Potassium Release Kinetics from Dioctahedral and Trioctahedral Minerals under Alkaline Conditions

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Keywords: mica, potassium, biotite, muscovite, alkaline pH, dissolution.

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Abstract- The agricultural significance of Potassium (K) has been comprehensively documented owing to its role in plant development and growth. The reserves of K in soil are not available to plant roots for uptake as 98% of the total soil K is mineral bound. The K bearing 2:1 type clay minerals can serve as an enormous and renewable pool of K supply in soil. The K releasing capacity of these minerals is governed by different agents like ionic strength, temperature and pH. Therefore, the release K from dioctahedral (Muscovite) and trioctahedral (Biotite) pure minerals were investigated at 25±1°C in batch reactors over the pH range of 8 to 12. The experiments performed until the steady state was achieved. At the start of each experiment, the high output solutions concentrations of Fe, Si, K and Al were recorded, after that a gradual reduction was observed leading to the establishment of steady state conditions. The release of Kwas more from the dissolution of biotite than muscovite dissolution. The both rates ranged at steady state between -10.13 mol g⁻¹ and -8.84 mol g⁻¹ at pH 8-12, respectively. The dissolution rates of muscovite (Rₚ) ranged between -9.64 mol g⁻¹ and -8.44 mol g⁻¹ at pH range 8 to 12, respectively. It is concluded that the solution pH has an affect significantly to the K release from biotite and muscovite dissolution. These results suggest that biotite-rich soils may have a relatively rapid leaching of K under alkaline conditions and have less K-fertilizer requirements as compared to muscovite dominant soils.

Keywords: mica, potassium, biotite, muscovite, alkaline pH, dissolution.

1. Introduction

Each nutrient plays distinctive functions in plants. In an agricultural context the significance of K is largely studied and documented due to its vital role in plant growth and development (Oborn et al., 2005). Different agricultural systems reported the deficiency of K(Zorb et al., 2014). Potassium has been declared as a limiting factor in soils Pakistan (30-35 %), China 25-75% and in South Australia (66%) (Akhtar et al., 2003; Jaiswal et al., 2016). On an average in Pakistani Soils K is added through fertilizers less than 1.0 kg K₂O ha⁻¹ while K output is about 15.0 kg K₂O ha⁻¹. Pakistani Soils are characterized by uncertain weathering of K containing minerals (Haider et al., 2016). According to the results of a study, the soil series of NWFP (35%), Sindh (8%) and Punjab (28%) had insufficient K levels. Potassium can be released at the rate of about 35-70 kg K ha⁻¹ from the soils rich in clay minerals(Simonsson et al., 2007). The Soils forms of K can be categorized into structural, exchangeable and non-exchangeable (Schneider et al., 2016). In soils, K is found in two major forms: exchangeable and non-exchangeable. The non-exchangeable K is fairly high in amount ranging from 90-98% of total K in soil and is mainly found as trapped between clay minerals inter layers.

It comprises of K in two interlayer sites of micaceous earth minerals, for instance illite and K from feldspar minerals. It is gathered that replaceable K ions are adsorbed on edges sites of earth minerals, soil natural issue and on trade destinations of smectite minerals (Dotaniya et al., 2016). The non-exchangeable K is released from illite and mica minerals as a result of the lowering of K level in soil solution and its exchangeable form due to plant uptake (Barre et al., 2007; Carey and Metherell, 2003; Singh and Schulze, 2015). According to literature, 2:1 type clay minerals serve as a major K pool having capacity of supplying K exceeding up to 3t ha⁻¹. The most important K-containing minerals common in soils are illite (32 to 56 g K kg⁻¹), K-feldspars (20 to 30 g K kg⁻¹), the trioctahedral mica: biotite (Mg mica, 36 to 80 g K kg⁻¹) and dioctahedral mica: muscovite (K mica, 60 to 90 g K kg⁻¹) (Jalali, 2006). The K found in fixed form can also be replaced by dissolution, by the conversion of mica into 2:1 layer silicates and also by ion exchange.

In any case, a sweep of the literature reveals that these examinations go back to not over 20 years or something like that. Soil K-bearing minerals, in the request of arrival of their K to plants are orthoclase, microcline, muscovite, and biotite. Mineral K is that part of total K that is accessible to plants after releasing and its availability is governed by different factors including degree of weathering, mineral K fraction, and K level in soil solution (Basak and Biswas, 2009; Dotaniya et al., 2016). The dissolution of minerals is the main phenomena affecting different biological, chemical and physical reactions in soil (Lerman and Meybeck, 2012). It specifically controls the nutrients supplying capacity of
soil essential for plant development (Wilson, 2004). Numerous studies have evaluated the muscovite and biotite dissolution; however, most of them were carried out in neutral and acid pH conditions (Li et al., 2014; Malmstrom and Banwart, 1997; Xue et al., 2016). The release of K from muscovite and biotite is significantly affected by the K ions movement in soil solution through cation exchange process. The dependence of phyllosilicate minerals dissolution on pH is generally considered to be the attachment of $\text{H}^+$ and $\text{OH}^-$ to Si and Al reaction sites (Brady and Weil, 2008) hence forming activated complexes of phyllosilicate minerals containing negative, positive and neutral charge at activated complexes of phyllosilicate minerals. Therefore, the main objective of the current investigation was to unravel the effect of varying alkaline pH (8-12) on biotite and muscovite dissolution kinetics at 25 °C and assessment of the release of K from biotite and muscovite.

II. Methodology

a) Collection and preparation of minerals

The fresh biotite and muscovite obtained from Excalibur Mineral Corporation, Charlottesville United States of America. Their chemical composition obtained from the company is given in Table 1. Both micas were in enormous crystal forms having few cm thicknesses. The minerals were cut in ethanol in a food processor using Knife blade for size reduction. Uniform particle sizes was achieved after separation of the <250 μm fractions in ethanol by wet sieving.

b) Experimental setup

The 200 mg each mineral sample reacted with 40 mL input solution with varying pH solutions (pH 8-12) in Teflon vessels placed in a thermostatic water bath (WB/OB 7-45, Memmert) at a temperature of 25±1 °C in controlled temperature room of University of Agriculture, Faisalabad. The ionic strength of all input solution was maintained constant at 0.01 M by NaCl. The experiment proceeds for a period of time until the steady state has been reached. When the consecutive samples showed <6% difference in Si concentrations it was considered that steady state has been reached (Bibi et al., 2011) and we confirmed the steady state for seven consecutive samples in this experiment.

c) Output solution analyses

From each batch the output solutions were collected after every 24 h hand filtered with Whatman filter paper 42. Immediately after collecting, the samples were subjected for pH measurement using a pre-calibrated combined pH electrode (HM-12P pH meter, accuracy ± 0.02 pH units). The Si concentrations were determined colorimetrically (UV visible spectrophotometer) by adopting molybdate blue method (Koroleff, 1976) and Al concentrations were measured colorimetrically by the catechol violet method (Dougan and Wilson, 1974). The Fe and K were determined by flame atomic absorption spectrophotometer (FAAS; Model Thermo S-Series, Thermo Electron Corporation, Cambridge, UK). The use of glassware was avoided at all stages of the experiment to prevent Si contamination.

From each group the output solutions were gathered after each 24 h and separated with Whatman filter paper 42. Promptly in the wake of gathering, the samples were subjected for pH estimation utilizing a pre-aligned joined pH cathode (HM-12P pH meter, precision ± 0.02 pH units). The concentration of Si was detected on spectrophotometer (UV visible) by embracing molybdate blue strategy (Koroleff, 1976) and Al fixations were measured colorimetrically by the catechol violet technique (Dougan and Wilson, 1974). The Fe and K were ditated by atomic absorption spectrophotometer (Thermo Electron Company, Cambridge, UK).

d) Dissolution rate calculations

The dissolution rate $R$ (mol g$^{-1}$ s$^{-1}$) was calculated from the data obtained when steady state was achieved from the output concentrations of Al, Fe and Si by adopting the following expression (Bibi et al., 2011; Rozalen et al., 2009):

$$ R = \frac{dC_{Si}}{dt} V_{Al/Si} M_{Mineral} $$

Whereas:

$R$ = dissolution rate (mol g$^{-1}$ s$^{-1}$), $dC_{Si}$ = concentration of Si in the steady state solution (μM).

$dt$ = time (days), $M_{sol}$ = mass of output solution (g), $M_{Mineral}$ = mass of mineral (biotite or muscovite) (g), $V_{Al/Si}$ = stoichiometric ratio.

e) Statistical analysis

The information was subjected to statistical investigation. The descriptive statistics was applied using Microsoft Word Excel program and software OriginPro® (Steel et al., 1997).

III. Results

a) Impact of pH on cations release

Figure 1 a-e shows the comparison between the Si release from biotite and muscovite dissolution with pH range of 8-12. The initial Si release was 158 μM and 170 μM at pH 12 while 45 μM and 58.06 μM at pH 8 from muscovite and biotite, respectively. It was also observed from the data the Si release more from biotite as compared to muscovite. The highest initial Al release rates was recorded at the highest pH 12 i.e., 52 μM and...
the lowest Al release rate recorded at the lowest pH 8 i.e., 29 μM. The release of Al was 43% more at pH 12 as compared to release at pH 8 from biotite. The maximum Fe released from biotite was found in output solution of pH 12 (250% more) at all days samples while minimum in pH 8 samples (Figure 3, a-e).

The comparison of K release from biotite and muscovite shows in Figure 5 a-i. Therelease of K from muscovite was at the most elevated pH 12 and the least at pH 8 with the estimations of starting discharge 1772 μM and 1014 μM, individually. Results indicated 42% more arrival of K at pH 12 than the most reduced pH 8. If there should arise an occurrence of biotite (Figure 4 f-j) at pH 8 the K initial discharge rate was 989 μM which is the most minimal from of all K initial discharge rates, at pH 12 it was 1817 μM which was most noteworthy beginning release rate in all pHs and this augmentation was 45% more when contrasted with the least pH 8. For the most part, as the pH expanded from 8 to 12 the underlying K discharge rates likewise expanded in both type of minerals.

b) Impact of Time on the Discharge of Elements

The release rates of Si, Al, Fe and K are plotted against time (days) in Figure 1, 2, 3 and 4, respectively. At the initial days of the experiments, Si was released at faster rate from both biotite and muscovite. The initial fast Si release was followed by a gradual decrease until becoming stable at the steady state (Figure 1). The state of stability (steady state) in release of Si achieved earlier in 25 days where input pH was greater than 10 but at lower pH 8 and 9 the stability achieved after 35 days. In case of Al in muscovite, the release (Figure 2, a-e) followed the same trend like Si; the concentration of Al was highest (255% more) at initial days of experiment but becomes lower after 25 days and achieved the steady state. These figures indicated that the discharge/release rates were changed with respect to time. It was also evident that the release was rapid during first few days and then gradually decreases to the stable form. It also shows that some variation in rates occurs throughout the experiments. In some cases the changes of rate correlate with deliberate or inadvertent changes in tentative situations. Figure 1 a-e shows the comparison between the Si release from biotite and muscovite dissolution with pH range of 8-12. At the initial stages of the experiments, Si was released at faster rate from both biotite and muscovite. The initial fast Si release was followed by a gradual decrease until becoming stable at the steady state (Figure 1).

c) Influence of pH on dissolution of biotite and muscovite

The mass based dissolution rates of biotite and muscovite calculated from Si release at the steady state are shown in Table 2 and Figure 6. Strongest pH dependence of both minerals on dissolution rates was observed. The dissolution rates of both minerals increased with an increase in pH from 8-12. The log normalized dissolution rate of biotite (R6) calculated from Si release at the steady state and initial mineral mass ranged between -10.13 mol g⁻¹s⁻¹ and -8.84 mol g⁻¹s⁻¹ at pH 8-12, respectively. The dissolution rates of muscovite (R5) ranged between -9.64 mol g⁻¹s⁻¹ and -8.44 mol g⁻¹s⁻¹ at pH range 8 to 12, respectively. Biotite dissolved at a much faster rate compared to muscovite at the whole pH ranges investigated in this study (Figure 6). The fractional reaction orders calculated from the linear regression of the plot of log R6 against pH (Figure 6) for biotite and muscovite are 0.34 and 0.28, respectively.

IV. Discussion

Underbasic, neutral and acidic conditions, the agents responsible for attack on the surface of minerals are hydroxyls, water molecules and protons, respectively. At every pH, the dissolution rate (R) is proportionate to order of protons (H⁺) activity. Typically the activity of water may be regarded as unity, and the water molecule-promoted dissolution rates will be approximately constant (Bibi et al., 2011). In the present study, during initial days of experiment, Si was released more as compared to later days. This higher release of Si at the initial stages probably because of the production of polymeric species, H₃SiO₆ and H₂SiO₄. The solubility of most Si containing oxides and mixed oxides increased due to the aggravated OH⁻ concentration (Rozalen et al., 2009; Bibi et al., 2011, 2012).

Similar decreasing trend of Al concentration followed by Si with time (Figure 1 and 2) due to the OH anions attack on the bridging O bonds of both Al-O-Si and Al₆-O-Si sites existing on the edge surfaces, catalysed by protonated Al-OH groups (Kuwahara, 2006). In all experiments, K release pattern showed similar trend as that of other cations, with higher release rate in start.

It has been demonstrated earlier that as a result of ion exchange reactions between mineral interlayer and solution, clay minerals firstly release interlayer cations. The rates of these reactions are controlled by diffusion. For example, Metz et al. (2005) revealed that the prompt release of Ca, Na and Mg from smectite causing in a reduction of the interlayer of muscovite, biotite and phlogopite. Though solid-state Fe oxidation can take place in the course of biotite alteration, this reaction does not necessarily cause stoichiometric Fe release to solution. Several studies have indicated that octahedral cations (primarily Al, Mg and Fe) are preferentially released during biotite dissolution (Acker and Bricker, 1992; Kalinowski and Schweda, 2007; Kuwahara, 2006; Newman and Brown, 1966). In this study, the release of K was totally dependent on pH (Figure 4) as more K was released with increasing of...
pH. Our results are accordance with Malmstrom and Banwart, (1997), they described that at high pH range, and release of interlayer K becomes more important for total dissolution of mica minerals. The desorption of H⁺ at basic pH was reported to be responsible cation release from biotite dissolution at basic pH.

The muscovite and biotite rates of dissolution are controlled by a pioneer complex made by the Si, Fe and Al release from the structure of biotite and muscovite(Oelkers et al., 2008). In alkaline conditions, the dissolution rates of muscovite and biotite depend on Si concentration in aqueous solution in addition to Fe and Al concentration. It has also been suggested that at basic pH, octahedral Al-O bond is the slowest to break; therefore the rates are controlled by both the removal of tetrahedral Si and octahedral Al from the mineral structure(Bibi et al., 2011; Rozalen et al., 2009). Among the mica minerals, biotite proved to be more weather able than muscovite because shortened K-O bond presence in muscovite which is resistant to the dissolution. Further the interlayer K is also less tightly bound in biotite than muscovite. Previously, Bickmore et al.,(2006)advocated that under alkaline conditions the quartz dissolution seemed to proceed by attacking of hydroxyl ions (OH⁻) which initiated by the existence of a silanol group (neutral). In the first mechanism, an OH⁻ ion outbreaks the oxygen atom of a siloxane group (>Si₂O) and is speed up by the existence of a >Si-OH group, this phenomenon evident that the rate of dissolution (R) may be proportional to the concentration of OH⁻. The first mechanism would tend to dominate at higher pH, since the concentration (or activity) of OH⁻ would go up with temperature for a given in situ pH but the fraction of deprotonated surface sites would remain constant. Our results are also agreement with the Kuwahara, (2006) who proposed that this mechanism can be applied to montmorillonite dissolution under alkaline conditions, that is, OH⁻ ions would outbreak the bonding of O bonds of mutually Al-O-Si and Al₂-O-Si sites present on the edge sides, more concentration of OH⁻ cause more dissolution of montmorillonite.

V. Conclusion

It is concluded that the dissolution of mica minerals (biotite, muscovite) increased with an increase in pH under alkaline range and the trioctahedral mineral (biotite) is easily dissolved than dioctahedral mineral (muscovite). Soils with high pH (>8) have large amount of K than that in low pH soils because dissolution rate of minerals high at such pH values. It is further recommended that K-fertilizer requirements for the soils having trioctahedral mineral (biotite) would be less as compared to soils containing dioctahedral mineral (muscovite).

References Références Referencias

Figure 1: Silicon (Si) release from biotite and muscovite dissolution experiments at pH 8-12, 25°C
**Figure 2:** Aluminum (Al) release from muscovite dissolution experiments at pH 8-12, 25°C
Figure 3: Iron (Fe) release from biotite dissolution experiments at pH 8-12, 25°C
Figure 4: Potassium (K) release from biotite and muscovite dissolution experiments at pH 8-12, 25°C
Figure 4: Potassium (K) release from biotite and muscovite dissolution experiments at pH 8-12, 25°C

Figure 5: Comparative dissolution rates of biotite and muscovite based on Si release
### Table 1: Chemical composition of mica minerals

<table>
<thead>
<tr>
<th>Composition</th>
<th>Biotite</th>
<th>Muscovite</th>
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</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>37.93</td>
<td>47.29</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>14.09</td>
<td>33.74</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>7.19</td>
<td>4.10</td>
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<tr>
<td>FeO</td>
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<tr>
<td>MnO</td>
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<tr>
<td>MgO</td>
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<td>CaO</td>
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<td>Na$_2$O</td>
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<td>K$_2$O</td>
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</tr>
<tr>
<td>TiO$_2$</td>
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<td>0.21</td>
</tr>
<tr>
<td>F</td>
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<td>0.20</td>
</tr>
<tr>
<td><strong>Σ</strong></td>
<td>97.30</td>
<td>98.98</td>
</tr>
</tbody>
</table>

**Biotite,**

$(Ca_{0.003}Na_{0.007}K_{1.82})(Al_{0.33}Fe^{3+0.82}Fe^{2+0.17}MnO_{0.00}Mg_{2.70}) (Si_{5.80}Al_{2.20})O_{20}(OH)_{3.91}F_{0.03}$

**Muscovite,**

$(Ca_{0.003}Na_{0.15}K_{1.62})(Al_{4.38}Fe^{3+0.40}Fe^{2+0.19}MnO_{0.04}Mg_{0.04}) (Si_{6.19}Al_{1.81})O_{20}(OH)_{3.91}F_{0.09}$

Ti omitted from the structural formulae.