uptake was higher in treatments with 0.5% OM (O_1) amendment, than that with 1% OM (O_2) amendment in pots containing phlogopite supplied with the K-free nutrient solution (Figure 2). This could be attributed to lower K concentrations in both root and shoot in the O_2 treatment as compared with that in O_1 (data not shown), which, in turn, appears to be due to less K availability to plants under the O_2 treatment because of the adsorption of soluble K on added OM.

3.3. Mineralogical changes

A 1.4 nm peak with a greater intensity than that of the control sample (before the experiment) was observed in samples collected from pots containing phlogopite in all OM treatments under either –K or +K nutrient solutions (Figure 3a), but such a peak was not detected in those collected from pots amended with muscovite (Figure 3b). Similar results had been obtained by Norouzi and Khademi (2009), who reported the alteration of phlogopite to vermiculite in alfalfa rhizosphere, but no XRD detectable transformation of muscovite.In the Mg-saturated samples collected from pots containing phlogopite, the relative intensities of 1.4 to 1.0 nm peaks for the samples supplied with the K-free nutrient solution are higher than those for the samples received +K nutrient solution (Table 1). The application of 0.5% (O_1) and 1% (O_2) cocopeat increased the rate of transformation of phlogopite, as compared to the treatment with no OM amendment (O_0). Under the K-free nutrient solution, the intensity ratio of 1.4 to 1.0 nm peaks for O_1 and O_2 treatments significantly increased from 0.08 to 1.38 and 1.26, respectively. The mean values for the same parameter under the complete nutrient solution (+K) were 0.65 for O_1 and 0.88 for O_2 treatments; levels that are significantly higher than that of the control (O_0) (Table 1).

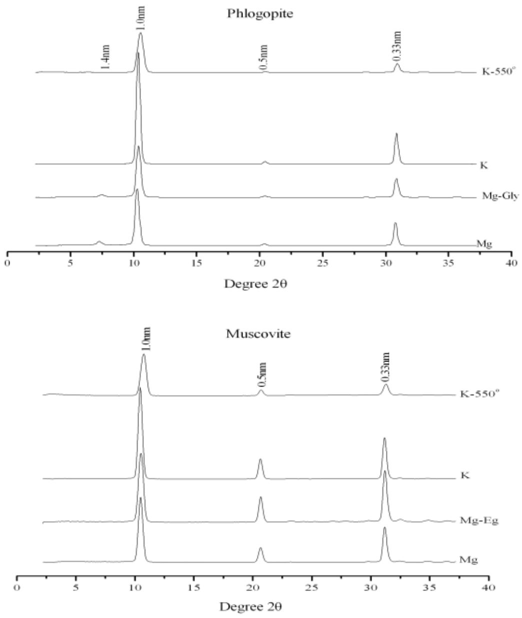

Figure 1. X-ray diffraction patterns of Mg-saturated (Mg), Mg-saturated and ethylene glycol solvated (Mg-Eg), Mg-saturated and glycerol solvated (Mg-Gly), K-saturated (K), and K-saturated and heated at 550 °C (K-550°) clay-sized phlogopite and muscovite samples used in the experiment (no interaction with rhizosphere)

In all the cases, XRD analysis of the ethylene glycol (Mg-Eg) treated samples showed that during the expansion, a part of the 1.4 nm peak expanded to 1.64 nm (Figures. 4a and 4b). A low intensity (data not shown) XRD peak at 1.7 nm after treatment with glycerol was observed in the O_0 –K, O_0 +K, O_1 +K, and O_2 +K samples, which was attributed to the formation of a low quantity of smectite in these treatments.In all the K-saturated treatments from pots amended with phlogopite, the 1.4 nm peak did not fully collapse to 1.0 nm (data not shown). Also, 0.71, 0.47, 0.354 and 0.284 nm peaks were observed in the Mg-saturated treatment (Figures 4a and 4b). These peaks in the Mg-saturated samples and the 1.4 nm peak in the K-saturated samples were attributed to the formation of chlorite from phlogopite transformation in the alfalfa rhizosphere. This appears to be the first report on the formation of chlorite from phlogopite under the influence of OM and plant rhizosphere. Brucite ($Mg(OH)_2$), resulting from the dissolution of phlogopite or its conversion to either vermiculite or smectite, seems to have attended the interlayers, which has, in turn, resulted in the formation of chlorite as suggested by Kohut and Warren (2002). The relatively high intensity of 1.4 nm peaks of XRD patterns in the Mg-saturated and ethylene glycol solvated samples from the rhizosphere amended with phlogopite clearly shows the formation of vermiculite. Besides, OM addition (O_1 and O_2) led to strong vermiculitization of trioctahedral mica (phlogopite) in the rhizosphere of alfalfa.

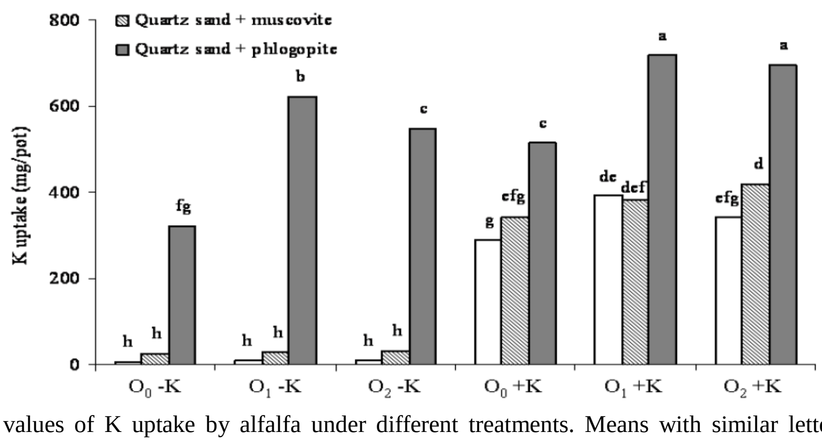

Figure 2. Mean values of K uptake by alfalfa under different treatments. Means with similar letters are not statistically significant at P≤0.05. O_0, O_1 and O_2 denote different OM amendments. –K and +K refer to K-free and complete nutrient solutions, respectively

Table 1. Mean XRD peak intensity ratios for Mg-saturated clay-sized particles separated from the growth media amended with phlogopite under K-free (-K) and complete (+K) nutrient solutions

Growth medium	1.4 : 1.0 nm	
	-K	+K
Quartz sand+phlogopite (O_0)*	0.27 [c]	0.17 [c]
Quartz sand+phlogopite (O_1)	1.38 [a]	0.65 [b]
Quartz sand+phlogopite (O_2)	1.26 [a]	0.88 [b]
Control (before the experiment)	0.08	

Means for both –K and +K treatments superscripted by the same letter are not statistically significant at P≤0.05.
*O_0: No organic matter (control), O_1: 0.5% organic matter, O_2: 1% organic matter

4. CONCLUSION

Addition of OM can greatly promote the K mobilization from minerals to soil solution and its absorption by the plant. The presence of OM in the growth medium in our experiments did not enhance K release in dioctahedral mica (muscovite) and no XRD detectable transformation of muscovite was recognized. Root activities and OM decomposition appear to have increased rhizosphere acidity which, in turn, facilitated K release from trioctahedral mica (phlogopite) in the K-deficient medium. The results obtained in this research show that OM plays a major role in the transformation of trioctahedral mica (phlogopite). It can induce the transformation of phlogopite to vermiculite and to a minor quantity of smectite and chlorite. Thus, the effect of OM on mineralogical changes greatly depends on the type of micaceous mineral. Organic matter also increases the rate of phlogopite transformation in the root zone through several mechanisms. It improves the physical conditions of the growth medium (Cecil and Tester, 1990; Barzegar et al., 2002) which, in turn, results in higher biomass production and higher K uptake. During the process of OM decomposition by microorganisms, CO_2 and organic acids are produced (Kelly et al., 1998), which reduces the pH of the medium. Both the K release from mineral and the likely dissolution of phlogopite occur at a higher rate under a low pH (Fanning et al., 1989). In addition, OM decomposition products, such as fulvic and humic acids, can directly chelate with metal ions including non-exchangeable and structural K in K-bearing minerals (Basak and Biswas, 2009). Despite the fact that all these mechanisms have been active under both +K and –K conditions, they seem to be more pronounced under K-deficient conditions.

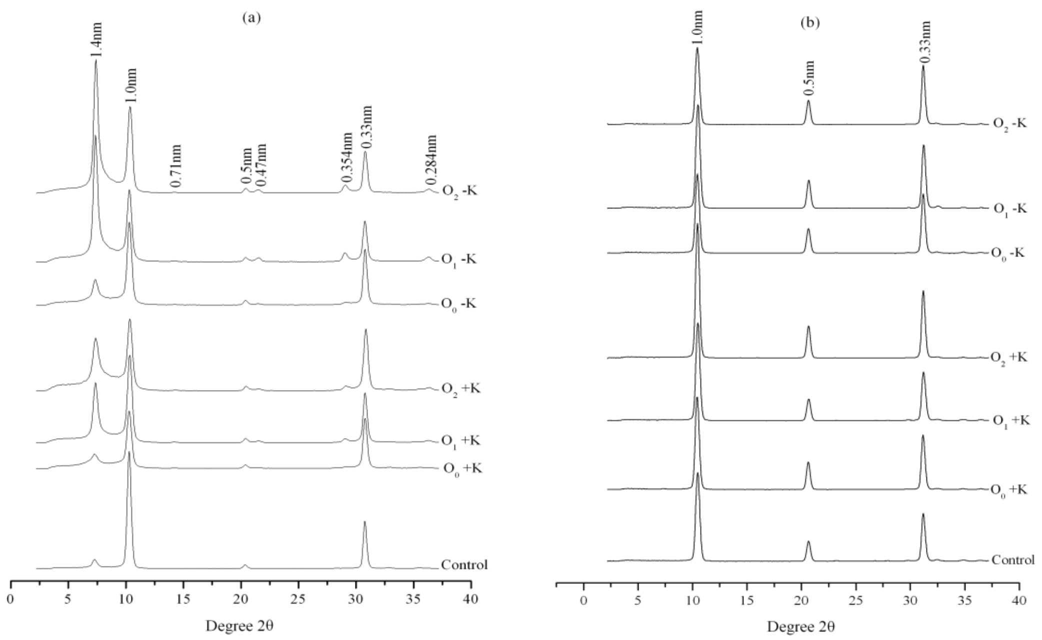

Figure 3. X-ray diffraction patterns of Mg-saturated clay-sized particles from the rhizosphere of alfalfa under different treatments at the end of the experiment as compared with those of the control. (a) Phlogopite amended pots, (b) Muscovite amended pots. O_0, O_1 and O_2 denote different OM amendments. –K and +K refer to K-free and complete nutrient solutions, respectively

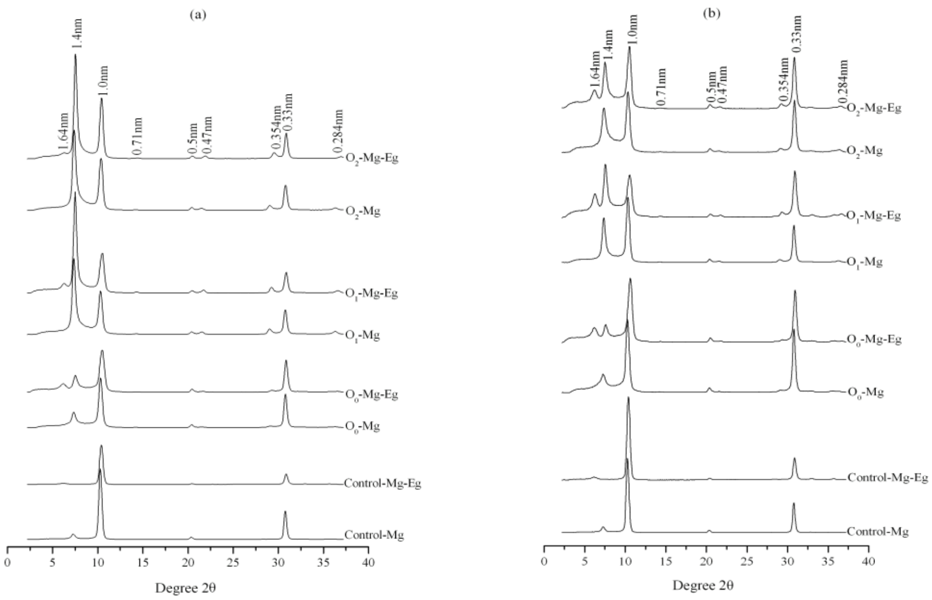

Figure 4. X-ray diffraction patterns of Mg-saturated (Mg) and Mg-saturated and ethylene glycol solvated (Mg-Eg) clay-sized particles from the rhizosphere of alfalfa amended with phlogopite under different treatments at the end of the experiment as compared with those of the control. (a) K-free nutrient solution, (b) complete nutrient solution. O_0, O_1 and O_2 denote different OM amendments

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