

## Expanding Clays in Rhizosphere Soils and its Implications to Nutrient Cycling

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### Abstract

Rhizosphere soils are the most active sites in the transformation of minerals in soil system. The presence of bacterial communities and mycorrhizal associations constantly modifies the soil solution composition leading to a dynamic nature of minerals in the root-soil interphase. The demand for K and Mg by organisms and host plants renders instability to K and Mg-containing silicates due to constant changes in pH and nutrient contents (e.g., K and Mg) in rhizosphere soils. Decreases in K or Mg concentrations in solution enhance the breakdown of micaceous or chloritic minerals into expanding 2:1 clays characterized by basal spacings ranging from 1.41 to 1.52 to 1.79 nm upon Ca-saturation and glycerol solvation depending on mycorrhizal species, nature of micaceous minerals, host plant species and growing season. Rhizosphere soils of *A. lasiocarpa* dominated by *Piloderma*, an ectomycorrhizal fungi, had significantly higher vermiculite+smectite to chlorite ratio (2.2) than other rhizosphere (1.9) and non-rhizosphere soils (1.6). These variations in ratios and spacing reflect differences in charge density and are measures of the ability of clay to store cations such as K and Mg. In addition, the breakdown of phyllosilicates to expanding clays is a reversible process. These expandable 2:1 clays play a role in biogeochemical cycling of K, Mg (and other cations) because of their ability to fix or release K, Mg (and other cations) as demanded by organisms and its associated host plants.

### Introduction

Rhizosphere soils (RS) provide nano- and microsites for the most intense interactions between organisms, mineral, gaseous and solution phases in soil systems. In forest ecosystems, plant roots are colonized by several ectomycorrhizal (EM) fungi where each symbiosis is a very specific RS system. There are a minimum of 347 and 280 different root-fungus symbioses (= RS = EM) associated with *Fagus sylvatica* and *Nothofagus dombeyi*, respectively (Kottke 2002). In agricultural soils, Blackwood and Paul (2003) and Miethling et al. (2003) described many unique bacterial community structures associated with various RS. These nano- and microenvironments are active sites for mineral precipitation, elemental speciation, nutrient cycling, soil structural formation and environmental remediation (e.g., Banfield and Navrotsky 2001, Benzerara et al. 2008, Hochella 2002). The rate of breakdown for mica and chlorite to 2:1 expandable clays and other hydroxyl-interlayered minerals (HIM) was predominant in RS compared to non-RS (e.g., April and Keller 1990, Courchesne and Gobran 1997, Glowa et al. 2004, Hinsinger et al. 2001, 2006).

Recently, Huang et al. (2005) summarized the implications of mineral-organic matter-microorganism interactions on the development of innovative management strategies to sustain ecosystem health on the global scale. They indicated that microbial activity can accelerate the breakdown of minerals by as much as six orders of magnitude. The interaction of organisms and minerals impacts agriculture, waste management, and the water industry, as well as the natural and semi-natural environment in the Earth's critical zone (Young and Crawford 2004, Brantley et al. 2006).

The objective of this presentation is to review the state-of-knowledge of biologically-mediated formation of clays in rhizosphere soils to elucidate nutrient cycling. Specifically, we

will determine the role of expanding clays as storage and/or reservoir for exchangeable cations, particularly potassium and magnesium, in forested and cropped areas.

#### Ectomycorrhizal fungi, clay mineral and chemical compositions

Smectites, vermiculites and hydroxyl-interlayered minerals (HIM) are the most common expanding clays found in rhizosphere soils. Hinsinger et al. (2006) reported that vermiculite formation from phlogophite was observed after 14 days when grown with rye grass (*Lolium multiflorum*); they further argued that similar high-charged clays can form from the transformation of mica within 2 days in the RS. However, these high-charge clays either are not stable and decreases in amounts (e.g., Courchesne and Gobran 1997) or may form in the RS zone (e.g., Hinsinger and Jaillard 1993; Kodama et al. 1994).

The amount and types of expanding clays are strongly influenced by the type of ectomycorrhizal fungus association in RS (e.g., Arocena et al., 1999; Glowa et al., 2004). The clay minerals produced by EM associated with roots of *Picea glauca* (white spruce) produce a significant amount of expandable clay (1.79 nm in Ca saturation and glycerol solvation) which largely collapses upon potassium saturation. Ca – saturation in the air dried state shows 1.41 nm spacing, instead of the normal hydrated (two water layer) state of 1.52 nm. The soil materials not associated with the EM (or non-rhizosphere) did not show significant expandable clay material but strong chlorite peak (Fig. 1)

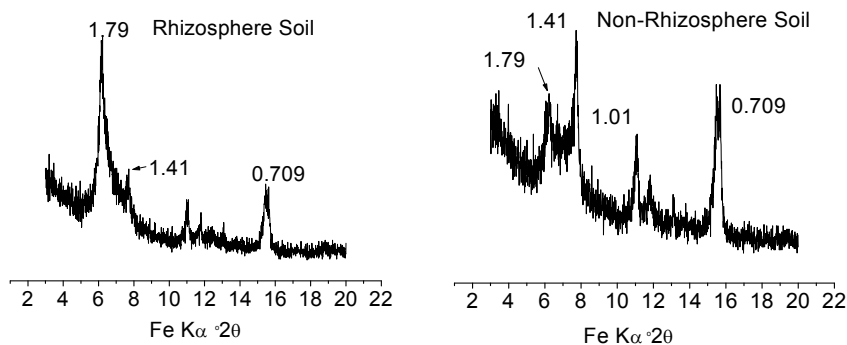


Fig. 1. X-Ray diffractograms of Ca-saturated and Glycerol-solvated clay fractions of rhizosphere and non-rhizosphere samples of hybrid spruce (*Picea glauca*) showing the relative intensities of the 1.7- and 1.4-nm reflections indicative of vermiculite (Vt) + smectite (Sm) and chlorite (Ch), respectively. The 1.0-nm peak suggests muscovite (Mus) (modified from Glowa et al. 2004)

The influence of fungal species on the nature of expandable clays in rhizosphere soils are summarized in Table 1. RS-A in the two studies are dominated by *Piloderma* and both had higher amounts of Vt+Sm compared to N-RS samples. In *A. lasiocarpa*, RS-A had significantly higher amounts of (Vt+Sm)/Ch than RS-B and N-RS. (Vt+Sm)/Mi ratios in RS-A and RS-B were not significantly different from each other. However, the ratios of (Vt+Sm) over mica or chlorite in RS-A and RS-B for both tree species were higher than N-RS samples.

Exchangeable cations in RS and N-RS samples varied according to the colonization by ectomycorrhizal fungi; the influence of fungi differed depending on the host tree species as well. In *P. glauca*, exchangeable K in RS-A and RS-B were similar and were significantly higher than N-RS while for *A. lasiocarpa*, K content in RS-A was significantly higher than in RS-B but both had higher exchangeable K than N-RS samples. Calcium and magnesium contents in RS soils were in *P. glauca* were not significantly different from each other; exchangeable Ca and Mg in RS-A were higher in RS-A than RS-B in *A. lasiocarpa*. In addition, Ca and Mg in the latter were similar to those in N-RS soils.

Reports on soil pH and other chemical properties between RS and N-RS soils sowed no consistent trends (Tables 1 and 2). Arocena et al. (1999) and Glowa et al. (2004) measured higher pH in RS than N-RS soil in contrast to similar soil pH in RS and N-RS soils determined by Turplault et al. (2007). Courchesne and Gobran (1997) reported that oxalate-extractable Fe and Al were significantly higher in rhizosphere than bulk soils (Table 2). Turpault et al. (2008) reported 8 mg Al kg<sup>-1</sup> soil citrate-extractable Al in rhizosphere soil compared to 6 mg Al kg<sup>-1</sup> soil citrate-extractable Al in bulk soil.

Table 1. Mean and (standard deviation) of the contents (g kg<sup>-1</sup>) of expandable phyllosilicates in clay fraction, and pH, exchangeable K, Mg and Ca (cmolc kg<sup>-1</sup> soil) in RS-A, RS-B and N-RS soils in two tree species (data from Arocena et al. 1999; Glowa et al. 2004)

	<i>Picea glauca</i> (n=6)			<i>Abies lasiocarpa</i> (n=3)		
	RS-A	RS-B	N-RS	RS-A	RS-B	N-RS
Vt + Sm	105 (10)	94 (7)	95 (22)	185a (24)	200a (24)	160b (14)
(Vt+Sm)/Mi	0.56 (0.04)	0.55 (0.08)	0.48 (0.09)	1.1b (0.13)	0.97b (0.14)	0.73a (0.06)
(Vt+Sm)/Ch	1.13 (0.37)	1.07 (0.42)	1.03 (0.47)	2.2b (0.28)	1.9a (0.23)	1.6a (0.04)
pH	4.1a (0.13)	4.3a (0.15)	5.1b (0.17)	4.6 (0.25)	4.9 (0.26)	5.2 (0.60)
Exch. K	0.29a (0.06)	0.32a (0.04)	0.17b (0.04)	0.32a (0.01)	0.25b (0.02)	0.15c (0.01)
Exch. Mg	0.84 (0.24)	1.11 (0.27)	0.78 (0.34)	1.1a (0.05)	0.74b	0.64b (0.05)
Exch. Ca	2.65ab (0.67)	3.34a (0.76)	2.36b (0.69)	8.1a (0.37)	5.6b (1.1)	4.2b (0.37)

Within each tree species, means followed by the same letter across each row are not significantly different ( $P > 0.05$ ); in *A. lasiocarpa*, RS-A = *Piloderma* (66 %); RS-B = *Mycelium radicans atrovirens* and cottony yellow-brown types or where *Piloderma* spp. colonization was <2% (Arocena et al. 1999); in *P. glauca*, RS-A = *Piloderma* (93 %); RS-B = *Inocybe lacera*-like and *Hebeloma*-like morphotypes or where *Piloderma* spp. colonization was <1 % (Glowa et al. 2004)

#### Seasonal variations in clay and chemical compositions

Variations in clay mineral and chemical composition in RS and N-RS environments are also influenced by the growing season (Turpault et al. 2008). They reported that the magnitude of 2:1 minerals that collapsed upon K-saturation was smaller for samples collected in rhizosphere than bulk soils. Also, the XRD reflection at 0.994 nm was higher in intensity in rhizosphere than those in the bulk sample.

The temporal changes in mineral composition are complemented by changes in cation exchange capacity (CEC) and chemical composition (Table 2). CEC and the ratio of exchangeable K/CEC measured in June were higher compared to observations in March for both bulk and rhizosphere soils. The ratios of exchangeable Mg and Ca to CEC exhibited trends in contrast to K/CEC ratio for RS and N-RS samples. Exchangeable Ca/CEC ratio in bulk soil was significantly higher in June than March, and CEC in determined in June were higher than observations in March for both bulk and rhizosphere soils.

Table 2 Mean (and SD) contents of selected chemical properties of bulk and rhizosphere in surface soils

	Bulk soil	Rhizosphere	Reference
Oxalate-extractable Al (g kg <sup>-1</sup> )	6.5a (1.3)	12.5b (3.1)	Courschesne and Gobran 1997
Oxalate-extractable Fe (g kg <sup>-1</sup> )	18.9a (4.1)	25.2b (4.3)	Courschesne and Gobran 1997
Citrate-extractable Al (g kg <sup>-1</sup> )	8	6	Turpault et al. 2008
pH	3.93 (0.13)	3.94 (0.09)	Turpault et al. 2007
<i>March</i>			
CEC (cmol kg <sup>-1</sup> soil)	17.0ax (2.1)	16.9ax (2.2)	Turpault et al. 2007
Exchangeable K/CEC	3.0ax (0.4)	5.6bx (1.6)	Turpault et al. 2007
Exchangeable Ca/CEC	16.5ax (3.6)	15.0bx (5.0)	Turpault et al. 2007
Exchangeable Mg/CEC	4.5ax (1.5)	3.6 bx (1.2)	Turpault et al. 2007
<i>June</i>			
CEC (cmol kg <sup>-1</sup> soil)	18.3Ay (2.2)	18.8Ay (2.5)	Turpault et al. 2007
Exchangeable K/CEC	3.7Ax (2.4)	7.0Bx (3.0)	Turpault et al. 2007
Exchangeable Ca/CEC	14.6Ay (2.7)	14.2Bx (3.8)	Turpault et al. 2007
Exchangeable Mg/CEC	4.1 Ax (0.9)	2.9 Bx (1.0)	Turpault et al. 2007

For Turpault et al. (2007), *a* and *b* are used to compare bulk and rhizosphere soils sampled in March; *A* and *B* compared soils sampled in June; *x* and *y* are used to temporal effect between March and June; means followed by different letters are significantly different at 95%

## Discussion and implications to nutrient cycling

### *Biologically-mediated mineral transformation*

Soil mineral transformations occur largely in soil microenvironments and processes vary considerably in space and time due to significant influence by microorganisms. Organisms in rhizosphere soils are responsible for the changes in the soil solution composition resulting from soil processes at the soil solid/soil solution interface (e.g., Arocena and Glowa 2000, Arocena et al. 2004, Hinsinger et al. 2006). For example, low pH in RS samples is believed to be a contributor to the breakdown of soil minerals and the increased availability of K<sup>+</sup> (and Ca<sup>2+</sup> and Mg<sup>2+</sup>) in soil solution (Arocena and Glowa 2000). Most of the changes in soil solution are associated with the increased uptake of water and nutrients by the host plants that are facilitated by mycorrhizal associations. Active plant uptake of nutrients such as K and P is known to lower their concentrations in rhizosphere soils, hence drive the soil processes towards the release of K (and P) and the breakdown of K (and P)-containing minerals (e.g., Hinsinger et al. 2001, Jungk 2002, Arocena et al. 2004, Hinsinger et al. 2005).

The uptake of K is of a special interest because it is required by plants in high quantities almost at levels equivalent to N (Hinsinger et al. 2001) implying a fast and high rate of removal from K-containing minerals. The most common source of K into the rhizosphere soil solution results from the release of non-exchangeable K from the interlayer K contained in K-bearing phyllosilicates such as micas and illites. The removal or release of K from phyllosilicates transforms mica and illites to expandable 2:1 minerals such as vermiculite and smectite (e.g., Arocena et al. 1999, Glowa et al. 2004, Hinsinger et al. 2006). K-released from interlayer free-up the negative charge and allows the K-free 2:1 structure to retain hydrated ions, hence its expansion to larger basal spacings (e.g., 1.5 to 1.8 nm) depending on the ambient conditions.

Fungal species are also known to influence the rate of K release, hence the transformation of micaceous minerals. Arocena et al. (1999) and Glowa et al. (2004) reported that the presence of *Piloderma* spp. *Inocybe lacera*-like and *Hebeloma*-like morphotypes in RS accelerate the transformation of mica (and chlorite) to 2:1 types of expandable clays compared to N-RS soils. *Piloderma* colonization increased the phosphorus uptake of Norway spruce seedlings (Arocena et al. 2004) and provides more available K to host plants through accelerated weathering of biotite (Glowa et al. 2003) when compared to soil not colonized by ectomycorrhizal fungi. The differential influence of ectomycorrhizal fungi on the breakdown of mica maybe attributed to the variations in physiological needs of the fungi and/or host plants for potassium.

#### *Implications to biogeochemical cycling*

It is well known that expandable 2:1 clay minerals fix and release K ions from and into solution depending on the environmental conditions. Officer et al. (2006) noted the significant relationship between plant available non-exchangeable K and 2:1 clay mineralogy. Hinsinger and Jaillard (1993) reported the release of K from phlogopite (a mica species) when the  $K^+$  concentration in the rhizosphere fell below  $80 \text{ mmol dm}^{-3}$  and resulted to the formation of expandable 2:1 clays. In addition, Barré et al. (2008) observed that the breakdown of phyllosilicates to expanding clays is reversible. This ability to fix or release K led Barré et al. (2007a, 2007b) to postulate that 2:1 minerals behave as a K reservoir in soils and significantly play a role in biogeochemical cycling of K.

The release and fixation of  $K^+$  in 2:1 clays in rhizosphere soils are influence by ectomycorrhizal fungi. In seedlings colonized by *Piloderma croceum*,  $K^+$  in soil solution close to the roots ( $<1.0 \text{ cm}$ ) of Norway spruce was significantly lower than those seedlings not-colonized by ectomycorrhizal fungus (Arocena et al. 2004). In Arocena and Glowa (2000), the concentrations as well as the activities of  $K^+$  in solutions followed the order RS-A  $>$  RS-B  $>$  N-RS (see Table 2 for the ectomycorrhizal colonizations of the samples).

The nutritional demands of plants and organisms for essential elements such as K influence the biogeochemical cycling. Turpault et al. (2007) reported that processes such as  $H^+$  production by roots and/or the organic matter degradation and uptake of K vary with season (e.g., March vs June), thus the differential formation of expandable clays in the rhizosphere soils. For example, hydroxy-Al polymers precipitated in vermiculite interlayers between March and June. Seasonal changes in mineral composition are further supported by the increase in CEC between March and June for the N-RS, and aluminium precipitation outside the interlayers for the RS samples. They concluded that rhizosphere mineral and chemical compositions as excellent indicators for understanding both the short- and long-term nutrient dynamics in ecosystems.

Knowledge of the elemental dynamics in rhizosphere soil is important to the understanding of nutrient availability to sustain life forms in the Earth's Critical Zone.

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