POTASSIUM FIXATION BY OXIDIZED AND REDUCED FORMS OF DIFFERENT PHYLLOSILICATES

by

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Abstract

Factors governing potassium fixation and release are poorly understood. This study was conducted to investigate the effects of clay mineralogy and structural iron oxidation state on potassium fixation. Five reference clays and two soil clays were used to capture a range in mineralogical compositions and potassium behaviors. Reference clays used were illite (IMt-1), kaolinite (KGa-1b), montmorillonite (STx-1b), nontronite (NAu-2), and vermiculite (VTx-1). Soil clays used were from the upper 15 cm of a Belvue loam (BEL) and a Cherokee silt (CHE). Potassium fixation capacities were measured on unaltered as well as sodium dithionite reduced forms of each clay. Ferrous and total iron contents were determined photometrically using 1, 10-phenanthroline. Potassium fixation was measured by potassium saturating the clays and washing off exchangeable and solution potassium with solutions of magnesium chloride; samples were then acid digested and the amount fixed was calculated as the amount of potassium in the acid digestion minus the amount originally in the sample. BEL released potassium rather than fixed it while CHE tended to release potassium in the unaltered form and fix potassium in the reduced form. Structural iron reduction significantly impacted the amounts of potassium fixed by VTx-1 and NAu-2, which had the highest total iron contents of all the clays evaluated. NAu-2 and VTx-1 both on average fixed less than 1 mg K g clay^{-1} in the unaltered form and an average of 6 and 11 mg K g clay^{-1}, respectively, in the reduced form. Regardless of being in the unaltered or reduced form, KGa-1b fixed essentially no potassium and IMt-1 and STx-1b fixed intermediate amounts of potassium—2 to 4 mg K g clay^{-1} on average. The effects of clay mineralogy and structural iron oxidation state on potassium fixation can largely be explained through an understanding of layer type, layer charge, and charge distribution. In order for potassium fixation to occur, interlayer sites need to be accessible and available. Generally, the greater the negative layer charge the greater the amounts of fixation, with tetrahedral layer charge favoring fixation more than octahedral layer charge, and layer charge being a function of structural iron oxidation state.

Table of Contents

List of Figures

List of Tables

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Dedication

For my mother, Linh Lam, who works so hard, gives so much, and smiles so brightly.

Preface

I initially began this project with the intent of evaluating just the effect of clay mineralogy and structural iron redox state on potassium fixation—a project with both agronomic and environmental relevance as it would (I hoped!) shed light on both nutrient and pollutant dynamics in soils and soil materials as related to both material composition and redox environment.

I never suspected that in order to accomplish this objective I would also end up wrestling with different ways to measure potassium fixation, bootstrapping a way to reduce structural iron in phyllosilicates, and delving waist deep into the old scientific literature. Though, in retrospect, it was these experiences that I ended up learning from the most.

One charming aspect of reading the old scientific literature is seeing scientists paw in the dark at the edges of what we now take for granted as common knowledge. It’s inspiring to read the work of someone hitting upon some great truth with such relatively limited analytical resources as well as it is encouraging to see scientists get it completely wrong.

Well, I don’t hope to hit upon any great truth here, and I hope the future will forgive me if I’ve gotten something completely wrong, but here’s to pawing at the truth.

Chapter 1 - Introduction

Potassium is the seventh most abundant element in the earth's crust. During the process of mineral weathering, as basic cations are largely lost through solution, potassium becomes relatively enriched in the soil compared to other common basic soil cations (Table 1.1). This is because potassium is uniquely retained in the soil in a way that the other common basic soil cations are not. This retention is referred to as potassium fixation (Meunier and Velde, 2004).

Table 1.1 Crustal abundances, soil abundances, and enrichment factors for common basic soil cations.

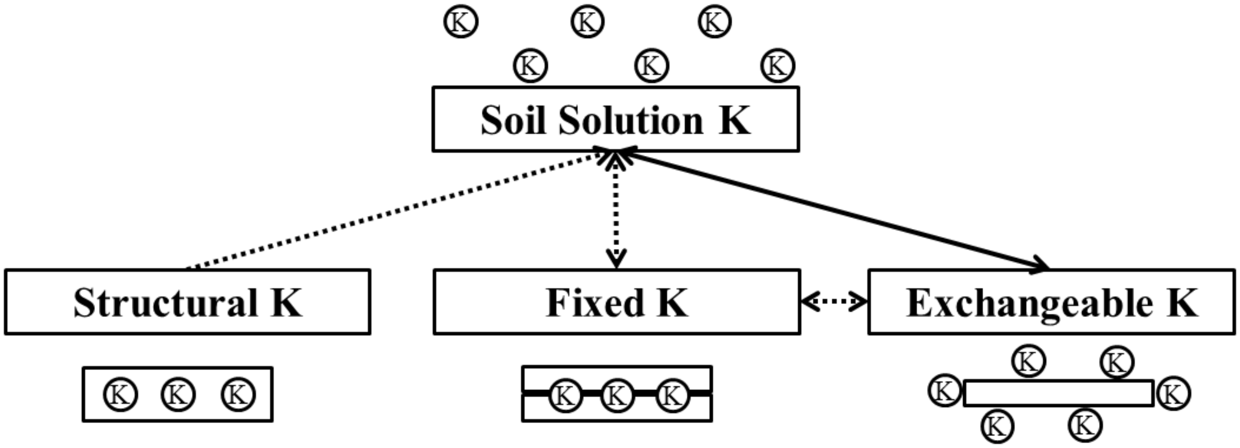
Element	Crustal abundance	Average soil abundance (USA)	Enrichment factor
Na	2.3%	1.2%	0.52
Mg	3.2%	0.9%	0.28
K	0.9%	1.5%	1.67
Ca	5.3%	2.4%	0.45

Source data in Appendix A. Crustal and soil elemental abundances vary by source and in some scenarios potassium abundances in the soil are less than in the crust. However, in these scenarios too, potassium still generally has the greatest enrichment factor of the common basic soil cations.

Soil potassium pools

While most basic cations exist in solution, exchangeable, and mineral form, potassium additionally exists in the fixed form (Figure 1-1).

Figure 1-1 Relationships between different pools of soil potassium.



Though this schematic for pools of soil potassium is fairly universal in terms of general concept, there are variations in the literature in terms of formally defining and measuring each pool. Solution potassium, which is the most clearly defined pool of soil potassium, is still subject to some interpretation in terms of measurement. Theoretically, solution potassium is aqueous potassium that is not in any way bound or attracted to soil minerals. Generally, solution potassium is measured by extraction with water or some solvent that will minimally disturb the double diffuse layer—e.g., ethanol. While the method of extraction can slightly alter the results yielded, measuring solution potassium is relatively straightforward.

Measuring exchangeable potassium, however, can be a bit more confusing. Exchangeable potassium is also referred to as replaceable and sometimes extractable potassium, which may be part of the reason for confusion. Often what can be extracted with a certain replacing solution is made synonymous with exchangeable potassium. The issue with this is that every combination of replacing solution parameters—e.g., solution volume, concentration, and type, and replacement method and duration—is going to yield a different amount of potassium. Exchangeable potassium, though, should refer to a specific value. It should refer to potassium ions attracted to mineral surfaces that are not fixed. Though it is difficult to establish this value as ever truly being measured, it is most commonly approximated by extraction with normal, neutral ammonium acetate (Quémener, 1978). This technique will also measure solution potassium. If solution potassium in the sample is considered to be large, then it can be subtracted off mathematically or removed prior to determination of exchangeable potassium. In most situations, however, solution potassium is considered to be negligible and no adjustment is made.

The fixed pool is the most difficultly defined and measured potassium pool, and the definition and measurement of the mineral pool is dependent on the definition and measurement of the fixed pool. At the most general level, fixed potassium refers to potassium held between collapsed phyllosilicate layers, and mineral potassium—also called structural and lattice potassium—refers to potassium that is part of a mineral structure[1]. To avoid any ambiguity as to where micas fall in this scheme, mineral potassium here will be further defined as potassium that is a part of the mineral structure in such a way that any release of potassium into solution would require the destruction of the mineral. This refined, though not universal, definition of mineral

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[1] For the sake of comprehensiveness, alternative, much less popular usages of the term potassium fixation can be found in Appendix B.

potassium, leaves the potassium in micas which can be released without the destruction of the mineral structure decidedly in the fixed pool.

Some authors take a more restrictive definition of fixed potassium than the one taken here, differentiating between native interlayer potassium—e.g., in primary micas—and non-native interlayer potassium—i.e., potassium fixed from solution. The reason for doing so is largely to do with their different release kinetics. Native interlayer potassium tends to be released more slowly than non-native interlayer potassium (Arnold and Close, 1961; Barshad, 1954; Haylock, 1956; Mortland and Ellis, 1959). However, since it is difficult to actually distinguish native interlayer potassium from non-native interlayer potassium in the laboratory and because native interlayer potassium shares more in common with non-native interlayer potassium than other forms of potassium, this distinction will not be made here.

Fixed potassium is frequently used synonymously with non-exchangeable and non-replaceable potassium. However, as discussed earlier, amounts of potassium that are replaceable and non-replaceable are highly dependent on replacement parameters. Additionally, there are a variety of procedures which will be discussed in Chapter 2 that are designed to replace and measure the non-exchangeable or non-replaceable fraction, making the terms “non-exchangeable” and “non-replaceable” a little counterintuitive. Furthermore, even if there were an extraction procedure that could be guaranteed to remove precisely just the solution and exchangeable fractions, the value obtained for the non-exchangeable fraction would inevitably include mineral potassium in addition to fixed potassium.

Mineral potassium determinations are typically made by the complete acid digestion of the sample. The value obtained gives total potassium, which in most situations is a fair estimate of mineral potassium. However, for a more precise measurement of mineral potassium, the other pools of potassium can be measured and subtracted off the total potassium value.

An added point of nebulosity to the measurement of these different potassium pools resides in the fact that all these pools are in equilibrium with each other, and whatever is done to the sample in the lab has the potential to impact these equilibriums. One of the difficulties in understanding potassium dynamics in the soil is trying to understand the factors governing potassium movement in and out of the various soil potassium pools.

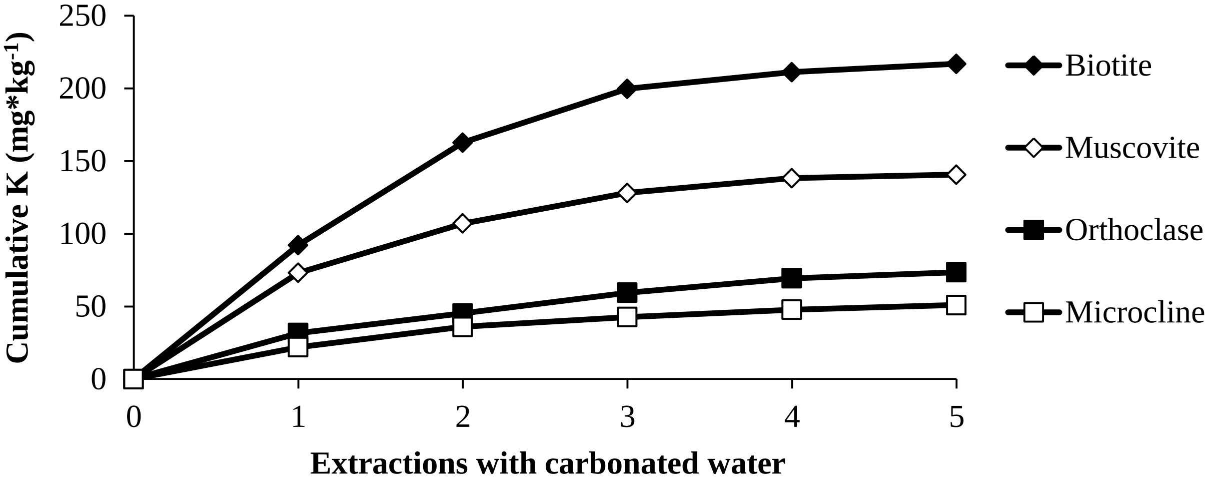
Soil potassium and plant availability

In addition to being an essential plant nutrient, potassium is also the third most frequently deficient plant nutrient. Making distinctions between different pools of soil potassium has much to do with the relative availability of different pools of potassium to plants. Though the amount of potassium in soils is often high, ranging from 3,000 to 100,000 kg K ha $^{-1}$ in the upper 20 cm of the soil, the amount of potassium that is readily available to plants is only a small fraction of the total potassium in the soil (Sparks, 2001a). The large majority of potassium in soils is tied up in mineral form—e.g., in potassium feldspars such as orthoclase or microcline. Exchangeable potassium and solution potassium, which are considered the readily available pools, only make up about 0.1 to 0.2% of the potassium in the soil with solution potassium only accounting for about 10 to 30 kg K ha $^{-1}$ (Mengel and Kirkby, 2001).

While the solution and exchangeable pools are considered the readily available pools, plants typically remove more potassium from the soil than is present in these two pools (e.g., Abel and Magistad, 1935, Hoagland and Martin, 1933; McLean and Simon, 1958; Natale et al., 2001; Quémener, 1988). This is possible because as both the solution and exchangeable pools are depleted of potassium by plant uptake, they are regenerated by the mineral and fixed pools (Pal et al., 2001; Wood and DeTurk, 1941). Rates of potassium release and regeneration, however, vary widely and are a function of cultural factors as well as environmental and mineralogical factors. Cooke and Gething (1979) compared two different soils, one which released approximately 20 kg K ha^{-1} annually and the other which released about 80 to 90 kg K ha^{-1} annually from the fixed and mineral pools. While there were many factors separating these two soils, the difference in potassium release may have been related to the more intense cropping of the former soil. Intense cropping leads to potassium exhaustion and potassium release rates decrease with the exhaustion of potassium reserves (Beckett and Nafady, 1967).

Various forms of soil potassium are described in different texts as being unavailable, difficultly available, slowly available, moderately available, and readily available—all relative and un-quantified classes of availability. The relative availability of potassium, however, is better characterized by a gradient than classes. For example, potassium associated with micas and potassium feldspars is often considered unavailable or slowly available to plants. However, minerals within these groups vary widely in terms of the readiness with which they yield their potassium to solution. Plummer (1918) evaluated how much potassium could be removed from common soil-forming minerals in five extractions with carbonated water and found that the amount of potassium released varied significantly (Figure 1-2).

Figure 1-2 Solubility in carbonated water of potassium in common soil-forming minerals.

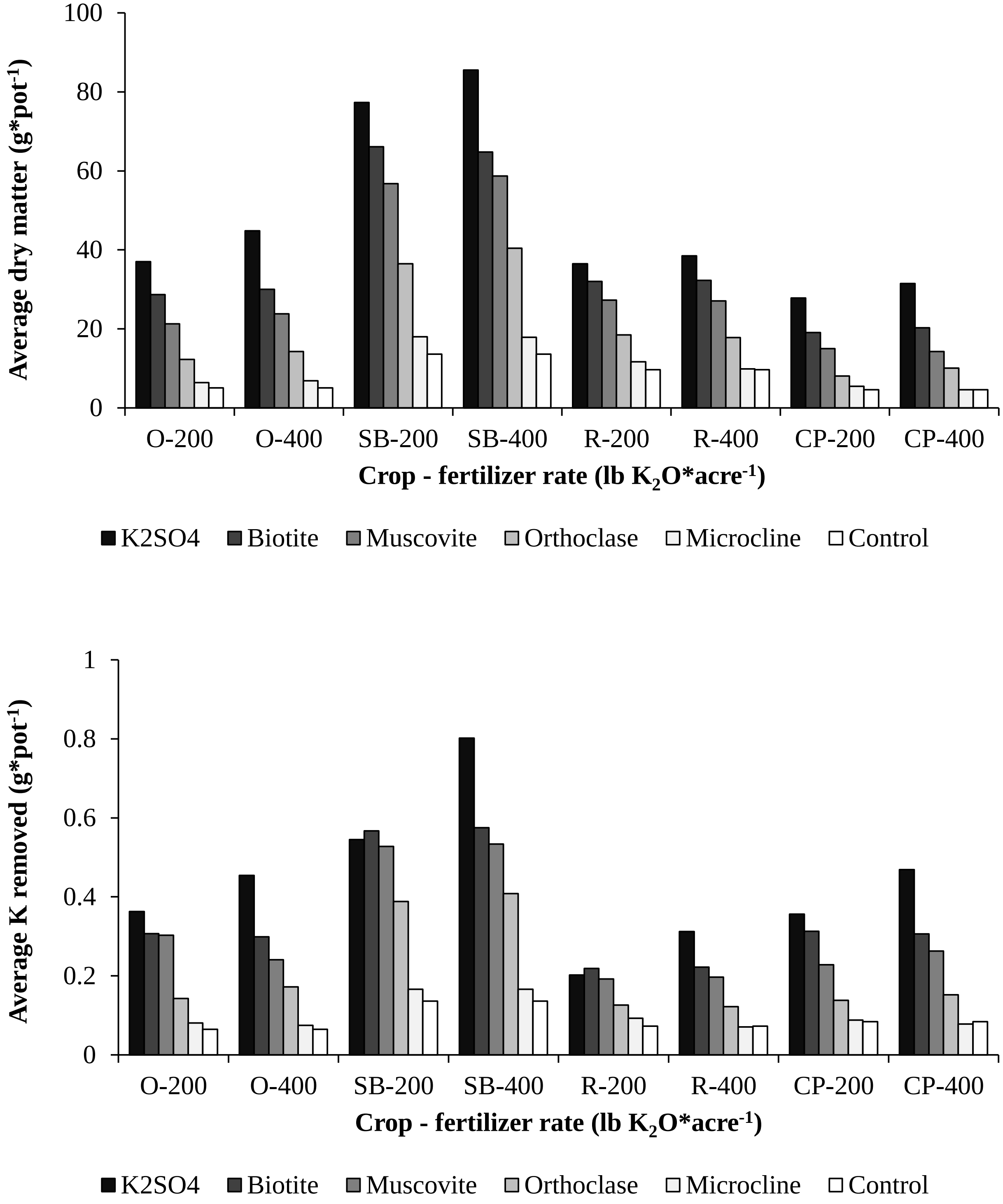


Data from Plummer (1918).

Plummer further investigated this relationship by conducting a number of pot studies where oats, soybeans, rye, and cowpea were grown. He fertilized the pots at two different rates—200 and 400 pounds of K_2O per acre—and used five different sources of potassium—potassium sulfate, and ground biotite, muscovite, orthoclase, and microcline. These experiments demonstrated both the ability of plants to extract significant amounts of potassium from potassium sources conventionally thought to be plant unavailable as well as a wide range in potassium availability between mineral types (Figure 1-3).

However, not all fixed potassium is readily available to plants. Potassium fixation in agricultural fields, in fact, can be so severe as to induce potassium deficiencies despite large additions of potassium fertilizer (e.g., Kovačević and Vukadinović, 1992). The most commonly cited reason justifying work on potassium fixation is the need to understand the agronomic value of fixed potassium as well as the factors governing potassium fixation and release. Potassium behavior has been hard to predict and explain which has led to potassium fertilizer recommendations based on soil test extractable potassium values failing to optimize agronomic performance. There is still much to learn about the factors governing not only the plant availability of different pools of potassium but also potassium fixation and release.

Figure 1-3 Average dry matter of and potassium removed by oats (O), soybeans (SB), rye (R), and cowpea (CP) when fertilized at the rate of 200 and 400 pounds of K_2O per acre by K_2SO_4, biotite, muscovite, orthoclase, and microcline.



Data from Plummer (1918).

Problems and objectives

A variety of workers have documented temporal variations in soil extractable potassium under a variety of land management practices and using a variety of different types of extractions (e.g., Bell and Thornton, 1937; Childs and Jencks, 1967; Gallagher and Herlihy, 1963; Garbouchev, 1966; Keogh and Maples, 1972; Koós and Németh, 2006; Leibhardt and Teel, 1977; Lockman and Molloy, 1984; Vitko et al., 2010). Generally, extractable potassium decreases during the growing season as potassium is being taken up by crops, reaching a minimum around harvest time. Afterward, during the winter, extractable potassium levels slowly rebound being replenished from non-extractable potassium sources and organic matter, sometimes to their original springtime high and sometimes to a lower level. In addition to the cycle of draw down during the growing season and replenishment during the winter months, there are other fluctuations in soil extractable potassium, the causes of which are less certain (Quémener, 1988).

There are a variety of reasons that could cause temporal variations in soil extractable potassium. Ignoring the variation caused by sampling and statistical factors like nutrient stratification and the number of cores in each sample, we can conceptualize the variations as being the result of shifting additions and losses to the soil extractable potassium pool (Table 1.2). This conceptualization takes for granted that extractable potassium accurately approximates solution and exchangeable potassium.

Table 1.2 Summary of general factors increasing and decreasing soil extractable potassium.

Additions to soil extractable potassium	Losses from soil extractable potassium
Release from mineral sources	Fixation by minerals
Release from organic sources	Uptake by plants
	Leaching from profile

Soil extractable potassium can be increased by release of potassium from both mineral and organic sources. Soil extractable potassium can be decreased by fixation, plant uptake, and leaching from the soil profile. The additions and losses from organic source release, plant uptake, and profile leaching are fairly easy to quantify, understand, model, and predict. The additions and losses to soil extractable potassium from potassium release and fixation by soil minerals are comparatively much more difficult to quantify, understand, model, and predict.

Many fluctuations in soil potassium are often attributed to soil fixation and release phenomena because the more easily understood potassium movement pathways fail to explain these fluctuations. Yet no explanation is proposed as to how potassium fixation and release would drive these fluctuations.

The rate and magnitude of potassium fixation and release has been documented to be related to both overlapping and seemingly disparate factors, including but certainly not limited to: soil type, soil horizon, soil mineralogy, previous mineral saturation, particle size distribution, particle size, grinding, soil weathering, soil fertilization, cropping intensity, soil pH, liming, plant cycling, potassium activity in solution, moisture conditions, temperature conditions, redox conditions, organic matter content, manure applications, biological activity, hydroxyl interlayering, and the presence of organic cations and molecules (e.g., Beckett, 1971; Goulding, 1987; Martin and Sparks, 1985). This overwhelming list of environmental, mineralogical, cultural, and biological factors affecting potassium fixation make predicting and understanding potassium seem daunting. However, these factors can be united rather elegantly into a single, coherent theory of potassium fixation by considering potassium fixation simply a phenomenon of contraction forces overcoming expansion forces. In order to further characterize and demonstrate this conceptual framework, the effects of clay mineralogy and structural iron redox state on potassium fixation were further evaluated in the laboratory.

Thus the objectives of this project were to:

1. Explore the effect of clay mineralogy on potassium fixation.

2. Explore the effect of structural iron redox state on potassium fixation.

3. Develop a coherent theory of potassium fixation using the results of this study and past studies.

Chapter 2 - Literature Review

Potassium fixation as a concept has been developed and refined over the years through many different kinds of observations. Early workers noted that there must be some sort of unique retention and release of potassium by the soil as potassium removal and addition rates alone failed to explain changes in soil extractable potassium over time. Additionally, workers observed poor crop response to potassium fertilizers in some regions despite apparent potassium deficiency, indicating the transformation of potassium from an exchangeable, available form to a less available form. Many different mineralogical, chemical, mechanical, and mathematical observations have helped to elucidate the mechanism by which potassium is uniquely retained—i.e., fixed. The development of the potassium fixation concept through all these observations will be discussed in the first portion of this chapter.

There are many different definitions of potassium fixation as well as many different methods used to measure both the potassium fixation capacity of a sample and the amount of fixed potassium in a sample. Since the results of potassium fixation determinations are the direct result of the methodology used and the methodologies used are often derived off different theoretical definitions of potassium fixation, the second portion of this chapter will be devoted to the topic of defining and measuring potassium fixation.

Throughout the first two portions of this chapter, most of the documented factors affecting potassium fixation and release will be discussed, with the exception of clay mineralogy and structural iron redox state. The effects of these factors will be discussed independently in the third and fourth sections of this chapter, respectively, to allow for more in depth coverage of each.

Development of the potassium fixation concept

Attempts at potassium accounting

One of the earliest recorded observations indicating the occurrence of a process akin to what is currently named “potassium fixation” was that of Dyer (1984) at Rothamsted. In Dyer’s efforts to evaluate various analytical determinations of available potassium, he documented that portions of potassium applied as fertilizer got converted into a form that was not dissolvable by one percent citric acid solution. Similar findings were made by Frear and Erb (1918) and Page and Williams (1925). In the study by Page and Williams, taking into account the amount of fertilizer applied and the amount of potassium removed during crop removal over about eighty years there should have been an excess of about 5100 kg extractable K ha^{-1} in the fertilized plots as compared to the unfertilized plots. In actuality, however there was only about an excess of 1400 kg extractable K ha^{-1} in the upper 46 cm of the fertilized soil. This suggested to the authors that there was a process by which the potassium was going from an extractable form to a non-extractable form in the fertilized soils and perhaps vice versa in the unfertilized soils.

An important note to make about these studies is that the transformation they suggest is thus far only characterized by potassium going from a form that is exchangeable by the exchanging process they choose to use to a form not exchangeable by this process. None of these authors suggest that potassium is being trapped between collapsed clay layers. Though Frear and Erb do use the term “fixation” they mean it in a more broad way than it is used currently. It is not until later, that workers begin to connect the idea of potassium fixation with entrapment between clay layers.

Another caveat to consider is that oftentimes in potassium accounting, potassium losses by erosion and leaching are considered negligible enough to be ignored. However, potassium leaching and erosional losses range widely. The losses from these two pathways can sometimes be significant. Leaching losses vary largely as a function of cropping system, rainfall, evapotranspiration, and soil texture and have been observed to range from 0 to 246 kg K ha^{-1} yr^{-1}, while erosional losses have been observed to exceed 150 kg K ha^{-1} yr^{-1} on agricultural land (Bertsch and Thomas, 1985; Lipman and Conybeare, 1936; Truog and Jones, 1938; Quémener, 1988; Volk, 1941). So, while it is tempting to attribute all unaccounted for potassium to potassium fixation, leaching and erosional losses can also sometimes be significant pathways of potassium removal from the soil extractable pool.

Crop potassium needs and crop response to potassium fertilizer

Some soils show poor responses to potassium fertilizer and this is frequently attributed to potassium fixation (Schuffelen and van der Marel, 1955). In some California cotton fields, unusually high rates of potassium fertilizer are needed to correct potassium deficiencies (Page et al., 1963). In these areas, which are dominated by vermiculite, fertilizer additions of up to 1500 kg K ha^{-1} are required to optimize cotton yield. Due to the ability of these soils to fix added potassium, traditional soil test potassium values are not a reliable metric with which to calculate fertilizer recommendations (Cassman, 1986; Cassman et al., 1989; Cassman et al., 1990).

Potassium balance and soil mineralogy

It has been well demonstrated in a variety of regions and under a variety of cropping systems that long term fertilization with potassium increases the mica and illite content of soils and that long-term, continuous cropping, decreases the mica and illite content with concomitant increases in the content of expandable clay minerals (e.g., Barré et al., 2007a, 2007b, 2008a, 2008b; Meunier and Velde, 2004; Meunier, 2005; Ross et al., 1985; Shaimukhametov and Mamadaliev, 2003; Simonsson et al., 2009; Sokolova et al., 1998; Volk, 1934). In a greenhouse study, Mortland et al. (1956) showed conclusively that plants can deplete micaceous substrates of potassium, transforming them into vermiculitic minerals.

While the content of micaceous minerals almost always increases with depth in soils, as weathering proceeds from the top of the profile down, there are two major exceptions to this pattern. The first is when there is a lithologic discontinuity present and the second is when there is an input of potassium at the surface (Thompson and Ukrainczyk, 2002). Ignoring the first exception, not only can fertilizer inputs at the soil surface increase mica content, but plant cycling of potassium to the surface can too (Swindale and Uehara, 1966).

Layer silicates have a limited fixation capacity which can be increased and decreased by removing or adding cations to fixation sites. For example, fertilized soils, when taken into the laboratory, tend to fix less potassium than their unfertilized counterparts (e.g., Pratt and Goulben, 1957; Volk, 1934)[2]. Similarly, potassium deficient field budgets—i.e., budgets characterized by potassium removal exceeding potassium addition—have been shown to favor increased potassium fixation (Shaimukhametov and Mamadaliev, 2003). Both of these observations can be replicated in laboratory settings. For example, Volk (1938) found that leaching the potassium out of a sample of mica increased its fixation capacity and many workers have found that prior fixation—either by potassium or by another fixable cation—decreases subsequent amounts of

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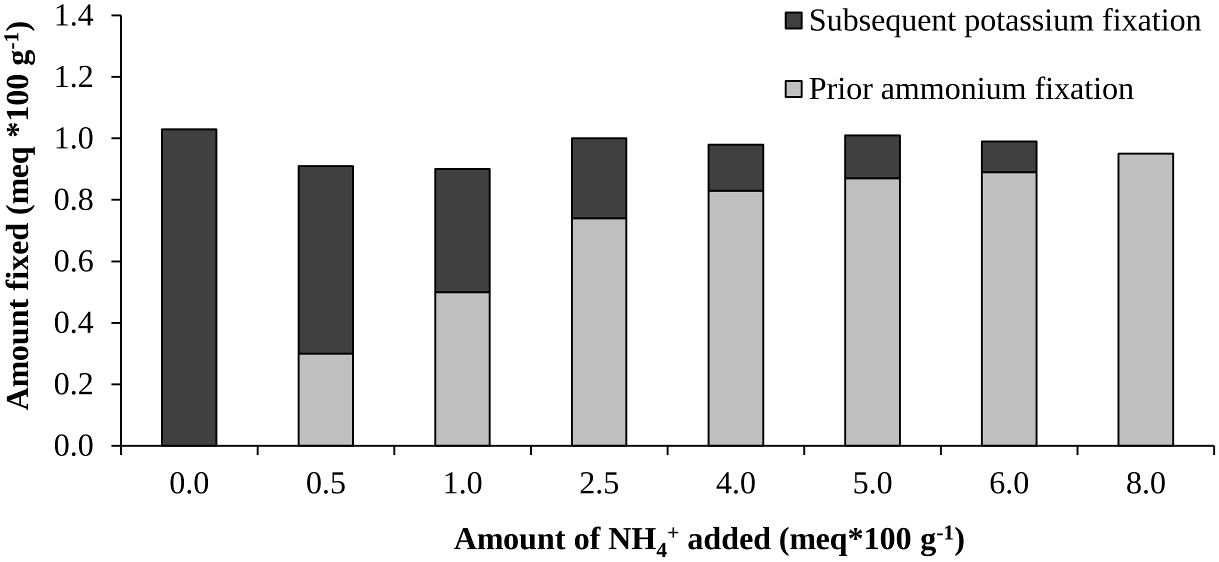
[2] Sardi and Csitari (1998) found that fertilized soils fixed more potassium than their unfertilized counterparts in some scenarios, however, in addition to fertilizing with potassium, they also fertilized with nitrogen and phosphorus, thus the conclusions that can be drawn from their study are limited as there was no comparison made between a completely unfertilized soil and a soil fertilized only with potassium.

fixation that can be induced in a sample (e.g., Hinman, 1966; Page et al., 1963; Stanford and Pierre, 1946; Wiklander, 1950) with the reduction in subsequent fixation equaling the amount of prior fixation (Figure 2-1).

Figure 2-1 Effect of prior ammonium fixation on subsequent potassium fixation.



Data from Stanford and Pierre (1946) for a Webster silty clay loam. Two and a half milliequivalents of potassium added to each sample after the ammonium addition.

Potassium fixation and lattice contraction

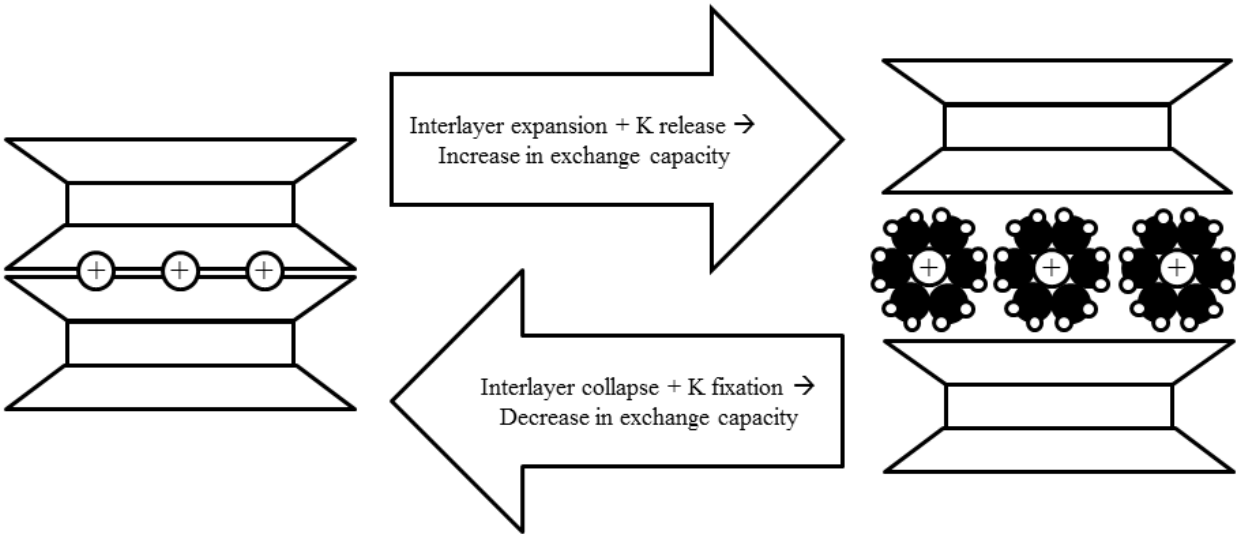
The formation of micaceous minerals associated with potassium fixation suggests that potassium fixation is the entrapment of potassium between collapsed layers. A variety of observations have corroborated this idea, unequivocally indicating that potassium fixation is a lattice contraction phenomenon. Most observations have pertained to the association of potassium fixation with decreases in exchange capacity and d-spacing. Though, Wear and White (1951) also showed potassium fixation to be associated with a decrease in hydrated clay volume.

Potassium fixation and decreases in exchange capacity

Potassium-fixation is sometimes described as the reversal of mica weathering (e.g., Jackson, 1963). When illite releases its potassium, it becomes vermiculite and when vermiculite fixes potassium it becomes illite (Barshad, 1948; Barshad, 1954). When micas weather, not only do their interlayers expand, they lose their potassium, and there is an equivalent increase in CEC (Reichenbach and Rich, 1975). This phenomenon can be observed in agricultural fields, where soil from unfertilized plots of land increase in exchange capacity over time as interlayers are opened up and potassium is taken up by plants (Scheffer et al., 1960).

Under a paradigm in which potassium-fixation is the reversal of mica weathering, it would follow that not only should potassium be held between collapsed clay layers during potassium-fixation, but there should be an equivalent decrease in CEC of the fixing material (Figure 2-2).

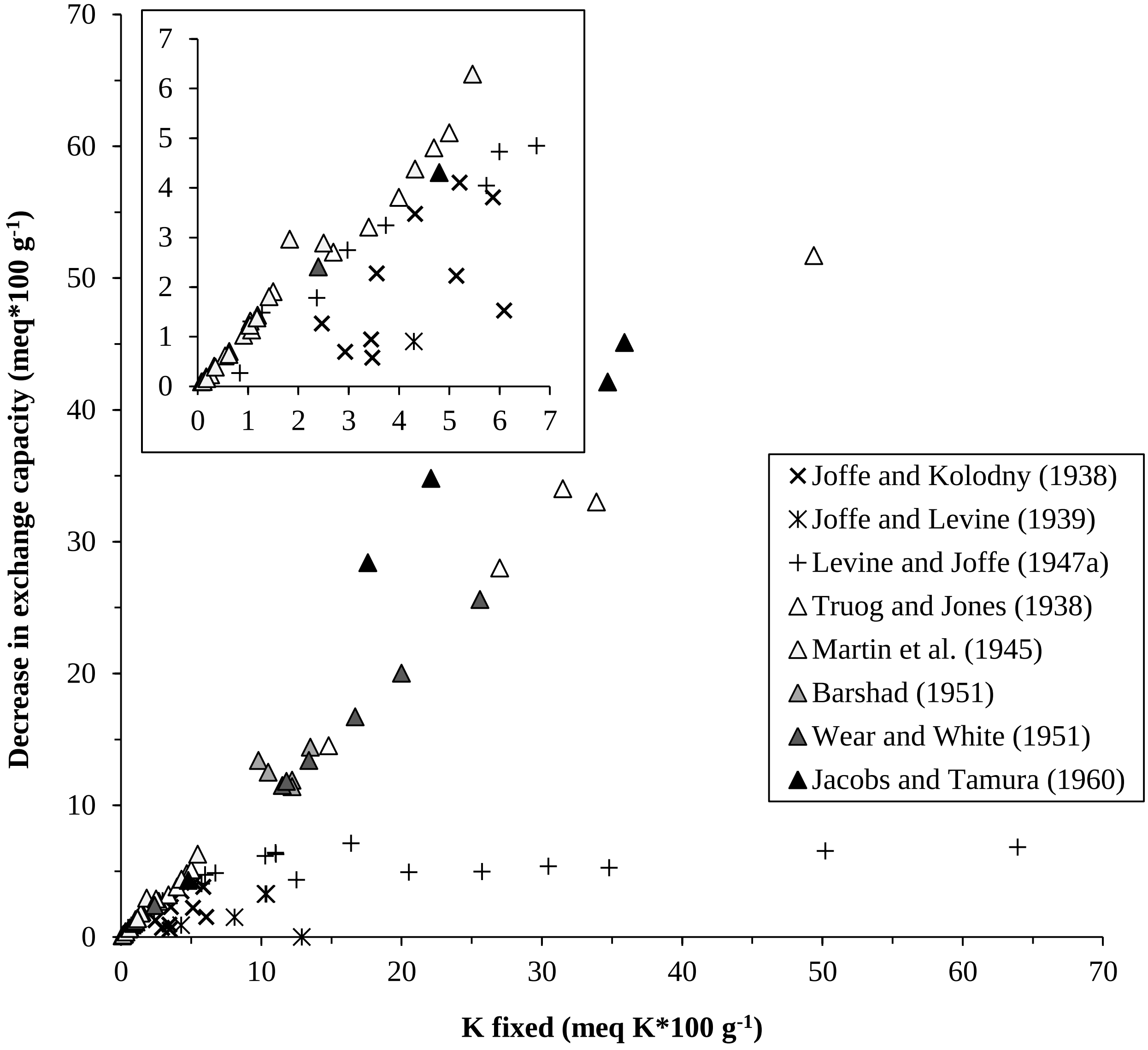
Figure 2-2 Conceptualization of potassium fixation as the reversal of mica weathering.



Many workers have observed a rough one to one relationship between both potassium and ammonium fixation and decreases in CEC (e.g., Barshad, 1951; Bower, 1950; Jacobs and Tamura, 1960; Martin et al., 1945; Shaviv et al., 1985; Truog and Jones, 1938; Wear and White, 1950). Page et al. (1963) even used decreases in fixation capacity as a proxy for determining the amount of potassium fixed.

However, Joffe and his coworkers observed instances where potassium fixation appeared not to be associated with an equivalent decrease in CEC (Joffe and Kolodny, 1938; Joffe and Levine, 1939; Levine and Joffe, 1947a). Figure 2-3 shows the two different patterns of results obtained by different workers on this topic.

Figure 2-3 Relationship between potassium fixation and decreased exchange capacity.



One gross outlier omitted.

Expanded inset included to show lower values with greater clarity.

The source of this discrepancy no doubt lies in differences in materials and methods. While there were no obvious differences between the types of materials being used (Table 2.1), there were significant differences in the procedures used both to measure potassium fixation and to measure CEC. While in some of the older papers, the methods are not described in sufficient detail as to allow repeating the procedure one point stands out in the procedure described by Joffe and Levine (1939).

Joffe and Levine took their initial CEC measurement after the samples had been potassium saturated. The final CEC was measured after the samples had been potassium saturated and subjected to multiple wetting and drying cycles. Joffe and Levine were no doubt working off the now no longer popular belief that wetting and drying cycles must occur for fixation to occur (Volk, 1934). It is however, now accepted that potassium fixation can proceed without drying and thus it is likely that much potassium saturation and CEC decrease had already occurred by the time Joffe and Levine measured initial CEC. This may explain the inconsistency of all the papers of Joffe with the rest of the literature.

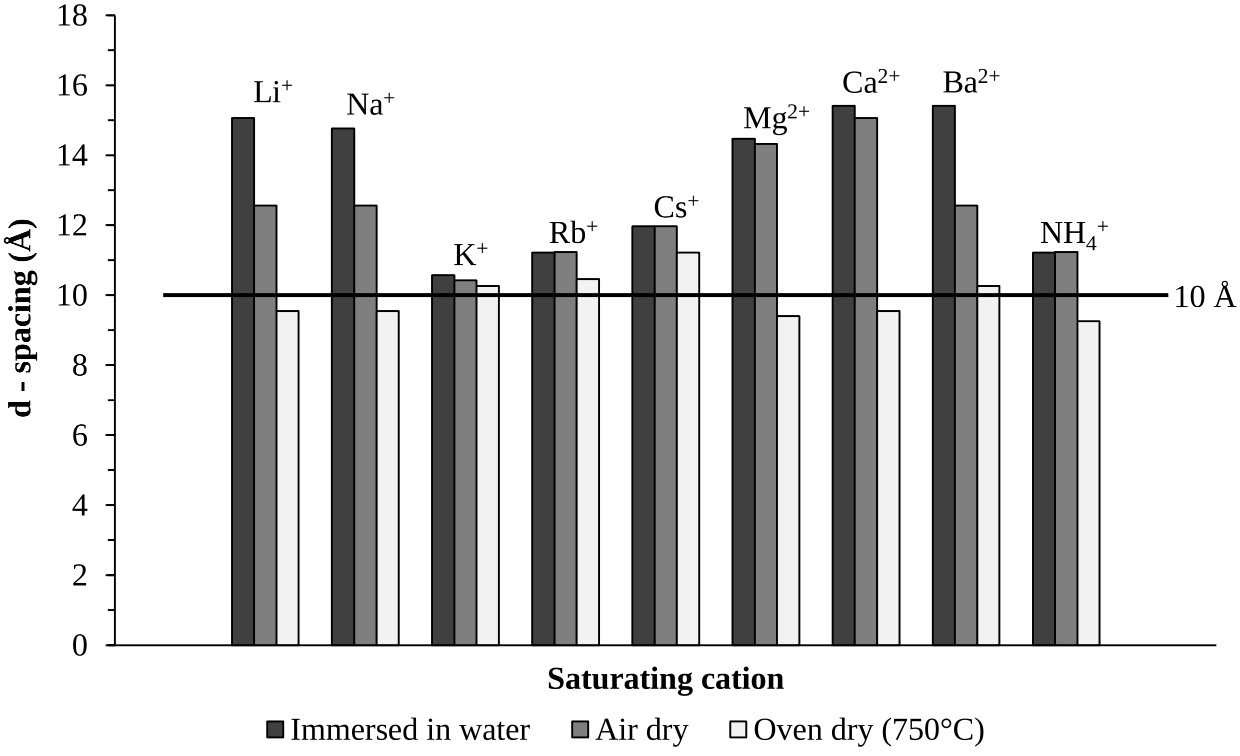
Table 2.1 Summary of materials used by different authors evaluating the relationship between potassium fixation and decreases in CEC.

Author(s), Year	Specimen samples	Soil samples
Truog and Jones, 1938	Bentonite Nontronite	Miami SiL (A, B horizons) Carrington SiL (A, B horizons) Richfield C (A, B horizons)
Joffe and Kolodny, 1938		Dover L (profile) Collington L (profile)
Joffe and Levine, 1939		Chester GR L(B horizon) Montalto SiL (B horizon, clay fraction) Gloucester GR L (B horizon)
Martin et al., 1945	Arizona bentonite California bentonite	Vina CL Ramona L
Levine and Joffe, 1947a	Wyoming bentonite	Montalto SiL (clay fraction)
Barshad, 1951		Sheridan clay loam (subsoil)
Wear and White, 1951	Wyoming bentonite California bentonite Illite	Putnam C (clay fraction)
Jacobs and Tamura, 1960	Vermiculite	
Shaviv et al., 1985		Domino series (profile) Pachappa series (profile) Altamont series (profile) Nord series (profile) Grangeville series (profile)

Potassium fixation and decreases in d-spacing

The d-spacings of vermiculites and montmorillonites are highly dependent on the type of cation they are saturated with. Potassium, ammonium, rubidium, and cesium saturated samples tend to have d-spacings similar to illite or mica—i.e., d-spacings of about 10 Å—whereas samples saturated with other cations tend to be more expanded (Barshad, 1948, 1950; Hendricks et al., 1940; van der Marel, 1954). This is due to the anhydrous nature of samples saturated with potassium, ammonium, rubidium, and cesium cations compared to the hydrous nature of samples saturated with calcium, magnesium, sodium, lithium, and barium cations (Barshad, 1948). A hydrated interlayer is much more expansive than an anhydrous interlayer. While potassium, rubidium, cesium, and ammonium saturated samples have anhydrous interlayers and approximately 10 Å d-spacings regardless of sample moisture status, lithium, sodium, magnesium, calcium, and barium saturated samples are expansive until drying expels interlayer water, at which point the clay layers collapse (Figure 2-4).

Figure 2-4 D-spacings for a vermiculite saturated with different cations and evaluated immersed in water, air dried, and oven dried at 750°C.



Source data from Barshad (1948, 1950).

Dehydration of interlayer spaces and potassium fixation facilitation

As another piece of evidence that potassium fixation is associated with the dehydration of interlayer spaces, samples allowed to stay continuously moist with added potassium tend to fix less potassium than samples that are dried and/or heated with added potassium. This pattern has been documented for a variety of soil and clay materials with regard to both potassium and ammonium fixation (e.g., Alexiades and Jackson, 1965; Barshad and Kishk, 1970; Black and Waring, 1972; Bouabid et al., 1991; Raney and Hoover, 1946; van Olphen, 1966)[3]. Additionally some materials require a drying step in order to fix any potassium (e.g., Attoe and Truog, 1945; Stanford, 1947; Volk, 1934). Martin et al. (1945) speculated that drying increased fixation because it increased the concentration of salts in soil solution, but Volk (1934) already tested this hypothesis and found that soils placed in highly concentrated potassium solutions still did not fix potassium until the drying step, indicating that the effect of drying on potassium fixation was more likely due to the loss of water than the increase in potassium concentration. When clay minerals are heated, they often dehydrate, collapse, and lose portions of their CEC (van Olphen, 1966). Thus, it is likely that the dehydration of the interlayer is the cause of potassium fixation increases associated with drying and heating.

Interestingly, Joffe and Kolodny (1938) demonstrated that heating a sample prior to potassium addition appeared to destroy the fixation capacity of the sample. Preheating temperatures above 550°C seemed to prevent any fixation of potassium by both soil and montmorillonite samples. This is likely due to the collapse of the clay layers during heating, which prevented the entrance of potassium ions when added later. York et al. (1953a) were of the opinion that moist and dry fixations were independent phenomena. However it seems likely that drying simply aids clay minerals that would otherwise not have the interlayer charge attraction for potassium to overcome potassium's energy of hydration. This idea corresponds well to observations that samples that are dried at higher temperatures with added potassium tend to fix more potassium than samples dried at lower temperatures. For example, potassium fixation tends to increase more with oven drying than with air-drying (Barshad and Kishk, 1968; Pratt and Goulben, 1957).

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[3] Page et al. (1967) noted that drying only increased potassium fixation at high potassium application rates. At low application rates however, the difference between moist and dry fixation was negligible.

Additionally, alternately wetting and drying samples with added potassium increases the rate and amount of potassium fixed with the amount fixed increasing with the number of wetting and drying cycles at a decreasing rate. This pattern has been documented with a variety of materials (e.g., Eberl et al., 1986; Eberl et al., 1993; Sucha and Siranova, 1991; Truog and Jones, 1938; Zeng and Brown, 2000; Volk, 1934). While interlayer dehydration is a requirement for potassium fixation, the presence of water still facilitates potassium fixation as it allows for the diffusion of potassium into the interlayer. It is likely then that wetting and drying cycles increase potassium fixation as compared to simply drying by facilitating the diffusion of potassium into more and more fixation sites and then collapsing the clay layers around them with subsequent dehydrations.

It should be noted, however, that the effects of drying and heating on potassium fixation are not always consistent (Mebdi and Ranjba, 1995) as drying and heating can affect more than the presence or absence of interlayer water—e.g., drying and heating can be associated with cationic substitutions in the mineral structure, production of protons, lowering of clay negative charge, warping of phyllosilicate structures, and changed relative energies of hydration of different cations (Inoue, 1983; Luo and Jackson, 1985; Rich, 1968; Sparks and Huang, 1985). Whatever combinations of mechanisms at work however, it seems that drying and increased temperature more often facilitate potassium fixation than inhibit it. Because these drying steps have so many unintended and difficult to account for effects and no analog to any field conditions, drying will not be incorporated in the potassium fixation methodology of this study.

Lattice contraction prevention and potassium fixation suppression

If interlayer collapse is a pre-requisite for potassium fixation, it should follow that if interlayer collapse can be prevented, potassium fixation should be suppressed. This has been demonstrated in a variety of ways, mostly by using or observing organic compounds and hydroxy interlayers as agents of lattice contraction prevention.

A few studies have shown how various organic compounds can prop up interlayer spaces preventing interlayer collapse and potassium fixation (Table 2.2). Page and Baver (1939) found that not only did adding various organic cations decrease potassium fixation in bentonites, the larger the radius of the organic cation, the greater the decrease in fixation. Stucki et al. (2000) observed that various organic compounds could disrupt smectite collapse, and Lee (2007) found that this disruption in layer collapse was associated with a decrease in potassium fixation ability.

Table 2.2 Organic compounds shown to inhibit potassium fixation and/or layer collapse.

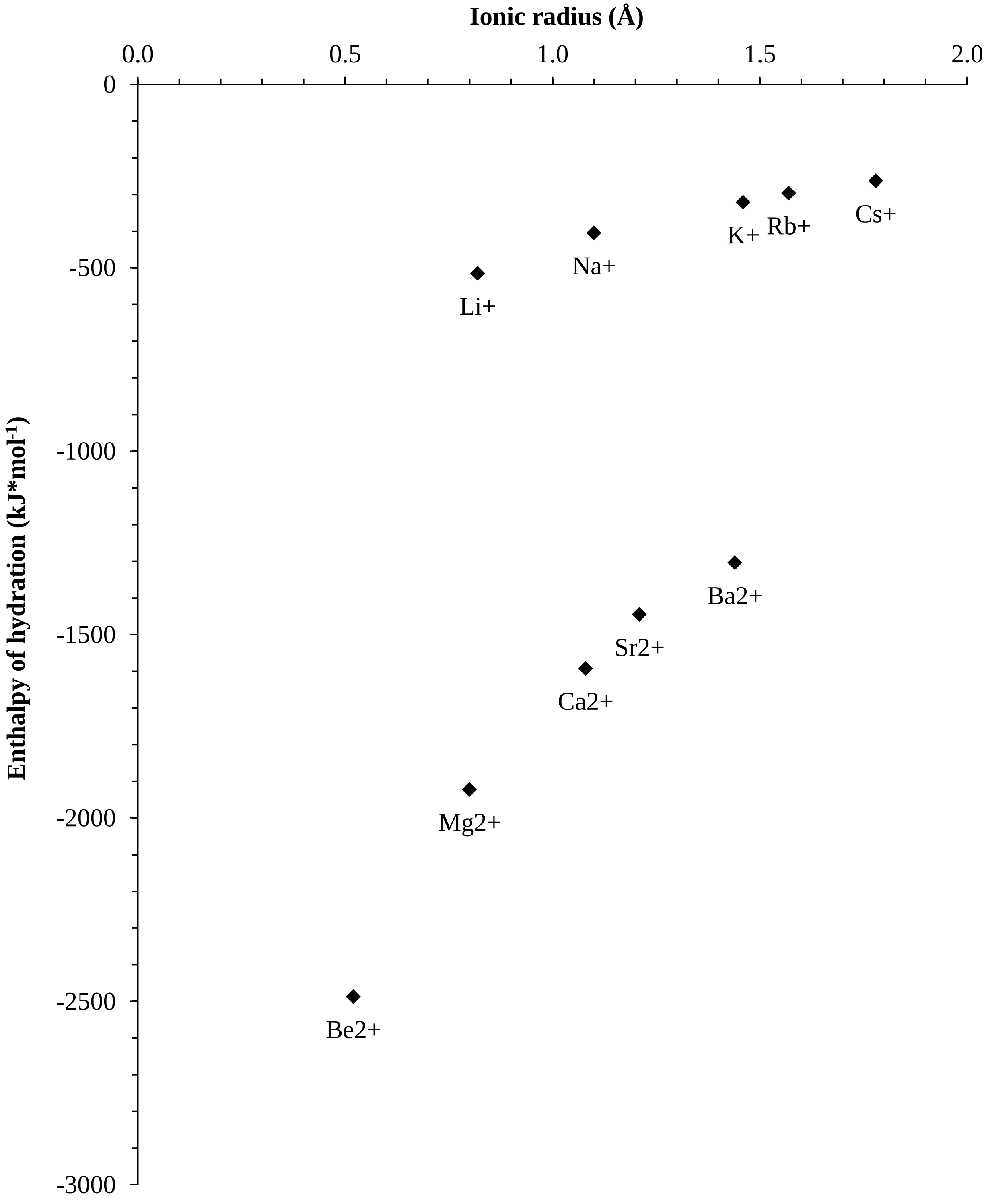
Author(s), Year	Material	Organic compound(s)	
Page and Baver, 1939	Bentonite	$(C_2H_5)_2NH_2^+$	$C_2H_5NH_3^+$
		$(CH_3)_2NH_2^+$	$CH_3NH_3^+$
Stucki et al., 2000	Smectite	Tetramethyl ammonium (TMA)	
		Trimethylphenylammonium (TMPA)	
		Hexadecyltrimethylammonium (HDTMA)	
Lee, 2007	Smectite	Trimethylphenylammonium (TMPA)	

In addition to various organic compounds, the presence of aluminum and iron hydroxides have also been found to prop apart interlayer spaces in such a fashion that prevents the collapse of the interlayer around potassium ions, thereby preventing fixation (e.g. Aide et al., 1999; Kozak and Huang, 1971; Rich, 1968; Rich and Black, 1964; Saha and Inoue, 1998; Simonsson et al., 2009). Frysinger and Thomas (1961) found that adding aluminum chloride to vermiculites hindered cesium fixation which may have been due to aluminum hydroxides forming in the interlayer.

Fixation as a function of ion size and valence

Potassium, ammonium, rubidium, and cesium ions are all fixed in a similar manner (e.g., Barshad, 1954; Coleman et al., 1963a; Martin et al., 1945; Meunier and Velde, 2004; Sucha and Siranova, 1991) whereas other cations such as sodium, calcium, magnesium, barium, and strontium are not fixed to any appreciable extent (e.g., Joffe and Levine, 1939). The similarities between cations that are fixed and their differences from cations that are not fixed give insight into the mechanism behind fixation. Potassium, ammonium, rubidium, and cesium ions are all monovalent, have similar, relatively large ionic radii and similar, relatively weak energies of hydration (Figure 2-5).

Figure 2-5 Enthalpy of hydration versus ionic radius of cations derived from Group I and Group II metals.

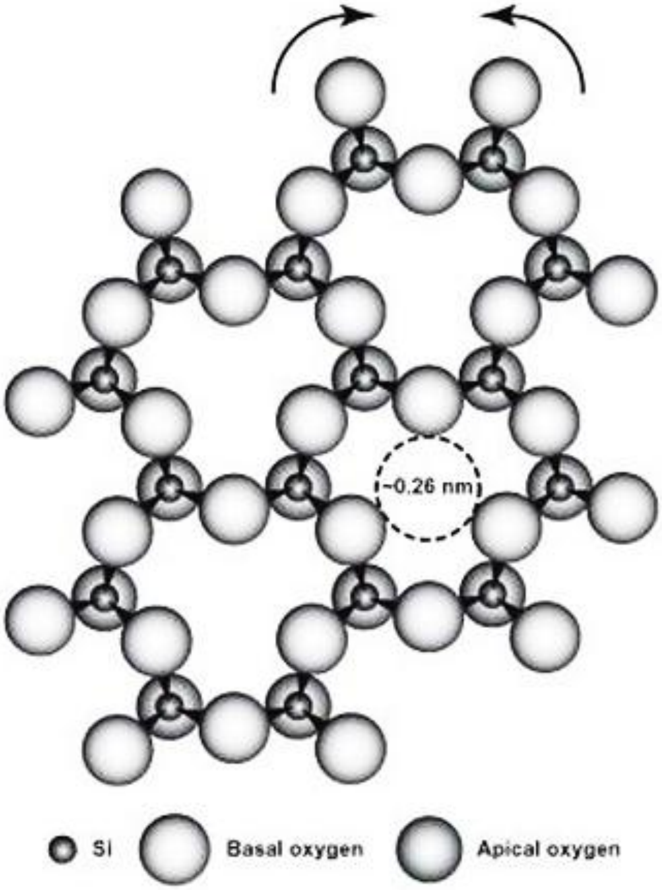


Source data in Appendix A.

Ammonium has a calculated ionic radius of approximately 1.48 Å (Barshad, 1950).

Page and Baver (1939) were the first to point out the correlation between having a larger ionic size and being fixed. A popularly held notion is that the reason certain cations are fixed is because their radii approximate the dimensions of the fixation sites—i.e., the siloxane ditrigonal cavities in tetrahedral sheets (Johnston and Tombácz, 2002). However, that explanation alone fails to explain why, for example, potassium ions which have ionic radii of about 1.46 Å are fixed but barium ions which have ionic radii of about 1.44 Å are not. In order to better explain why some ions can be extensively fixed and other ions can not be, the valence of the ion also needs to be taken into account. While potassium and barium ions have similar ionic radii, potassium ions are monovalent, whereas barium ions are divalent, which has a profound impact on their relative hydration energies. A combination of monovalency and large ionic size contribute to relatively low energies of hydration for potassium, ammonium, rubidium, and cesium. Low hydration energies allow for the dehydration and collapse of the interlayer. In order for cation fixation to occur, the electrostatic attraction between the cation and interlayer surface must exceed the energy of hydration such that water molecules can be excluded from the interlayer space (Hurst and Jordine, 1964; Kittrick, 1966).

Figure 2-6 Schematic of siloxane ditrigonal cavities on planar surface of a phyllosilicate.



From Essington (2004).

Another theory as to why only monovalent ions are fixed is that monovalent cations are able to match the local negative charge of the ditrigonal cavities in the tetrahedral sheet, whereas divalent cations, due to their excess charge, are more likely to be positioned between ditrigonal holes rather than in them (Reichenbach and Rich, 1975).

Potassium fixation: definitions and measurement

Conceptual definition of potassium fixation

The Soil Science Society of America (SSSA) defines potassium fixation as:

> The process of converting exchangeable or water soluble K to that occupying the position of K^+ in the micas. They are counter ions entrapped in the ditrigonal voids in the plane of basal oxygen atoms of some phyllosilicates as a result of contraction of the interlayer space. The fixation may occur spontaneously with some minerals in aqueous suspensions or as a result of heating to remove interlayer water in others. Fixed K^+ ions are exchangeable only after expansion of the interlayer space.

This is but one of many conceptual definitions of potassium fixation. Occasionally potassium fixation has been more broadly defined to include any removal of potassium from solution. These types of potassium fixation can be found summarized in Appendix B. However, for the purposes of this study, potassium fixation will be used to exclusively refer to when potassium is held between collapsed clay layers.

Some authors take more restrictive definitions of potassium fixation than the one put forth by the SSSA. Alexiades and Jackson (1965) maintained that fixation could only occur by vermiculites. Kittrick (1966) asserted that potassium fixation should be associated with irreversible layer contraction. However, since potassium can be held in the interlayer spaces of smectites and illites in a similar manner to vermiculites, and no layer contraction is truly irreversible, these more restrictive definitions will be eschewed.

The SSSA definition of potassium fixation is purely conceptual and does not include a way to measure potassium fixation. In contrast, many potassium fixation definitions in the literature are purely empirical and based on the response of potassium to certain extractions. While the values obtained using these laboratory definitions are used to quantify the amounts of potassium fixed as conceptually defined, little work has been done to actually verify this correspondence. The many different ways of measuring potassium fixation and fixed potassium will be discussed in the next two sections.

Laboratory definitions of potassium fixation

Laboratory determinations of potassium fixation vary widely with almost no two workers in the area using the same exact approach. A summary of methods to measure fixation can be found by Quémener (1979), who notes that while much work has been done measuring fixed potassium, little work has been done toward developing a systematic method of analysis. Since the amount of potassium measured as fixed is highly dependent on the methodology used it is difficult to compare results across studies using different methodologies (Agarwal, 1960b; Cassman et al., 1990; Simonis et al., 1998).

While the conceptual definition for potassium fixation rests strongly on the notion that the potassium be retained between collapsed clay layers, very few studies on potassium fixation use the collapsed portion of this definition as a criterion for potassium fixation. Most potassium fixation studies rely on extractions which are assumed to remove either the non-fixed fraction of potassium or the fixed fraction of potassium. Unfortunately these assumptions are not always accurate. For example, ammonium is the most popularly used replacing ion because it is believed to remove all exchangeable cations but not any fixed cations. However ammonium can both fail to remove all non-fixed potassium and remove portions of fixed potassium, leading to the over and underestimation of potassium fixation, respectively (e.g., Mosser-Ruck et al., 2000).

Similar issues are associated with extractions of fixed potassium. For example, out of four popular methods of extracting fixed potassium—extraction with hydrochloric acid, with aqua regia, with boiling nitric acid, and exchange with hydrogen saturated resin —none are capable of completely extracting fixed potassium, leading to the underestimation of fixed potassium (Andrist-Rangel et al., 2006; Maclean, 1962; McLean and Simon, 1958). Overestimation can also occur when the extraction process is too vigorous (Reitemeier, 1951).

Due to these kinds of inadequacies in procedure, it is probably more appropriate to refer to potassium fixation values as indices of fixation rather than actual measurements of fixation. Though many of the procedures in use may not be able to accurately measure the amount of potassium fixed in a system, they can still be used to compare the relative fixing abilities of different materials.

Most potassium fixation procedures fall into three general categories of approach. The most popular approach is to add a known amount of potassium to a system, allow it to equilibrate, and extract off all the unfixed potassium with a salt solution. The amount of potassium fixed is calculated as the difference between the amount of potassium added and the amount of potassium extracted. However, even within this general approach there is an enormous amount of variation in terms of experimental setups (Table 2.3).

Table 2.3 Summary of some of the variations in experimental parameters for different potassium fixation procedures.

Sample weight	Potassium source	Equilibration time	Extraction solution	Extraction method
50 mg	KCl	< 1 hour	NH_4OAc	Equilibration → Filtering
to	K_2SO_4	to	NH_4Cl	Equilibration → Centrifugation →Decantation
800 g	$KHCO_3$	5 years	MgOAc	Leaching
	KOH		$MgCl_2$	
	K_2HPO_4		HCl	
	Mixed fertilizer		HNO_3	
	Manure			

Though many different sample weights have been used, most of these procedures use somewhere between one and five grams of sample. While many potassium sources have been used, potassium chloride is overwhelmingly the most commonly used. Earlier studies tended to use longer equilibration times—weeks to years, whereas current studies tend to use shorter equilibration times—hours to days. Throughout the history of potassium fixation studies, neutral, normal ammonium acetate has been the preferred extraction solution. The different extraction methods include equilibration of the system with the extraction solution followed by filtering the extract off, equilibration of the system with the extraction solution followed by centrifugation and decantation of the extract—i.e., washing, and leaching the system with the extraction solution.

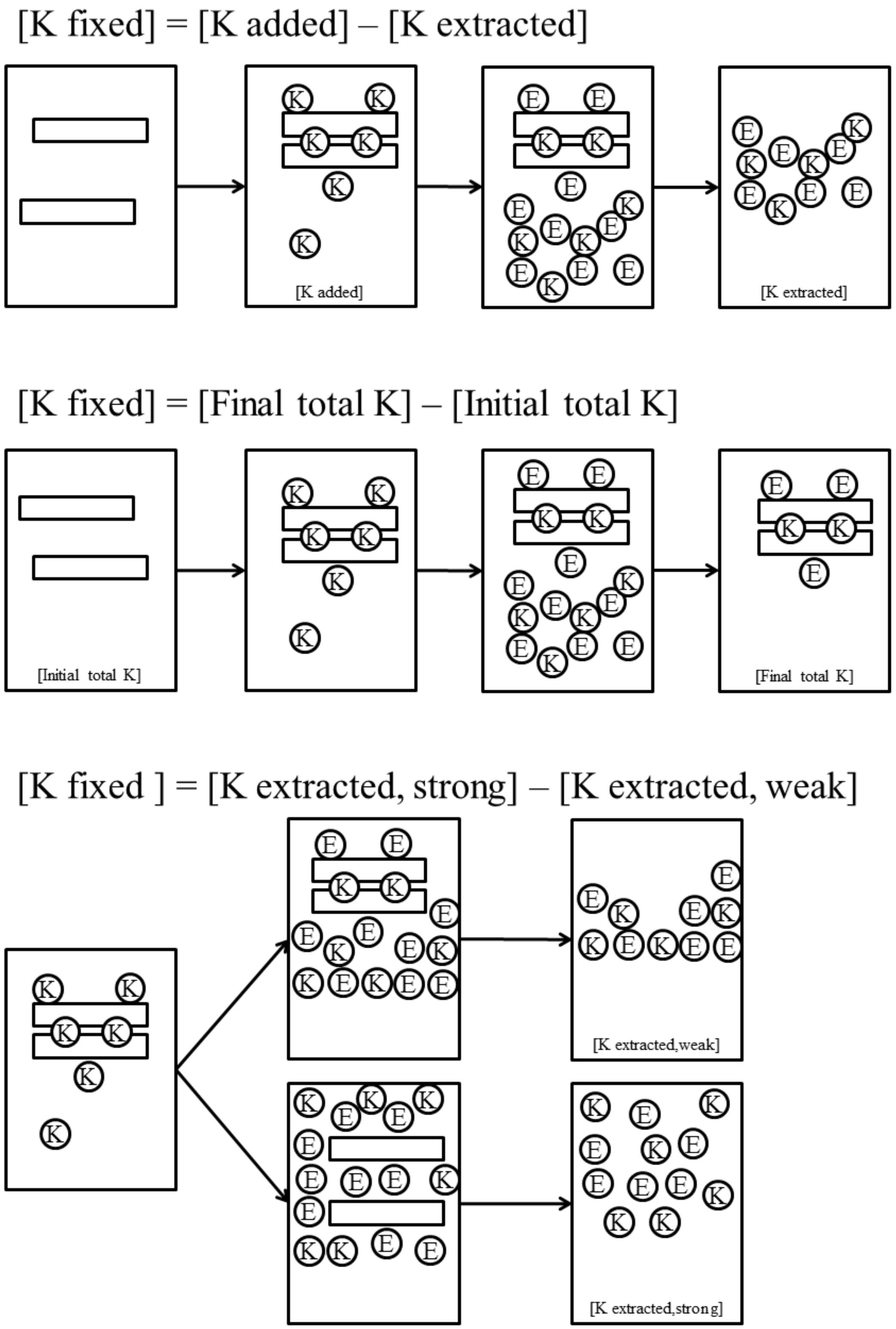
Other variations between procedures include variations in the volumes and concentrations of the potassium and extraction solutions as well as the temperature and pH of the extraction solution, and the duration and number of extractions. Additionally, many procedures include steps in which the soil and solution are agitated—e.g., through manual or mechanical shaking—and/or dried at a particular temperature for a particular duration during or after equilibration with potassium. Despite all of these variations associated with this one general approach to measuring potassium fixation, very little has been done to evaluate the effect of altering these different variables on potassium fixation measurements.

The second general approach is quite similar to the first approach except in what is measured. Much like in the first approach in the second approach, the system is first saturated with potassium and then extracted with a solution intended to remove all solution and exchangeable potassium. The remaining mineral material is then completely acid digested in order to determine the amount of fixed potassium in the system. In order to determine if this potassium was fixed by the fixation treatment or originally part of the mineral, a baseline potassium determination is made on the sample prior to potassium fixation. The amount fixed is then calculated as the difference between the final amount of potassium in the sample and the initial amount of potassium in the sample.

The third general approach was only used by Barshad (1951, 1954) but will be mentioned here for the sake of comprehensiveness. In Barshad’s opinion, the amount fixed could be determined by measuring the amount of potassium that could be extracted from a potassium saturated system by a relatively weak extractant that would only remove exchangeable and solution potassium and the amount of potassium that could be extracted from a potassium saturated system by a relatively strong extractant, which would remove exchangeable, solution, and fixed potassium. The amount fixed is calculated as the difference between these two values. Barshad used ammonium as the weak replacing ion and sodium as the strong replacing ion. When measuring ammonium fixation, potassium would be used as the weak replacing ion. The logic was that other fixable cations could not replace fixed cations whereas strongly hydrated, non-fixable cations—such as sodium—could.

All of these approaches (Figure 2-7) suffer from the same issues: (1) they all depend heavily on the assumption that the extraction processes are removing the correct potassium pools, (2) there is little documented correspondence between the values obtained and the amount of layer collapse, and (3) none of their experimental parameters have been standardized or evaluated for their influence on the potassium fixation values yielded. Nonetheless, values obtained from these methods can be used to help understand potassium fixation via their ability to rank different materials in terms of their potassium fixation capacity and assess the relative effect of different treatments on potassium fixation capacity.

Figure 2-7 Schematic of different approaches used to assess potassium fixation. (K) = potassium ions. (E) = extraction ions.



In addition to measuring the amount of potassium that can be fixed by a material, it is often of interest to measure the amount of fixed potassium already in a material. Much like methods for measuring potassium fixation, the methods for measuring fixed potassium are many. A brief summary of the different approaches used to measuring non-exchangeable potassium can be found in Table 2.4. Similar to the methods for measuring potassium fixation, the extractions associated with measuring fixed potassium can be successive or single and can be done through continuous leaching, decantation after equilibration, or filtering after equilibration. Additionally the concentrations, temperatures and extraction times associated with each of these extraction solutions vary from method to method. Where exhaustive cropping is used as the extraction technique, the different crops used include legumes like clover and alfalfa and grasses such as perennial ryegrass, weeping-lovegrass, oats, and Sudan grass.

Table 2.4 Extraction methods used to determine nonexchangeable levels of potassium.

Acid	Electrolyte	Electric current	Plant	Ion-exchange resin
	NaCl			
HCl	$MgCl_2$	Electrodialysis	Exhaustive cropping	H-saturated
HNO_3	Sodium tetraphenylboron	Electroultrafiltration		Ca-saturated
	Sodium cobaltinitrate			

Adapted from Addiscott and Talibudeen (1969), Martin and Sparks (1985), Quémener (1978).

While most authors agree that exhaustive cropping of soils gives the best and most functional estimate of fixed potassium, they also agree that such experiments are time consuming (e.g. Addiscott and Talibudeen, 1969; Reitemeier, 1951). While laboratory methods for determination of fixed potassium are preferable for their convenience, the values derived from these methods yield little information about the timing of the release of fixed potassium in the field (Johnston, 1988). While the different approaches to measuring fixed potassium yield different results, they nonetheless typically rank samples in the same order in terms of potassium release (Addiscott and Talibudeen, 1969).

Laboratory procedure parameter variations and impact on potassium fixation results

Sample pretreatment

While the effects of standard soil pretreatment procedures are not usually considered in potassium fixation studies, it merits noting that soil grinding, organic matter removal, and initial cation saturation have documented if not entirely clear effects on potassium fixation capacities.

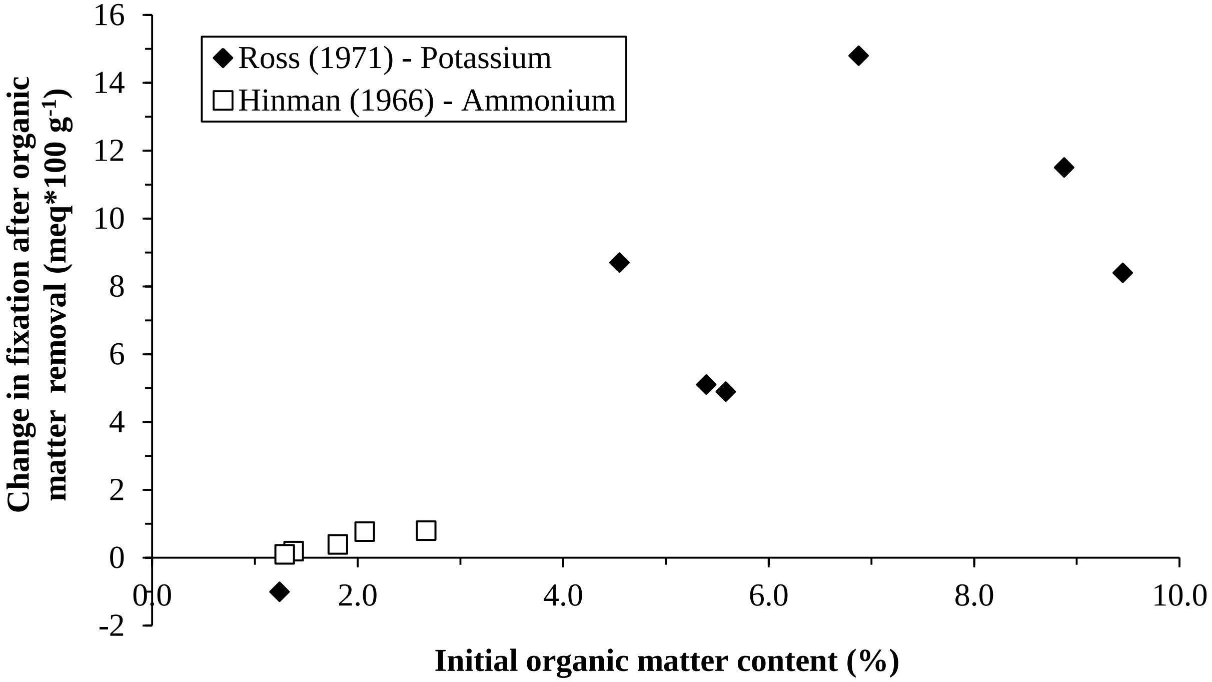
Grinding

Sample grinding has been found to both decrease and increase the amounts of potassium fixed by different samples (e.g., Barshad, 1954; Volk, 1938). It is not entirely clear what causes this though it may be related to increases in potassium release and/or sample oxidation associated with grinding (Barshad, 1954; Jackson and Truog, 1940; Martin et al., 1945).

Organic matter removal

Organic matter removal has been found to both increase and decrease the amounts of potassium fixed by different samples (Hinman, 1966; Martin et al., 1945; Ross, 1971). Collectively, these three studies only represent fourteen distinct determinations of the effect of organic matter removal on potassium fixation. Hinman and Ross found that organic matter removal resulted in an increase in fixation capacity roughly proportional to the amount of organic matter in the sample—i.e., the amount removed (Figure 2-8). Ross hypothesized that organic matter blocks fixation sites and by removing organic matter, fixation sites can be made accessible to potassium. Alternatively, Martin et al. found that organic matter removal resulted in the destruction of soil potassium fixation capacity and attributed this to the acidic conditions promoted by digestion with hydrogen peroxide rather than the direct effect of organic matter removal. Another possible way organic matter could affect potassium fixation is by providing additional sites for potassium exchange which would partially divert potassium from fixation sites. In this scenario, organic matter removal would be expected to increase potassium fixation. Yet another factor to consider is that organic matter removal promotes sample dispersion. A more dispersed sample could conceivably allow for more access to its interlayer fixation sites. It is difficult to disentangle the effect of not having organic matter and the effect of the process of removal. Since organic matter removal is a common sample preparation procedure and the effects of it on potassium fixation results are unclear, further investigation is warranted.

Figure 2-8 Relationship between initial organic matter content and change in fixation capacity after organic matter removal



Prior cation saturation

It is a common procedure to saturate clay samples with a particular cation prior to any analysis, however the type of cation used to saturate the sample can affect the cation fixation capacity of the sample (Inoue, 1983). For example, Tamura and Jacobs (1960) found synthetic sodium saturated fluorophlogopite to be more selective for cesium ions than synthetic potassium saturated fluorophlogopite, which may be due to the potassium saturation already satisfying some of the fixation site in the fluorophlogopite. Generally, samples that are saturated with potassium and other highly fixed cations such as ammonium have a lower fixation capacity than samples saturated with less fixed cations such as magnesium, calcium, and sodium. While this is the general rule, there also appear to be other more subtle effects of initial cation saturation of potassium fixation. For example, Dennis and Ellis (1962) found calcium-saturated vermiculite to fix more potassium than sodium-saturated vermiculite, which may be related to sodium cations having lower hydration energies than calcium cations. Workers in the field of potassium fixation should be conscious that prior cation saturation can significantly affect potassium fixation results.

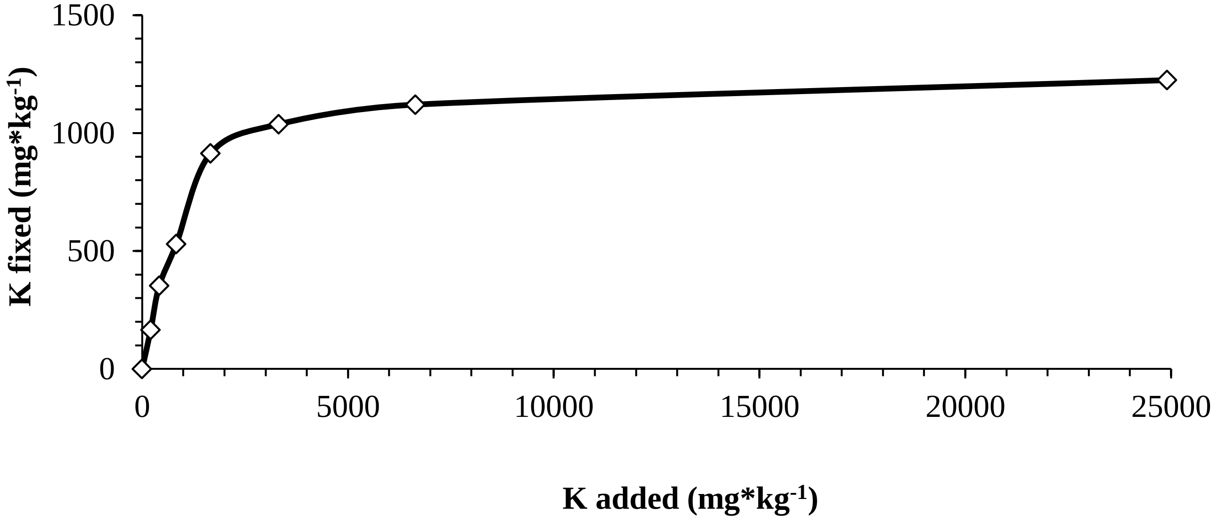
Potassium fixation procedure

There are a number of different ways that procedure methodology can affect potassium fixation results. Highlighted here are the procedural parameters that both vary the most from procedure to procedure and have some of the more established effects on potassium fixation. Not included here is a discussion of the effect of drying or wetting and drying cycle treatments as the effects of these treatments were discussed in an earlier section.

Potassium amount and concentration

Increasing the concentration of the potassium solution or the amount of potassium added to the soil or clay system increases the amount of potassium fixed by the system at a decreasing rate until all the accessible fixation sites are occupied (Figure 2-9). After this saturation point, additional inputs of potassium do not yield additional fixation. This pattern has been documented using a variety of soils, soil clays, and specimen clays and for ammonium and cesium fixation as well as potassium fixation (e.g., Arifin et al., 1973; Attoe, 1948; Barber, 1979; Bouabid et al., 1991; Bower, 1950; Cassman et al., 1990; Chittamart et al., 2010; Inoue, 1983; Jacobs and Tamura, 1960; McLean and Simon, 1958; MacLean, 1962; Martin et al., 1945; Mebdi and Ranjba, 1995; Page et al., 1967; Pratt and Goulben, 1957; Ranjha et al., 1990; Rider et al., 2006; Scott et al., 1957a; Sears, 1930; Simonis et al., 1998; Stanford and Pierre, 1946; Volk, 1934; York et al., 1953a; Wood and DeTurk, 1941).

Figure 2-9 Effect of the amount of potassium added on the amount of potassium fixed.



Adapted from Volk (1934); for a Miami silt loam.

Potassium source

Potassium chloride is the most commonly used source of potassium in potassium fixation studies, which is appropriate as potassium chloride is the most widely used potassium fertilizer in the world (Stewart, 1985). Though potassium chloride is the most popular source of potassium to use in potassium fixation studies other potassium sources have also been used with some variation in result. A summary of various studies evaluating the effect of potassium source on potassium fixation can be found in Table 2.5. While conclusions are generally consistent across studies there are a few discrepancies which can possibly be explained by variations in materials and method between studies.

Table 2.5 Summary of studies evaluating the effect of potassium source on fixation.

Author(s), Year	Observations about the effect of potassium source on potassium fixation.
Hoagland and Martin, 1933	$KCl \approx K_2SO_4$
Wood and DeTurk, 1941	K_2HPO_4 > KCl (application rate = 500 mg K/ kg soil)
Hoover, 1944	KCl > K_2HPO_4 (application rates $\leq$ 400 mg K/ kg soil)[a]
	K_2HPO_4 > KCl (application rates = 2,160 mg K/ kg soil)
Raney and Hoover, 1946	KCl > K_2HPO_4 (application rates = 400 mg K/ kg soil) [b]
Joffe and Levine, 1947b	KAc > KCl
Mortland and Gieseking, 1951	K_2SiO_3 > KOH[c]
Scott et al., 1957a	KCl > KOH
MacLean, 1962	$KCl \approx K_2CO_3$
Heller-Kallai and Eberl, 1997	$K_2CO_3 \approx KHCO_3 > KCl \approx KAc \approx KOx$[d]

[a] One exception out of seven total pairs of data to this pattern.

[b] Re-presents data from Hoover (1944) with the addition of new data.

[c] One exception out of seven total pairs of data to this pattern.

[d] KAc = CH_3CO_2K = potassium acetate. KOx = $K_2O_4C_2$ = potassium oxalate.

Generally, the higher the pH created by the potassium source, the greater the fixation of potassium—e.g., carbonate and bicarbonate forms of potassium which create relatively alkaline environments are more fixed than the chloride form of potassium which does not significantly alter the solution pH. Heller-Kallai and Eberl (1997) proposed this to be due to the deprotonation of structural hydroxyl groups at high pH which would increase layer charge and the need for additional potassium to maintain electroneutrality. Joffe and Levine (1947b) proposed this to be due to the removal of exchangeable hydrogen at high pH and the freeing up of fixation sites for potassium. Regardless of the mechanism, York et al. (1953b) found that potassium added as the chloride was more plant available than potassium added as the carbonate which could have conceivably been due to carbonate ions promoting potassium fixation.

Potassium hydroxide creates highly alkaline environments but appear to lead to less fixation than other forms of potassium (Mortland and Gieseking, 1951; Scott et al., 1957a). Eberl et al. (1993) indicated that wetting and drying cycles with potassium hydroxide destroys smectites. It is possible that where samples were dried with potassium hydroxide, their structures were destroyed this was a more significant process than any increase in fixation that might have been facilitated by the increased pH.

While there appears to be no discernible difference between additions of potassium chloride and potassium sulfate in terms of potassium fixation, there is a marked though inconsistent difference between additions of potassium chloride and potassium phosphate. It appears that high potassium application rates tend to favor more fixation by the phosphate form of potassium whereas lower application rates tend to favor more fixation by the chloride form of potassium. It could be at high concentrations of phosphate, aluminum is precipitated out as aluminum phosphate, which prevents it from competing with potassium for fixation sites (Stanford, 1947). It could also be that at high concentrations of phosphate, the precipitation of potassium bearing phosphates is promoted. Interestingly, Wrenshall and Marcello (1940) found that adding monocalcium phosphate along with potassium chloride to agricultural fields rendered the potassium less available to plants as compared to when potassium chloride was added alone. This may have been due to phosphate ions either precipitating potassium ions out directly or precipitating out cations competing with potassium for fixation sites, thereby facilitating potassium fixation.

Equilibrium time

The amount of potassium fixed by a system increases with time at a decreasing rate until a saturation point is reached (e.g., DeTurk et al., 1943; Hanway and Scott, 1957; Hoover, 1944; Inoue, 1983; Martin et al., 1945; Stanford and Pierre, 1946; Whitney, 1990; Wood and DeTurk, 1941; York et al., 1953a). The time it takes for soil systems to reach equilibrium with added potassium ranges widely and appears to vary by potassium application rate, sample type, and fixation treatment. Wetting and drying cycles hasten fixation whereas increased applications of potassium prolong the equilibrium time. Montmorillonites have been documented to reach equilibrium significantly quicker than vermiculites and micas, which may be a function of the relative accessibility of the interlayer—the interlayer of montmorillonites being more expansive and accessible than interlayers of vermiculites and micas (Sparks and Huang, 1985).

Fixed potassium ions become increasingly difficult to replace the older the system is allowed to become. Thus, not only does increasing the equilibrium time increase the amount of potassium fixed by a system, but it also increases the tenacity with which the potassium is fixed. Wood and DeTurk (1941) partitioned the fixed potassium pool into acid soluble and acid insoluble groupings and found that over time, more potassium transitioned from the acid soluble pool to the acid insoluble pool. This could possibly be reflective of the movement of potassium from peripheral interlayer sites to deep interlayer sites (Reitemeier, 1951).

Extraction procedure

In most efforts to measure potassium fixation, it is desirable to be able to selectively remove exchangeable and fixed potassium. However, there is no universally established method to measure either of these pools and the approaches that are used not only vary by general method but the extraction solutions used vary by type, pH, concentration, volume, temperature, and extraction time. Each combination of these factors extracts a different amount of potassium which leads to a different amount of potassium determined as fixed. The effect of each of these parameters will be discussed briefly here.

Extraction method

There are multiple methods that can be used to extract potassium off of a sample. In some cases, the sample is shaken with an extraction solution, centrifuged, and the supernatant extract is decanted. A variant of this is to withdraw an aliquot from the supernatant for analysis. In other cases the sample is shaken with an extraction solution and then the sample is filtered out of the extraction solution. Another method yet is to leach the sample with the extraction solution. A variant of this approach is to leach the sample multiple times. Multiple extractions always recover more potassium than single extractions (e.g., Pratt et al., 1956; Raney and Hoover, 1946; Shaw and MacIntire, 1936). The relative efficacy of the different methods at replacing potassium has not been investigated.

Extraction solution concentration

All other factors being equal, the more concentrated the extraction solution, the more potassium will be released into solution (e.g., Dyer, 1984; Frear and Erb, 1918; Levine and Joffe, 1947b; Mortland, 1958; Page and Baver, 1939).

Extraction solution volume

The greater the volume of extraction solution used, the more potassium will be released into solution (e.g., Dyer, 1894; Page et al., 1967). While it has become fairly standard to use a soil to solution ratio of one to ten, the soil to solution ratio also has the potential to affect the amount of potassium extracted. The point seems potentially trite, as it has long been appreciated that the pools of potassium are in equilibrium with each other and to dilute the concentration of potassium in solution is to cause more potassium to be brought into solution. However, this point is often overlooked when developing and modifying methods with which to measure potassium fixation.

Extraction solution temperature

The temperature of the extraction solution affects the release of potassium into solution. Typically, the greater the temperature, the greater the potassium release (e.g., Frear and Erb, 1918; Barshad, 1951; Mortland, 1958).

Extraction time

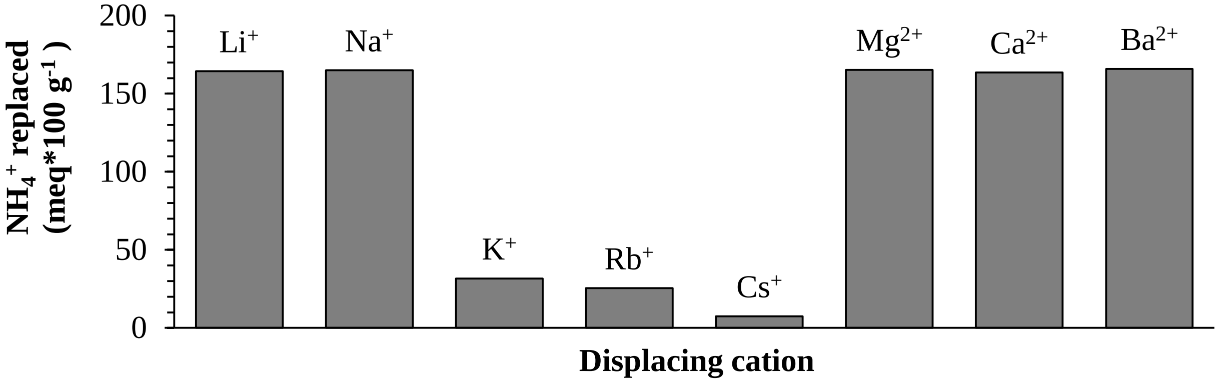
Extraction time carries different meanings with different extraction methods, but generally speaking it refers to the duration with which the extracting solution has time to interact with the system—whether that is equilibrium, leaching time or electrodialysis time. The greater the extraction time, the greater the potassium release, with the rate of release decreasing over time (e.g., Agarwal, 1960a; Dyer, 1984; Frear and Erb, 1918; Barshad, 1951, 1954; Jalali and

Zarabi, 2006; Mortland, 1958; Mortland and Ellis, 1959; Munn et al., 1976; Ross, 1971; Smith et al., 1968; Steffens and Sparks, 1997).

Extraction solution type

There are many different types of extraction solutions used with the intention to remove exchangeable potassium. Most popular amongst them are various chlorides (e.g., NH_4Cl, NaCl, $MgCl_2$, $CaCl_2$, $BaCl_2$), acetates (e.g., NH_4OAc, NaOAc, MgOAc), and acids (e.g. HNO_3, HCl). Interestingly, NaCl, $MgCl_2$, HNO_3, and HCl solutions are also used with the intention of removing fixed potassium which is a testament the varying efficacies with which different solutions remove potassium. Thus the type of extraction solution used to remove potassium from the soil profoundly affects calculated potassium fixation results (Alexiades and Jackson, 1965; Bray, 1937; Demumbrum and Hoover, 1958; Hanway and Scott, 1959; Martin et al., 1945; Rich, 1964). Extraction solution type has a profound effect on the amount of potassium removed for a variety of reasons. The main reason however is that different cations are able to remove fixed cations with different amounts of efficacy (Figure 2-10).

Figure 2-10 Amounts of ammonium replaced from ammonium saturated vermiculites by different cations in the hydroxide form.



Source data from Barshad (1948).

Typically, ions that are extensively fixed—i.e., potassium, ammonium, rubidium, cesium—are much less effective at removing fixed cations than the ions that have relatively high energies of hydration—e.g., sodium, magnesium, calcium, and barium ions (Barshad, 1948, 1951, 1954). It is suspected that this has to do with the relative inability of the aforementioned ions to hydrate and open interlayer spaces.

While the ability of a particular cation to replace a fixed cation is the main determinant for the efficacy of replacing solution, there are also a host of other smaller, less understood factors controlling the efficacy of the replacing solution. For example, it may be that certain extraction solutions are not universally stronger than others, but rather an interaction between the material being evaluated and the extraction solution determines the efficacy of the replacement. For example, typically magnesium ions are a better than ammonium ions at replacing potassium ions. However, in some soils ammonium acetate is a more effective replacer than magnesium acetate (Rich and Black, 1964). Similarly, there appears to be an interaction between the amount of potassium added and the extraction solution type in determining the relative efficacy of the extraction solution (Martin et al., 1945). Yet another point to be considered is the flocculating ability of the replacing cation. There are extraction solutions that at certain concentrations also are flocculants. The flocculation of clays has the potential to hinder the free exposure of the surfaces of clay particles and thus access of the exchanger to the exchangeable cations.

Extraction solution pH

Many workers have demonstrated that potassium release is increased by lowering solution pH. For example, York et al. (1953) found that using an extracting solution of ammonium acetate with a pH of 4.8 lead to greater potassium recovery than using the same extracting solution at a pH of 7.0. In fact, the more acidic extracting solution was able to entirely recover all added potassium. Rich and Black (1964) found similar results, concluding that small hydronium ions in acid systems were more effective at exchanging with potassium than large hydrated basic cations. Thus, magnesium chloride was found to be a more effective exchanger of potassium than magnesium acetate because magnesium chloride allowed hydronium ions in acid systems to replace potassium as compared to magnesium acetate which made the solution neutral. Not all replacing solutions are equally responsive to pH changes though as there appears to be an interaction between pH and replacing cation type on the replacement efficacy of the cation (Rich, 1964). For example, ammonium extractions appear to be minimally affected by pH compared to the extractions with lithium and magnesium (Figure 2-11).

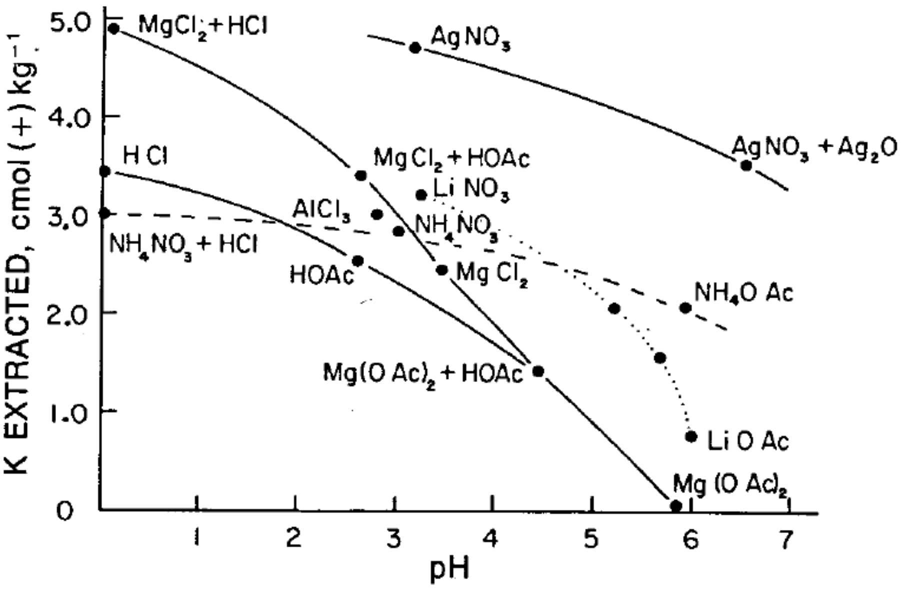


Figure 2-11 Potassium extracted from soil as affected by pH and extracting solution. All solutions are normal with respect to the component indicated.

From Rich (1964).

A variety of studies have demonstrated that increasing the pH of a soil or clay system tends to increase subsequent fixation whereas decreasing the pH of a soil or clay system tends to decrease subsequent fixation. These manipulations in pH have been accomplished by pretreatment with calcium carbonate, calcium hydroxide, barium hydroxide; sodium hydroxide, sodium carbonate, hydrochloric acid, and acetic acid, and have been applied not only to soils but reference samples of montmorillonite, vermiculite, and illite (e.g., Barshad, 1954; Harris, 1937; Inoue, 1983; Joffe and Levine, 1947; MacLean, 1962; Mebdi and Ranjba, 1995; Stanford, 1947; Stanford and Pierre, 1946; Volk, 1934; York et al., 1953a).

These observations about pH and potassium fixation are not confined to the laboratory. There have been studies demonstrating that calcareous soils tend to fix more than acidic soils. Evaluating soils from different corn fields in Iowa, Allaway (1939) found that acid soils fixed markedly less potassium than calcareous soils. Ten acid soils sampled fixed an average of 6.5 mg K kg^{-1} soil whereas twenty-two calcareous soils sampled fixed an average of 76.5 mg K kg^{-1} soil. Simonis et al. (1998) noticed that not only did the amounts of potassium fixed by soils derived from basic rocks typically exceed that fixed by soils derived from acidic rocks, but of the calcareous soils evaluated there was a significant correlation between calcium carbonate content and the amount of potassium fixed. While these correlations do not demonstrate causation, they are consistent with what might be expected based on the results of the aforementioned laboratory experiments.

There are two main theories as to why fixation should be greater at higher pH and lesser at lower pH. The first one is that hydronium ions compete with potassium ions for fixation sites in acidic environments. The second theory is that soil acidity promotes the protonation of oxygen atoms shared by tetrahedral and octahedral sheets which weakens electrostatic bonds with interlayer potassium ions through decreasing layer charge and/or through changing the geometry of octahedral hydroxyl groups (de Villiers and Jackson, 1967; Rich, 1964; Rich, 1968; Stanford, 1947; Thompson and Ukrainczyk, 2002).

Effect of clay mineralogy on potassium fixation and release

Empirical observations

Different soils fix widely different amounts of potassium (e.g., Hoagland and Martin, 1933; Volk, 1934). Volk noticed early on that potassium fixation tended to increase with the clay content of a soil[4]. Since then, many other workers have confirmed this early observation and as a consequence most potassium fixation studies center on potassium fixation by clays (e.g., Barber, 1979; MacLean, 1962; Mebdi and Ranjba, 1995; Ranjha et al., 1990).

The general rule of potassium fixation increasing with clay content does not apply when the clay is predominately kaolinitic. This is because relationship between clay content and potassium fixation has less to do with particle size and more to do with particle mineralogy. It just happens that the potassium fixing minerals tend to be clay-sized. Kaolinite particles, though clay-sized, have inaccessible interlayers due to hydrogen bonding which prevent them from fixing potassium. Additionally, coarser than clay-sized particles can fix substantial amounts of potassium if they are composed of potassium fixing minerals. Considerable potassium and

---

[4] Potassium and ammonium fixation generally tends to increase with depth, i.e., subsoils tend to fix more potassium than surface soils (e.g., Aide et al., 1999; Hanway and Scott, 1957; Hinman, 1966; Joffe and Kolodny, 1937; Pratt and Goulben, 1957; Rühlicke, 1985; Shaviv et al., 1985) with few exceptions (Joffe and Kolodny, 1937). While these observations are frequently cited as added evidence that potassium fixation increases with clay content which tends to increase with depth, there could also be other factors also at work. Shaviv et al. (1985) suggested that this may be due to the addition of inputs of potassium to the surface, which would partially saturate the fixation capacity of the soil surface. This external input of potassium may be through external fertilization or internal cycling—i.e., plants drawing potassium to the surface. Another possibility is the enrichment of organic matter in the surface soil could be impeding potassium fixation.

ammonium fixation has been documented in silt-sized and even very fine sand-sized vermiculite and hydrobiotite (Murashkina et al., 2007; Rider et al., 2006). The general prevailing logic is that the greater proportions of potassium fixing material in the soil, the stronger the potassium fixation (Rich, 1968).

While it is agreed that potassium fixation by soils is largely related to both clay content and mineralogy (e.g., Shaviv, 1985; Simonis et al., 1998; Zhang et al., 2009), it is not entirely agreed upon what the main potassium fixing materials are in the soil. Vermiculite is the often cited as the principal agent of potassium fixation (e.g., Brown, 1953; Rich, 1968) though micas have also been mentioned (e.g., Barshad, 1951; Barshad, 1954; Ranjha et al., 1990). While there is some controversy as to whether vermiculites or micaceous minerals fix more potassium, all sources agree that vermiculitic, micaceous, and smectitic minerals all fix more potassium than kaolinite which should fix no potassium (e.g., Martin and Sparks, 1985; Williams et al., 2010; Wolf, 1999).

When vermiculite was assumed to be the only mineral capable of cation fixation, the amount of potassium that could be fixed by a soil clay was used as a way to calculate the amount of vermiculite in the sample (e.g., Alexiades and Jackson, 1965; Coffman and Fanning, 1974). Murashkina et al. (2007) demonstrated the inadequacies of this procedure by using rubidium fixation values to calculate vermiculite contents. This technique leads to the overestimation of the amount of vermiculite because smectites with large amounts of tetrahedrally-derived charge also fixed substantial amounts of rubidium.

Table 2.6 summarizes fixation capacity rankings of various clay minerals as determined by different studies, and shows that there are some discrepancies between studies in terms of the ways that different clay mineral types are ranked in terms of their fixation capacity. The causes for these discrepancies are likely many-fold and include the fact that relative fixation capacity rankings appear to be dependent on pH, drying treatment, potassium concentration, and charge (e.g., Richards and McLean, 1963; Stanford, 1947; Sawhney, 1970).

Clay minerals are classified mainly by two criteria—layer type and octahedral sheet type. Clay minerals can have 1:1, 2:1, or 2:1:1 layers, and each of these kinds of layers can have either di- or trioctahedral octahedral sheets. The 2:1 mineral group is further classified on the basis of interlayer charge (Meunier, 2005). The effect of each of these classification criteria on potassium fixation will be discussed in the next three sections.

Table 2.6 Summary of fixation capacity rankings of various clay minerals as determined by different studies.

Author (s), Year	Fixation capacity ranking
Truog and Jones, 1938	bentonite > mica > kaolinite = 0
Volk, 1938	bentonite > kaolinite ≠ 0 some micas > kaolinite, other micas < kaolinite.
Fine et al., 1940	bentonite > illite
Hoover, 1944 / Raney and Hoover, 1946	montmorillonitic soil > kaolinitic soil
Stanford, 1947	montmorillonite > illite (pH < 6) illite > montmorillonite (pH > 6)
Mortland and Gieseking, 1951	illite > montmorillonite > kaolinite ≈ 0
Wear and White, 1951	montmorillonite > illite
Barshad, 1954 [a]	vermiculite > smectite
Demumbrum and Hoover, 1958	vermiculite > illite = 0
Tamura and Jacobs, 1960 [b]	illite > montmorillonite > biotite – vermiculite > kaolinite
Richards and McLean, 1963	vermiculite > illite > bentonites > kaolinite ≈ 0 (dried) bentonites > illite > vermiculite > kaolinite ≈ 0 (kept moist)
Acquaye et al., 1967	vermiculitic soil > kaolinitic soil
Barber 1979	montmorillonitic soil > kaolinitic soil
Rühlicke, 1985	vermiculitic soils > smectitic soils
Chen et al., 1987	nontronite > montmorillonite
Douglas, 1989	vermiculite, beidellite > montmorilloite
Bouabid et al., 1991	smectitic, vermiculitic soil clays > mixed mineralogy soil clays
Saha and Inoue, 1998	vermiculite > montmorillonite
Scherer and Zhang, 2002	vermiculite > illite

[a] Rankings determined for ammonium fixation.

[b] Rankings determined for cesium fixation.

Layer type

While there may be some disagreement about which 2:1 layer silicates fix more potassium, most agree that 2:1 layer silicates, rather than 1:1 and 2:1:1 layer silicates are the fixers of potassium in soils. While there has been some limited documentation of kaolinite fixing potassium (e.g., Volk, 1934), these are most likely situations where the extraction of exchangeable potassium was insufficiently vigorous and thus what was truly exchangeable potassium got considered fixed potassium and/or situations where it was difficult to precisely measure potassium, and small inaccuracies extrapolated out into significant amounts of fixation.

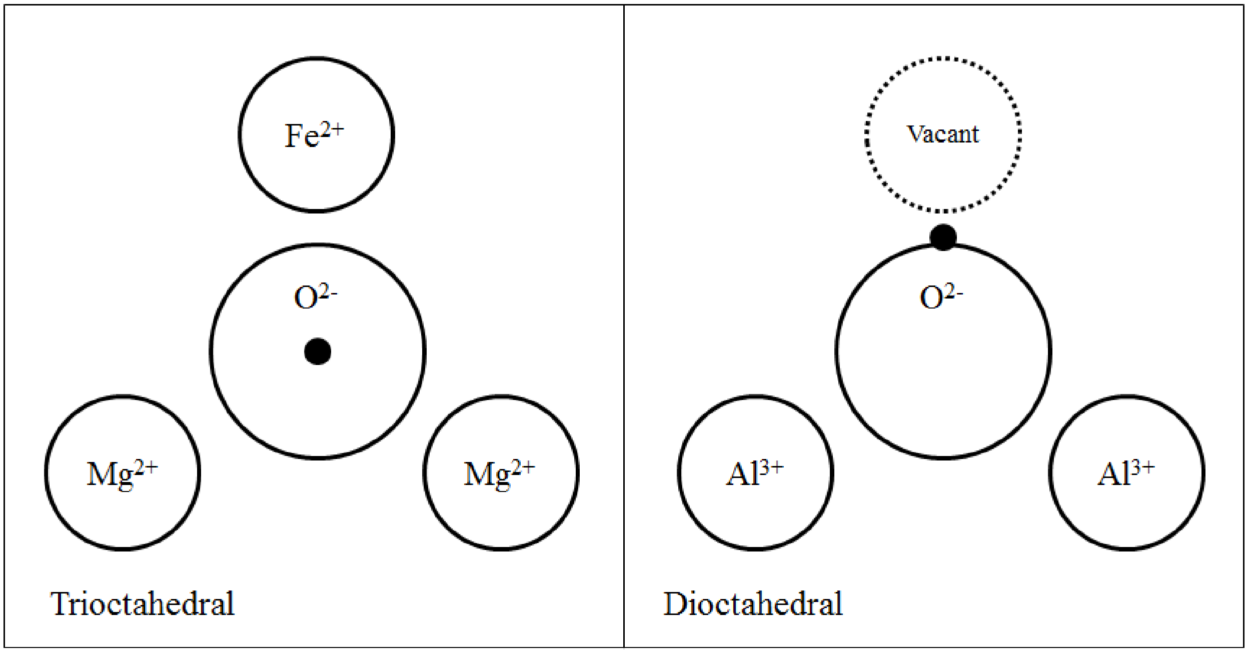
The theoretical justification for disbelieving fixation by kaolinite and other 1:1 layer silicates is that the interlayer of these minerals should be inaccessible due to hydrogen bonding between the layers. For a similar reason, 2:1:1 layer silicates ought not to fix potassium because their interlayers are occupied by hydroxide layers which prevent both interlayer access and collapse. The ability of potassium ions to access the interlayer and the ability of the interlayer to collapse are both prerequisites for potassium fixation and 2:1 layer silicates are unique in their satisfaction of these requirements.

Octahedral sheet type

In trioctahedral minerals, the hydroxyl dipole is perpendicular to the octahedral sheet whereas in dioctahedral minerals, the hydroxyl dipole is oriented on more of an incline (Figure 2-12). Sawhney (1972) suggested that it may be due to this geometry that potassium ions are more tightly held in dioctahedral minerals as compared to trioctahedral minerals. The inclined hydroxyl orientation in dioctahedral minerals shortens the octahedral layer allowing potassium ions to be closer to octahedral oxygen atoms, thereby creating a stronger electrostatic attraction between the potassium ions and adjacent oxygen atoms.

Not only does the dioctahedral versus trioctahedral nature of the clay affect the orientation of the hydroxyls, so does the type of cation occupying the octahedral sites. Different octahedral occupancies give way to different levels of potassium stability do to their effect on hydroxyl orientations. Additionally, the substitution of fluorine ions for hydroxyl ions has been demonstrated to increase the strength with which potassium is held because there is no longer the repulsive force of hydrogen being exerted on interlayer potassium ions (Sparks and Huang, 1985).

Figure 2-12 Effect of octahedral sheet type of micas on hydroxyl orientation. Planar view. (●) = hydrogen ion.



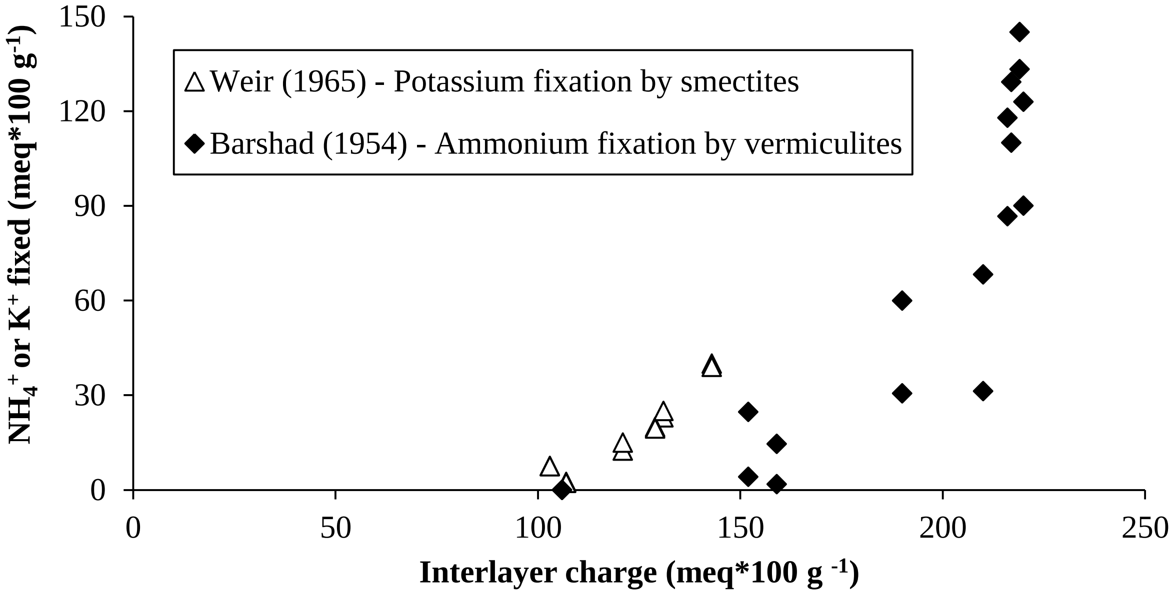
Adapted from Sparks and Huang (1985).

Layer charge

Cation fixation and release is heavily influenced by interlayer charge which affects the electrostatic attraction of the interlayer for the cations (Rich, 1968). Other factors being equal, greater layer charge is often correlated with greater fixation (e.g., Barshad, 1954; Bouabid et al., 1991; Inoue, 1983; Lee, 2007; Weir, 1965).

Using vermiculites with a range of interlayer charges, Barshad (1954) found that vermiculites with greater interlayer charge fixed more ammonium than vermiculites with less interlayer charge. Similarly, using montmorillonites with a wide range of charges and charge locations, Weir (1965) found that montmorillonites with greater layer charge fixed more potassium than montmorillonites with less layer charge and that montmorillonites with low layer charge fixed negligible amounts of potassium. Additionally, despite there being differences in methodology and the difference of ammonium versus potassium fixation, overlaying the datasets of Barshad and Weir, a more holistic view of fixation can be observed (Figure 2-13). While generally fixation increases with layer charge, the pattern is not perfect and this is likely do to the effects of other factors on cation fixation.

Figure 2-13 Fixation of ammonium and potassium by variably pre-treated vermiculites and smectites of varying purity as affected by total interlayer charge of crystal lattice.



Using a single smectite and manipulating its layer charge via structural iron reduction, Lee (2007) found that the smectite samples with greater layer charge fixed greater amounts of potassium. Using a single montmorillonite and manipulating its layer charge via heating, Inoue (1983) found that the montmorillonite samples with greater layer charge also fixed greater amounts of potassium. Eberl (1986) found that subjecting different sodium-saturated smectites to alternate wetting and drying in the presence of potassium bearing minerals such as potassium feldspars and micas not only lead to illitization of the smectites, but more illite was formed—i.e., more potassium was fixed—with smectites of greater negative layer charge.

If potassium fixation is related to layer charge it might follow that it is also related to CEC, which is a direct function of layer charge. Using forty-four soil clays, three montmorillonites, and one vermiculite, Bouabid et al., (1991) found potassium fixation capacity to be well correlated with total CEC ($r^2 > 0.73$). However, Chittamart et al. (2010) and Rider et al. (2006) determined there to be a poor relationship between CEC and cation fixation capacity. This inconsistency however, may be rooted in the fact that both the latter studies used soil clay and bulk soil samples which may have introduced a number of confounding factors such as the CEC of minerals that do not fix potassium

Often charge location is considered as important of a factor as charge magnitude in controlling fixation and release. Negative charge originating from the tetrahedral sheet retains cations more strongly than equivalent negative charge originating from the octahedral sheet due to the proximity of the charges to the interlayer surface (Reid-Soukup and Ulery, 2002). This has been somewhat substantiated by Bouabid et al., (1991), who found potassium fixation capacity to be well correlated with tetrahedral CEC ($r^2 > 0.52$) but poorly correlated with octahedral CEC ($r^2 < 0.13$). Total charge, however, was still a better predictor than either tetrahedral or octahedral CEC.

Effects of structural iron oxidation state on potassium fixation and release

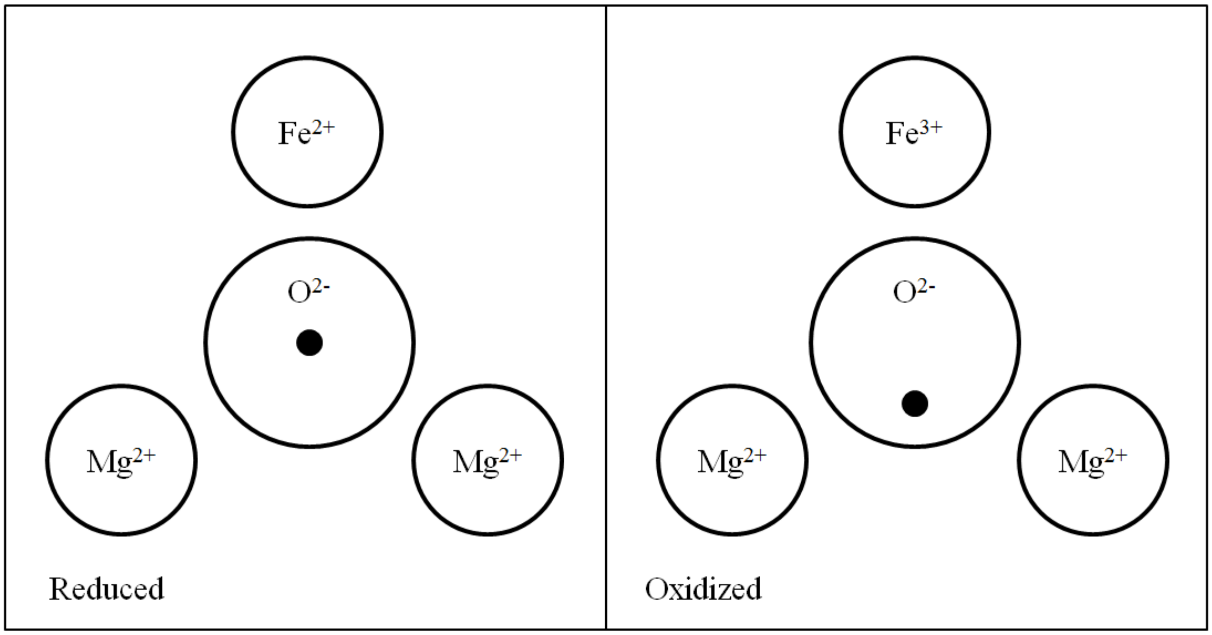
Many physical and chemical properties of phyllosilicates are affected by the redox state of their structural iron. The redox state of structural iron directly affects phyllosilicate layer charge, CEC, swelling pressure, specific surface area, and structural geometry. Through its effect on these characteristics, iron redox state can also profoundly influence potassium fixation and release.

Most of the work done on the effect of the oxidation state of structural iron and layer charge has been done using smectites. Results from both laboratory and field experiments using both soil clays and reference clays have indicated that reduction of octahedral ferric iron in smectites increases negative layer charge and CEC (e.g., Favre et al., 2002; Stucki and Kostka, 2006; Stucki et al., 1984b). At slight levels of iron reduction, increases in CEC are equivalent to the amount of iron reduced. At more intense levels of reduction, however, CEC ceases to increase and begins to decrease. This latter phenomenon has been attributed to the dehydroxylation and dissolution of the smectites at high levels of reduction (e.g., Drits and Manceau, 2000; Heller-Kalai, 1997; Lee, 2007; Neumann et al., 2010; Ribeiro et al., 2009; Stucki and Roth, 1977). Reduction facilitated increases in CEC can be somewhat reversed by re-oxidation of structural iron (e.g., Favre et al., 2002; Favre et al., 2004; Favre et al., 2006ab).

Structural iron reduction in smectites and corresponding increases in charge density have been related to decreases in swelling pressure and specific surface area and larger, more compact flocs (e.g., Gates et al., 1993; Kim et al., 2005; Kim et al., 2003; Komadel et al., 2005; Kostka et al., 1999b; Lear and Stucki, 1989; Shen et al., 1992; Stucki and Kostka, 2006; Stucki et al., 2000). This is due to increased coulombic attraction between interlayer surfaces and cations facilitating interlayer collapse. Dong et al. (2003) used electron microscope images to show that unreduced smectite had layer spacings of about 15 Å while reduced smectite had layer spacings of about 11 Å. With these kinds of changes observed in reduced smectitic materials, it should follow that smectite reduction also be associated with an increase in cation fixation and indeed it is (Chen et al., 1987; Khaled and Stucki, 1991; Lee, 2007; Shen and Stucki, 1994). Additionally, Chen et al. (1987) found that increases in fixation were directly related to changes in ferrous iron content—i.e., the greater the reduction the greater the increase in fixation.

The work done the oxidation state of structural iron and potassium fixation in non-smectitic minerals has been much less extensive and much less clear. Barshad and Kishk (1968, 1970) found that the oxidation of vermiculites and biotites increased their potassium fixation which is contrary to what might be expected if oxidation resulted in a decrease in layer charge. However, Barshad and Kishk found that layer charge was not significantly altered by oxidation—indicating perhaps compensatory deprotonation of hydroxyl groups with oxidation. They proposed that the increased retention associated with oxidation was due to the tilting of the octahedral hydroxyl dipole from the perpendicular to the inclined, increasing the attractive forces between interlayer potassium ions and adjacent oxygen ions (Figure 2-14).

Figure 2-14 Effect of octahedral iron oxidation state of micas on hydroxyl orientation. Planar view. (●) = hydrogen ion.



Adapted from Sparks and Huang (1985).

In contrast to the findings of Barshad and Kishk, Scherer and Zhang (2002), using soils samples as well as a vermiculite and illite specimens, found that ammonium fixation increased with octahedral iron reduction and additionally, the greater the reduction, the greater the increase in fixation—though this relationship was not stoichiometric, much like the relationship between reduction and layer charge.

The methods used by Barshad and Kishk were quite different than those used by Scherer and Kishk. Variance in method no doubt gave rise to their differences in conclusion. While Barshad and Kishk oxidized their samples using a highly alkaline solution of sodium hypochlorite, Scherer and Zhang reduced their samples using a buffered solution of sodium dithionite. While Barshad and Kishk noticed no effect of oxidation on layer charge, Scherer and Zhang found that reduction of their samples increased negative layer charge. While it would be expected that iron oxidation would be associated with a decrease in layer charge, the highly alkaline conditions of the sodium hypochlorite solution most likely promoted the deprotonation of structural hydroxyls on the layer silicate, compensating for the loss in electrons.

Since potassium fixation is in many ways analogous to mica weathering, it might follow that since mica weathering is typically associated with structural iron oxidation, interlayer expansion, and loss of potassium, potassium fixation should be associated with potassium entrapment between collapsed layers and structural iron reduction (Mortland and Lawton, 1961; Scott and Amonette, 1988). While Barshad and Kishk demonstrated that the oxidation of biotites increases the difficulty with which interlayer potassium is removed in highly alkaline conditions, in more natural environments the oxidation of iron in micas is more associated with potassium loss (e.g., Craw, 1981).

Ultimately oxidation of structural iron in micas can either stabilize or destabilize interlayer potassium depending on both the pH environment and on whether the oxidation of structural iron leads to the ejection of the iron atoms or not from the octahedral sheet (Thompson and Ukraniczyk, 2002). When the oxidation of octahedral iron in micas leads to iron ejection, the hydroxyl ions to orient toward the empty octahedral site, allowing the potassium ions to nest closer into the ditrigonal cavity and subsequently be held more tenaciously (Juo and White, 1969; Barshad and Kishk, 1970; Farmer et al., 1971).

A summary of all the studies on the topic of structural iron redox state in phyllosilicates on potassium fixation can be found in Table 2.7. Most of the work has been done on smectites and through the manipulation of the oxidation state of octahedral iron. The study presented here in this thesis hopes to expand on this work by including kaolinite, illite, vermiculite, and two soil clays in addition to two smectites and by manipulation the oxidation state of tetrahedral iron as well as octahedral iron.

Table 2.7 Summary of materials used by various authors evaluating the effect of oxidizing or reducing structural iron in phyllosilicates on potassium fixation.

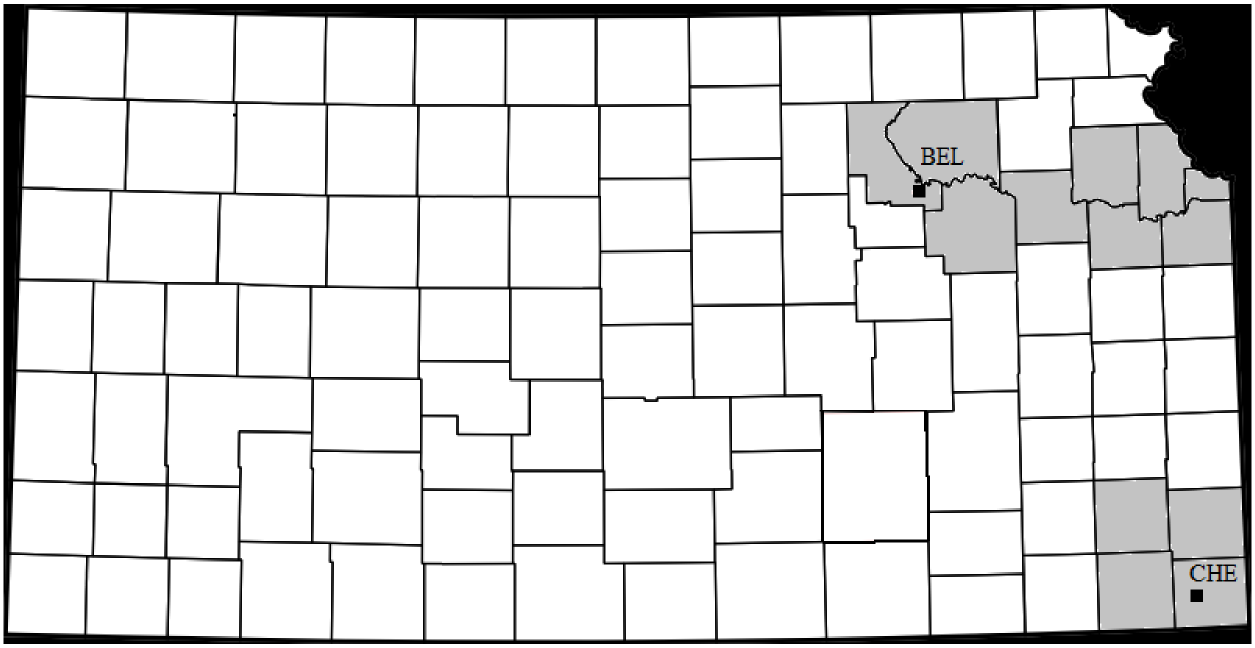
Author(s), Year	Materials
Barshad and Kishk, 1968	4 vermiculitic soil clays 2 biotites
Barshad and Kishk, 1970	11 vermiculitic soil clays
Chen et al., 1987	4 montmorillonites 1 nontronite 6 soil clays
Khaled and Stucki, 1991	2 montmorillonites
Shen and Stucki, 1994	2 montmorillonites 1 illite 3 soil clays
Scherer and Zhang, 2002	2 soils 1 vermiculite 1 illite
Lee, 2007	1 montmorillonite

Chapter 3 - Materials

Research sites

This study uses the upper fifteen centimeters of soils from two sites previously studied by the primary investigator. The sites selected for study were Cherokee (CHE), a southeastern Kansas site in Cherokee County and Belvue (BEL), a northeastern Kansas site in Riley County (Figure 3-1).

Figure 3-1 Map indicating sampling locations (■) and counties in which the Belvue (BEL) and Cherokee (CHE) soil series are mapped in Kansas.



These two surface soils have similar physical, chemical, and mineralogic characteristics (Table 3.1) but differ in that the Cherokee soil displays inexplicable potassium fluctuations throughout the year, whereas Belvue soils do not. Additionally, despite having similar amounts of ammonium acetate extractable potassium, potassium deficiencies are more frequently observed at the Cherokee site.

Even though the BEL sample is a loam and the CHE sample is a silt, a closer evaluation of their particle size fractions reveals that their particle size distributions are quite comparable. Each of the samples has approximately 10% of their weight in the clay sized fraction and 85% of their weight in the medium silt- to fine sand-sized fractions. The main difference in terms of particle size distribution between the two samples is that BEL has more of this latter weight in the sand fraction, and CHE has more of it in the silt sized fraction. The two samples have comparable amounts of carbon, nitrogen, and organic matter and close pH values though the BEL sample is slightly more acidic.

The Cherokee and Belvue series are both extensively cultivated with each of the research sites being used for soybean production. Climatically, Belvue series soils experience a mean annual temperature of 12 to 13°C (53 to 55°F). The more southern Cherokee series soils experience a warmer mean annual temperature in the range of 14 to 18°C (57 to 65°F). The Belvue series is drier than Cherokee series—receiving approximately 760 to 890 mm (30 to 35 in) of precipitation a year compared to the 1020 to 1140 mm (40 to 45 in) of precipitation received annually by the Cherokee series. The Cherokee series is somewhat poorly drained compared to the well-drained Belvue series.

Table 3.1 Classification and physical and chemical properties of soils.

ID	Soil Series	Taxonomic Class
BEL	Belvue	Coarse-silty, mixed, superactive, nonacid, mesic Typic Udifluvents
CHE	Cherokee	Fine, mixed, active, thermic Typic Albaqualfs

ID	Particle Size Distribution (wt. %)											Textural Class
	Clay	Silt				Sand						
	Total	F	M	C	Total	VF	F	M	C	VC	Total	
BEL	9.4	1.8	9.8	31.5	43.1	30.0	14.0	2.3	0.3	1.0	47.5	Loam
CHE	10.2	5.2	42.9	37.0	85.1	3.0	1.1	0.3	0.2	0.1	4.7	Silt

ID	Total C (%)	Total N (%)	OM (%)	NH_4OAc Extractable Bases and Acidity (meq*100 g^{-1})					CEC (meq*100 g^{-1})	pH	
				Ca	Mg	Na	K	Acidity	Summation	0.01 M $CaCl_2$ (1:2)	H_2O (1:1)
BEL	0.6	0.1	1.5	3.9	1.2	0.05	0.5	1.2	6.9	5.0	5.4
CHE	0.6	0.1	1.4	5.0	0.6	0.05	0.4	0	6.0	5.5	6.3

Reference clays

Five reference clays were used for this study—kaolinite (KGa-1b), illite (IMt-1), nontronite (NAu-2), montmorillonite (STx-1), and vermiculite (VTx-1). The vermiculite sample was courtesy of Dr. Jerry Bigham and was originally from the Source Clay Minerals Repository of the Clay Minerals Society in Columbia, Missouri. The other four reference clays came directly from the Source Clay Minerals Repository of the Clay Minerals Society in Chantilly, Virginia. Source and characterization data for these reference clays can be found in Table 3.2.

Table 3.2 Reference clay characterization data.

ID	**Name**	**Origin**
KGa-1b	Kaolin	Washington County, Georgia, USA
IMt-1	Illite	Silver Hill, Montana, USA
NAu-2	Nontronite	Uley Mine, South Australia
STx-1b	Montmorillonite	Gonzales County, Texas, USA
VTx-1	Vermiculite	Llano County, Texas, USA

ID	**Chemical Composition (wt. %)**											
	SiO_2	**Al_2O_3**	**TiO_2**	**Fe_2O_3**	**FeO**	**MnO**	**MgO**	**CaO**	**Na_2O**	**K_2O**	**F**	**P_2O_5**
KGa-1b	44.2	39.7	1.4	0.1	0.1	tr	tr	tr	tr	0.1	0.0	tr
IMt-1	49.3	24.3	0.6	7.3	0.6	tr	2.6	0.4	0.0	7.8	0.0	0.1
NAu-2	57.0	3.4	0.0	37.4	0.0	0.0	0.3	2.7	0.1	tr	0.0	0.0
STx-1b	70.1	16.0	0.2	0.7	0.2	tr	3.7	1.6	0.3	0.1	0.1	tr
VTx-1	27.8	0.59	tr	1.1	tr	0.1	29.7	14.6	tr	tr	0.0	tr

ID	**Structural Formula**
KGa-1b	$(Mg_{.02}\ Ca_{.01}\ Na_{.01}\ K_{.01})[Al_{3.86}\ Fe^{(III)}_{.02}\ Mn_{tr}\ Ti_{.11}][Si_{3.83}Al_{.17}]\ O_{10}(OH)_8$
IMt-1	$(Mg_{.09}\ Ca_{.06}\ K_{1.37})\ [Al_{2.69}\ Fe^{(III)}_{.76}\ Fe^{(II)}_{.06}\ Mn_{tr}\ Mg_{.43}\ Ti_{.06}]\ [Si_{6.77}\ Al_{1.23}]\ O_{20}(OH)_4$
NAu-2	$(M^{+}_{.97})[Al_{.52}\ Fe_{3.32}\ Mg_{.7}]\ [Si_{7.57}\ Al_{.01}\ Fe_{.42}]\ O_{20}(OH)_4$
STx-1b	$(Ca_{.27}\ Na_{.04}\ K_{.01})[Al_{2.41}\ Fe^{(III)}_{.09}\ Mn_{tr}\ Mg_{.71}Ti_{.03}][Si_{8.00}]O_{20}(OH)_4$
VTx-1	$(Mg_{2.27}\ Ca_{2.92}\ K_{.01})[Mg_{5.98}\ Mn_{.01}\ Ti_{.01}][Si_{7.71}\ Al_{.13}Fe^{(III)}_{.16}]O_{20}(OH)_4$

Data from van Olphen and Fripiat (1979).

Rationale

The Belvue and Cherokee sites were selected for being similar in terms of physical, chemical, and mineralogical characteristics but differing in terms of potassium behavior. Soil clays in general were included to evaluate the potassium fixation behavior of mixed mineralogy soil clays.

Kaolinite, illite, smectite, and vermiculite reference clays were selected because they reflect the diverse mineralogy of the soil clays selected as well as the soil clays of temperate regions. KGa-1b, IMt-1, NAu-2, Stx-1b, and VTx-1 were selected specifically to reflect a wide range of iron contents and iron locations. Two types of smectite (STx-1b and NAu-2) were included for their low and high iron contents—0.8% and 23%, respectively. While most of the iron in the reference clays is octahedrally coordinated, NAu-2 has a small amount of tetrahedral iron and VTx-1 has only tetrahedral iron and no octahedral iron. While the reference vermiculite selected (VTx-1) is trioctahedral, most soil vermiculites are dioctahedral. While dioctahedral vermiculite would have been preferred for the sake of more accurately representing soil minerals, no pure samples of dioctahedral vermiculite are available.

Since the main action of iron redox state on potassium fixation is thought to be through an action on layer charge, the five reference clays were additionally selected to reflect a range of layer charges and charge locations. While most of the layer charge for IMt-1, NAu-2, and VTx-1 is derived from the tetrahedral sheet, the layer charge for STx-1b is derived wholly from the octahedral sheet.

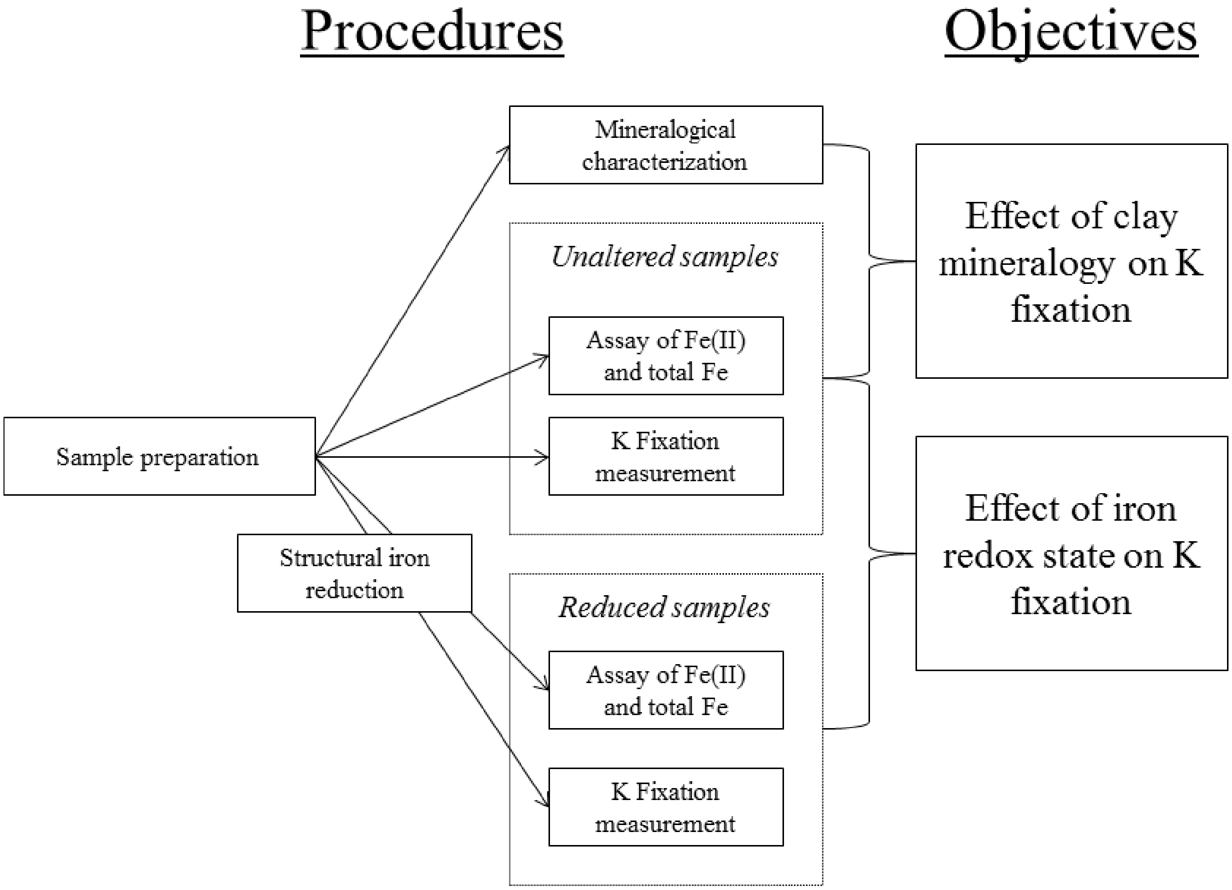
Thus, not only did this spread in mineralogical characteristics allow for the evaluation of the effect of clay mineralogy and iron redox state on potassium fixation, it also allowed for some inferences to be made about the relationship between charge location and magnitude on potassium fixation.

Chapter 4 - Methods

Experimental design

The objectives of the laboratory experiments were to evaluate the effect of clay mineralogy and iron redox state on potassium fixation. In order to accomplish the objectives, the soil and reference clays were first fractionated, sodium saturated, freeze-dried, and homogenized. After this sample preparation, clay mineralogy was determined for the soil clays and confirmed for the reference clays by x-ray diffractometry. One set of samples, without further alteration, was evaluated for ferrous iron and total iron content as well as potassium fixation capacity. A second set of samples was reduced and then subjected to the same iron and potassium fixation determination as the unaltered samples.

Figure 4-1 Generalized flow chart of experimental design.



Sample preparation

Freeze dried clays were prepared using the methods of Jackson (1975). Soil samples were air dried and passed through a two millimeter sieve. Approximately forty grams of each soil were pretreated with 1 M NaOAc solution to remove carbonates and thirty percent hydrogen peroxide to remove organic matter. Samples were washed once with 1 M NaCl solution and then with deionized water until they dispersed. A 300 mesh sieve was used to catch the sand fraction while silt and clay fractions were caught in two liter bottles. Sand fractions were oven dried and stored.

A series of eight sedimentation cycles were used to separate the silt fraction from the sand fraction. Silt fractions were oven dried and stored. Clay fractions were flocculated and consolidated by additions of $MgCl_2•H_2O$ crystals, centrifugation, and decantation. Clay suspensions were saturated with sodium by washing three times with 1M NaCl solution and then with deionized water until dispersion. Dispersed suspensions were sonified and quick frozen in a dry-ice bath. The quick frozen clays were freeze dried, homogenized, and stored for later analysis. Hence, the freeze-dried clay specimens were Na-saturated.

The same procedure was followed for the preparation of the reference clays with the following exceptions: (1) it was necessary to grind IMt-1, NAu-2, and VTx-1 with a mortar and pestle prior to their being passed through a two millimeter sieve and (2) none of the reference clays were pretreated with sodium acetate or hydrogen peroxide.

Mineralogical characterization

Mineralogical characterizations were carried out via the use of x-ray diffractometry. All x-ray diffractometry work was done using a Phillips XRG-3100 generator, an APD 3520 X-ray diffractometer with Theta compensating slit, graphite monochromator, and scintillation detector, and VisualXRD software (GBS Scientific Equipment Pty. Ltd., Victoria, Australia). Copper Kα radiation was used at 35 kV and 20 mA. Step size for all scans was set at $0.02°2\theta$ with a time per step of 0.6 seconds.

Six parallel oriented mounts were made of each of the clay samples in order to characterize their mineralogy. Three of the preparations included potassium saturation of the clays, pipetting onto glass slides, and drying at 25°C, 350°C, and 550°C (treatments denoted as K-25, K-350, and K-550, respectively). Clay suspensions were saturated with potassium by washing three times with 1 M KCl solution and then with deionized water until dispersion.

The remaining three preparations included magnesium saturation of the clays. Clay suspensions were saturated with magnesium by washing three times with 1 M $MgCl_2$ solution and then with deionized water until the specimens dispersed. Two slides were made by pipetting the Mg-saturated clay onto a glass slide and drying at 25°C. One slide was allowed to remain and the other was additionally heated to 60°C in a container of ethylene glycol (treatments denoted as Mg-25 and Mg-EG respectively). Another slide was made by using 1% (v/v) glycerol instead of deionized water to wash the Mg-saturated clays. This Mg-saturated and glycerol-solvated sample was pipetted onto a glass slide and dried at 25°C (treatment denoted as Mg-GLY). Each pipetting placed two milliliters of solution containing thirty milligrams of clay onto each glass slide.

All slides were scanned from 2°2θ to 15°2θ with the Mg-25 slides being scanned from 2°2θ to 34°2θ. Semi-quantitative analysis of the relative proportions of different clay minerals in the soil clays were made by comparing peak heights to pure sample peak heights.

Silt samples were analyzed as randomly oriented powder mounts and scanned from 18°2 θ to 54°2θ.

Structural iron reduction

Fifty milligram samples of freeze dried, sodium saturated clay were placed into 50 mL centrifuge tubes with 50 mL of citrate-bicarbonate buffer. The citrate-bicarbonate buffer was made with eight parts 1 N sodium bicarbonate, one part 0.3 M sodium citrate, and thirty-six parts deionized water. The clay was allowed to disperse in the reaction tube by shaking gently overnight.

After dispersion, a solution of dithionite was made up such that a five milliliter aliquot of the solution contained 600 mg of sodium dithionite. Five milliliter aliquots of this dithionite solution were then immediately added to the centrifuge tubes. The tubes were capped and placed into a water bath at 70°C for four hours to allow the reaction to progress.

The samples were then centrifuged for five minutes at 1800 rpm. If the supernatants were cloudy, the samples were centrifuged again for another five minutes. Once the supernatant became clear, it was decanted and discarded. The samples were then either transferred with deionized water into 125 mL amber HDPE bottles for ferrous and total iron analysis or potassium saturated for the potassium fixation procedure.

This procedure was extensively modified from the procedure by Stucki et al. (1984b). Further information about the development of this procedure can be found in Appendix C.

Assay of ferrous iron and total iron

Ferrous iron and total iron contents were determined by a colorimetric method recommended by Amonette and Templeton (1998). Fifty milligram samples were dissolved by 15 mL of boiling acid matrix—containing 12 mL of 10% sulfuric acid, 1 mL of 48% HF, and 2 mL of a 10% solution of 1, 10-phenanthroline in 95% ethanol—in 125 mL amber HDPE bottles. After allowing the sample to be digested in a boiling water bath for 30 minutes, 10 mL of 5% boric acid and 90 mL of deionized water were added to the sample to stabilize and dilute the digestate. To determine the ferrous iron content of the digestate, 1 mL subsamples of the digestates were combined with 10 mL of 1% sodium citrate solution in 30 mL amber glass bottles. Absorbances of these solutions were measured at 510 nm in 1 cm path length quartz cells by a Genesys 20 spectrophotometer. To determine the total iron content of the digestates, 1 mL subsamples were combined with 10 mL of 1% sodium citrate, 1% hydroxylamine solution. Hydroxylamine served to reduce any ferric iron in the digestate, causing the measure of ferrous iron to be equivalent to a measure of total iron. Absorbances of these solutions were measured in the same fashion as in the ferrous iron determination. A standard curve was constructed using ferrous ammonium sulfate. The necessity of using amber containers throughout the procedure was to prevent photoreduction of the digested sample iron.

Potassium fixation measurement

A few different methods were attempted to measure potassium fixation, but a modification of a method used by both Lee (2007) and Shen (1994) was settled on for its precision and consistency in terms of repeating experimental results.

Fifty milligram samples of Na-saturated, freeze dried clay, either unaltered or reduced, were washed three times with 50 mL of 1 M KCl solution to potassium saturate them. The samples were then washed five times with 50 mL of 0.5 M $MgCl_2$ solution, and these washes were weighed and saved for potassium analysis in order to verify complete removal of solution and exchangeable potassium. Using a small amount of deionized water, the washed samples were transferred into Teflon decomposition vessels. The vessels were placed in an oven at 110°C until the samples were dry. This step merely served as a way to ensure there was enough space in the small vessel for the acid digestion to occur.

After drying, 0.5 mL aqua regia and 5 mL of 48% HF were pipetted into the vessel. The vessels were then capped and placed into Parr digestion bombs. The bombs were placed in the oven for 1 h at 110°C. They were then removed and allowed to cool to ambient temperature. Once cool, the bombs were opened, and the contents of the Teflon vessels were quantitatively transferred into 100 mL Nalgene volumetric flasks already containing 2.80 g of boric acid powder using deionized water. Flasks were brought to volume using deionized water and shaken to dissolve the boric acid powder. Potassium concentrations of the acid digestions and $MgCl_2$washes were determined using a Varian model 720-ES inductively coupled plasma optical emission spectrometer. Baseline mineral potassium contents were determined in the same manner but omitting the initial steps of potassium saturation and washing with $MgCl_2$ solution.

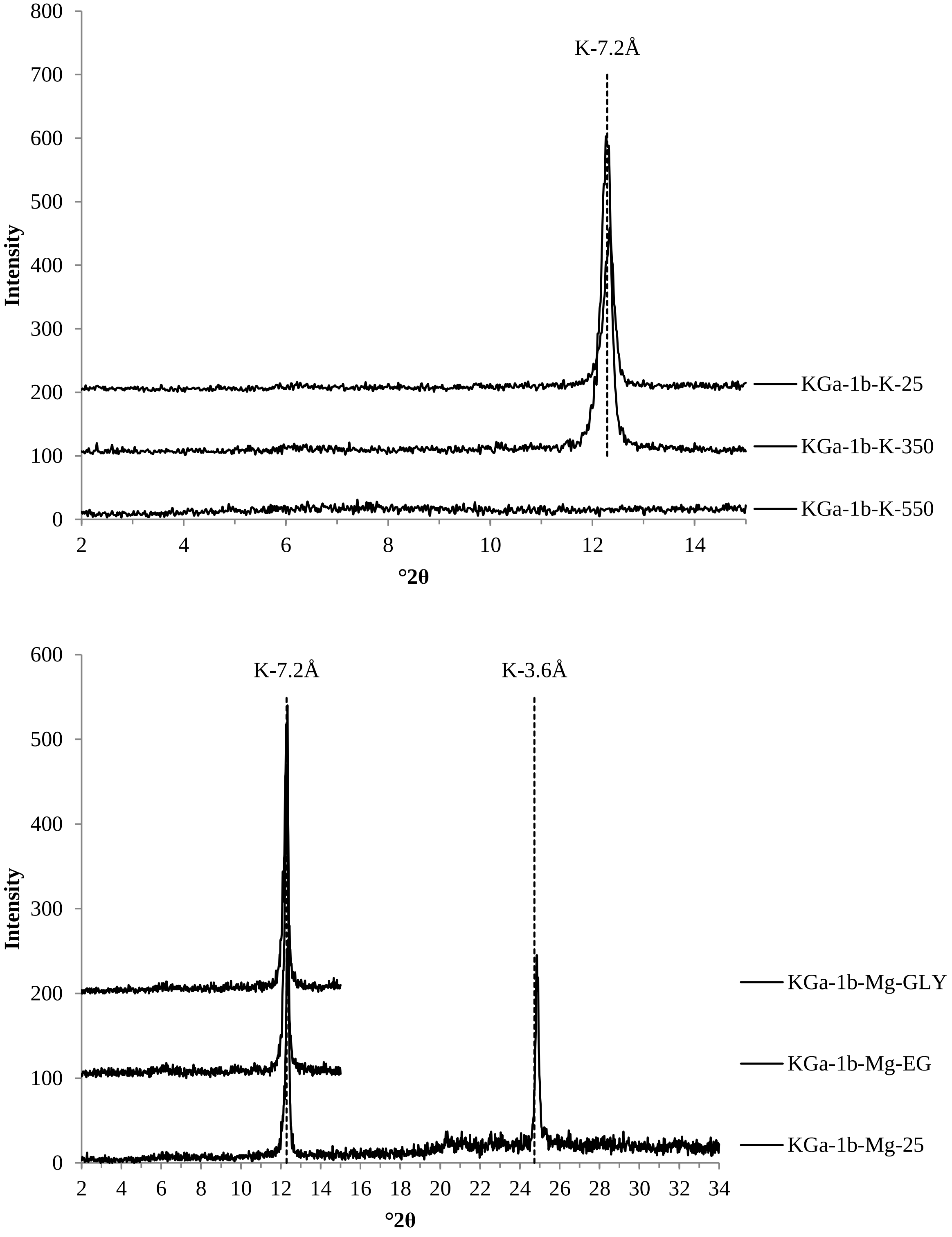
Chapter 5 - Results

Mineralogical characterization of materials by x-ray diffractometry

Reference clays

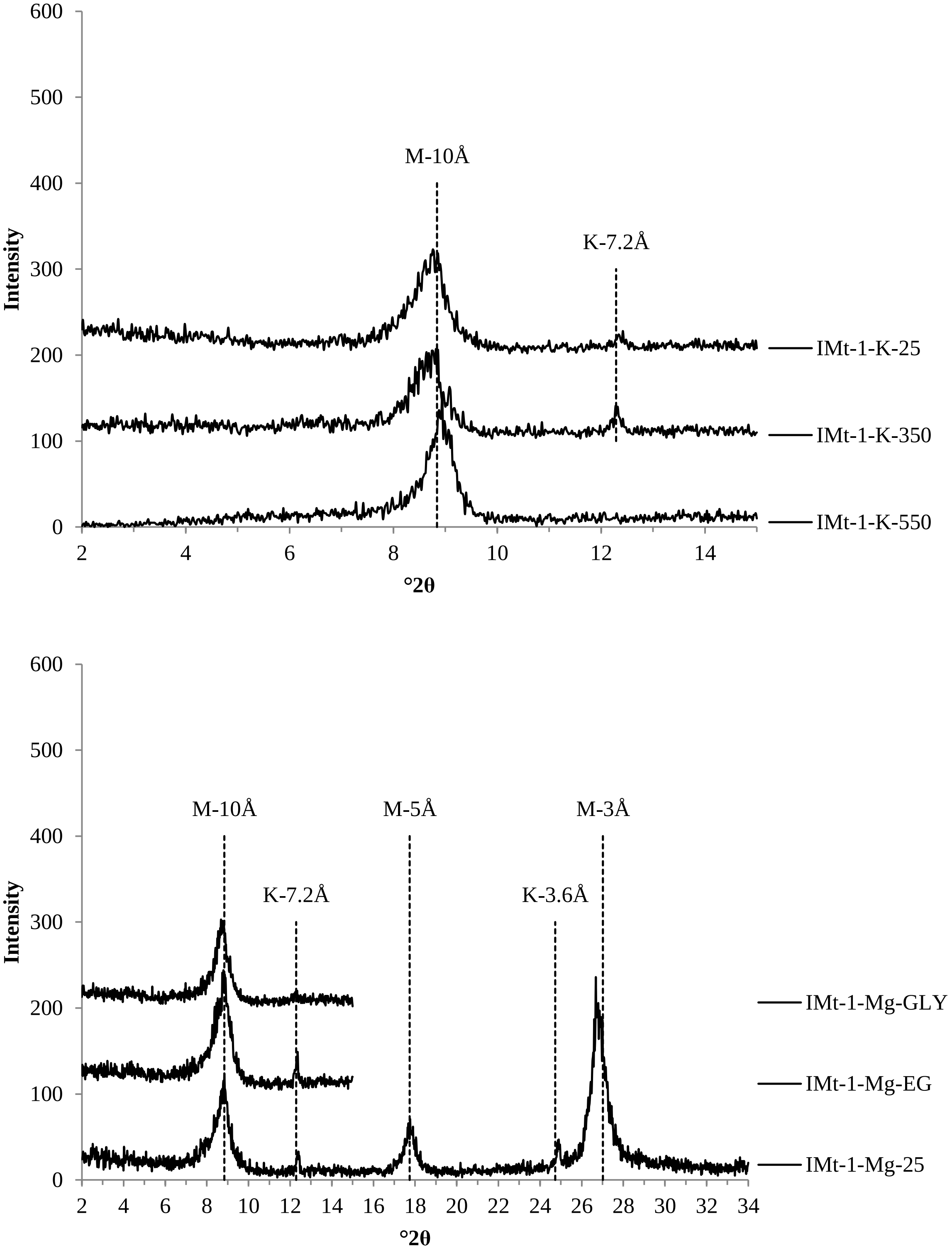
The reference clay minerals were characterized by x-ray diffractometry not only to confirm their identity and reveal any crystalline impurities that might exist in the sample, but also to demonstrate how potassium saturation and heating differently affect the clay minerals. KGa-1b demonstrated a classic kaolinitic response to the different treatments (Figure 5-1). Due to hydrogen bonding between layers, kaolinite interlayer spaces are inaccessible to cations and organic molecules. Thus, regardless of the sample being saturated with potassium, magnesium, glycerol, or ethylene glycol, the d-spacing remains a strong 7.2 Å. Heating to 550°C however disorders the layers, causing a loss in the 7.2 Å peak. X-ray diffraction patterns for IMt-1 (Figure 5-2) indicated the presence of some kaolinite with the presence of a small 7.2 Å peak that disappears with heating to 550°C. Mostly, however the patterns confirm that the bulk of the sample is micaceous with a strong 10 Å peak regardless of treatment. Similar to kaolinite, the interlayer spaces of illites are also inaccessible to the different cations and organic molecules used to saturate the sample. However, in the case of illite, interlayer inaccessibility is due to clay layers being contracted around potassium ions.VTx-1 contained the diagnostic 14.5 Å peak in the magnesium patterns and the characteristic collapse of a 12Å peak to a 10Å peak with the heating of the potassium saturated samples (Figure 5-3). Magnesium has a larger hydrated radius than potassium, and thus, an interlayer of hydrated magnesium ions is more open than an interlayer of hydrated potassium ions. The collapse of the 12 Å peak to a 10 Å peak with the heating of the potassium saturated samples is due to the dehydration of the interlayer. Thus, a K-saturated vermiculite heated to 550°C has a diffraction pattern quite similar to micas. The VTx-1 specimen also contained some smectite as indicated by a small peak at 17-18 Å for the Mg-EG and Mg-GLY treatments. NAu-2 and STx-1b demonstrated classic smectitic responses to the different treatments (Figures 5-4 and 5-5). Due to having a less of a negative charge than vermiculite, smectites permit the entrance of bilayers of glycerol versus monolayers and hold onto potassium with less tenacity than vermiculites, leading to more expanded interlayer spaces. Nevertheless, smectites, like vermiculite, collapse into mica like structures when K-saturated and heated.

Figure 5-1 XRD patterns for KGa-1b.



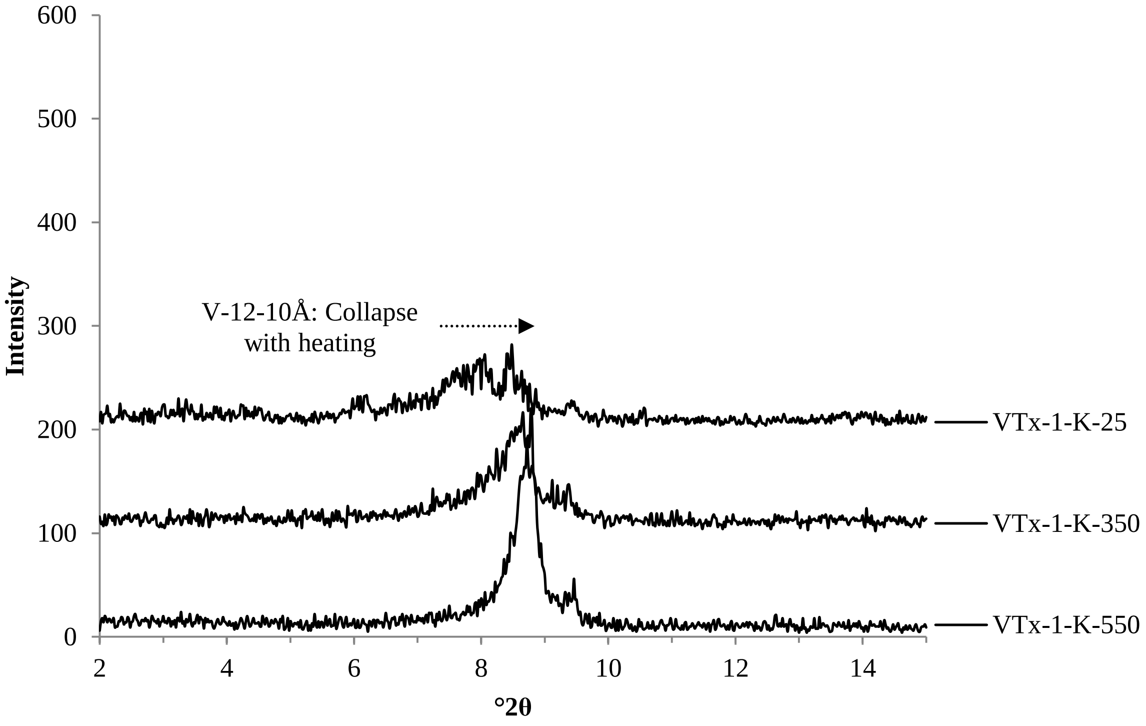
K = kaolinite.

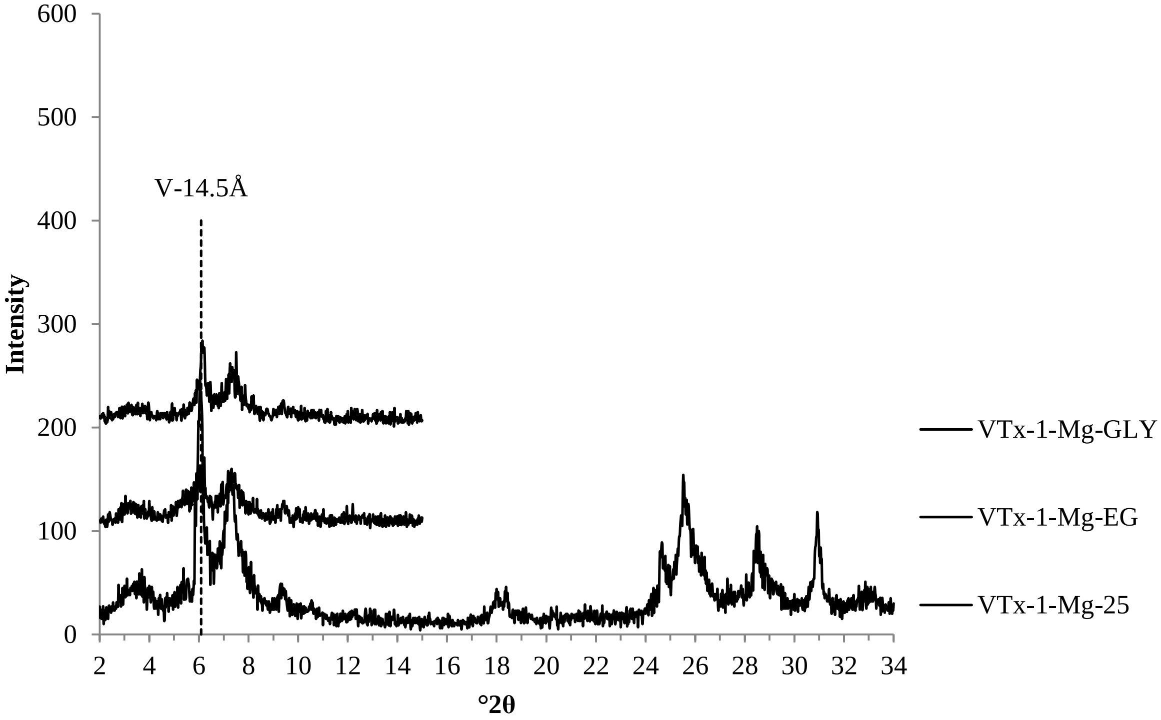
Figure 5-2 XRD patterns for IMt-1.



K = kaolinite. M = mica.

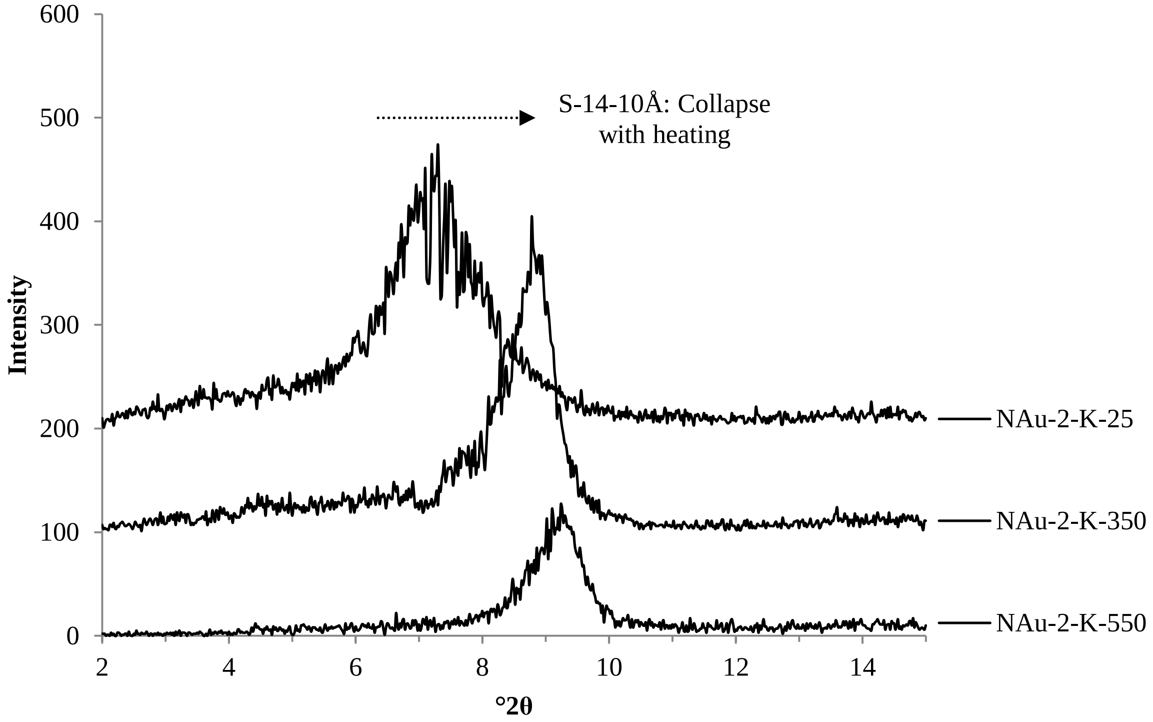
Figure 5-3 XRD patterns for VTx-1.

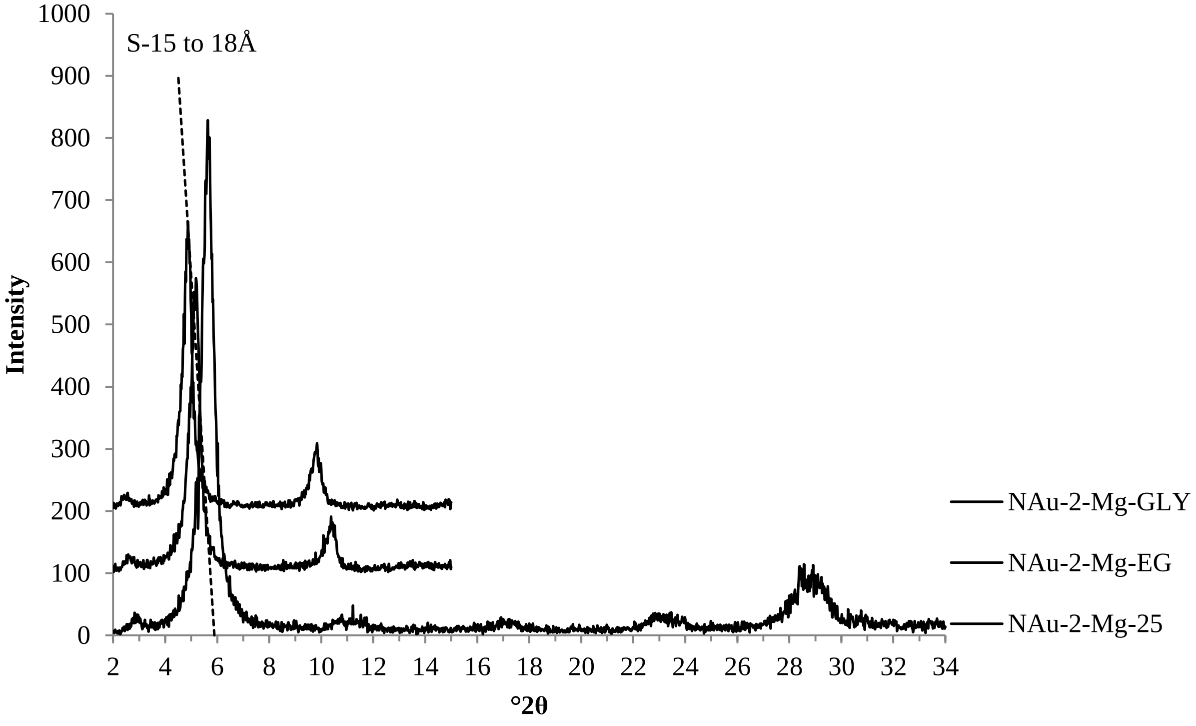




V = vermiculite.

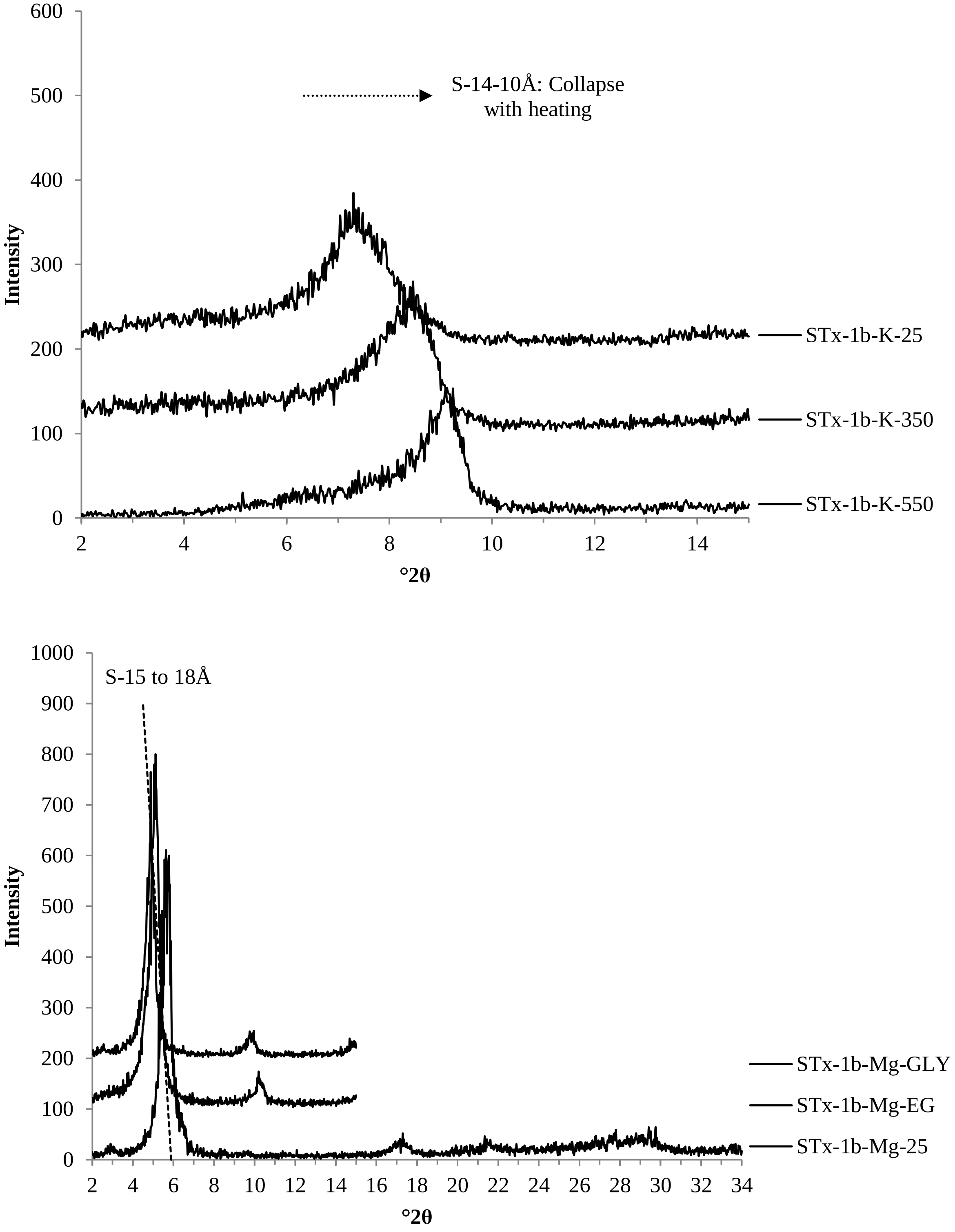
Figure 5-4 XRD patterns for NAu-2.





S = smectite.

Figure 5-5 XRD patterns for STx-1b.

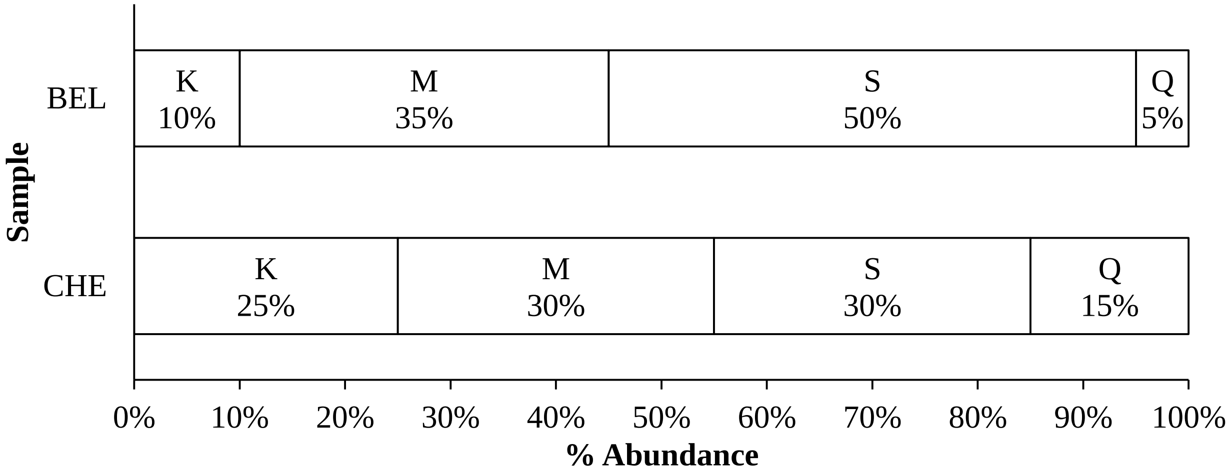


S = smectite.

Soil clay and silt fractions

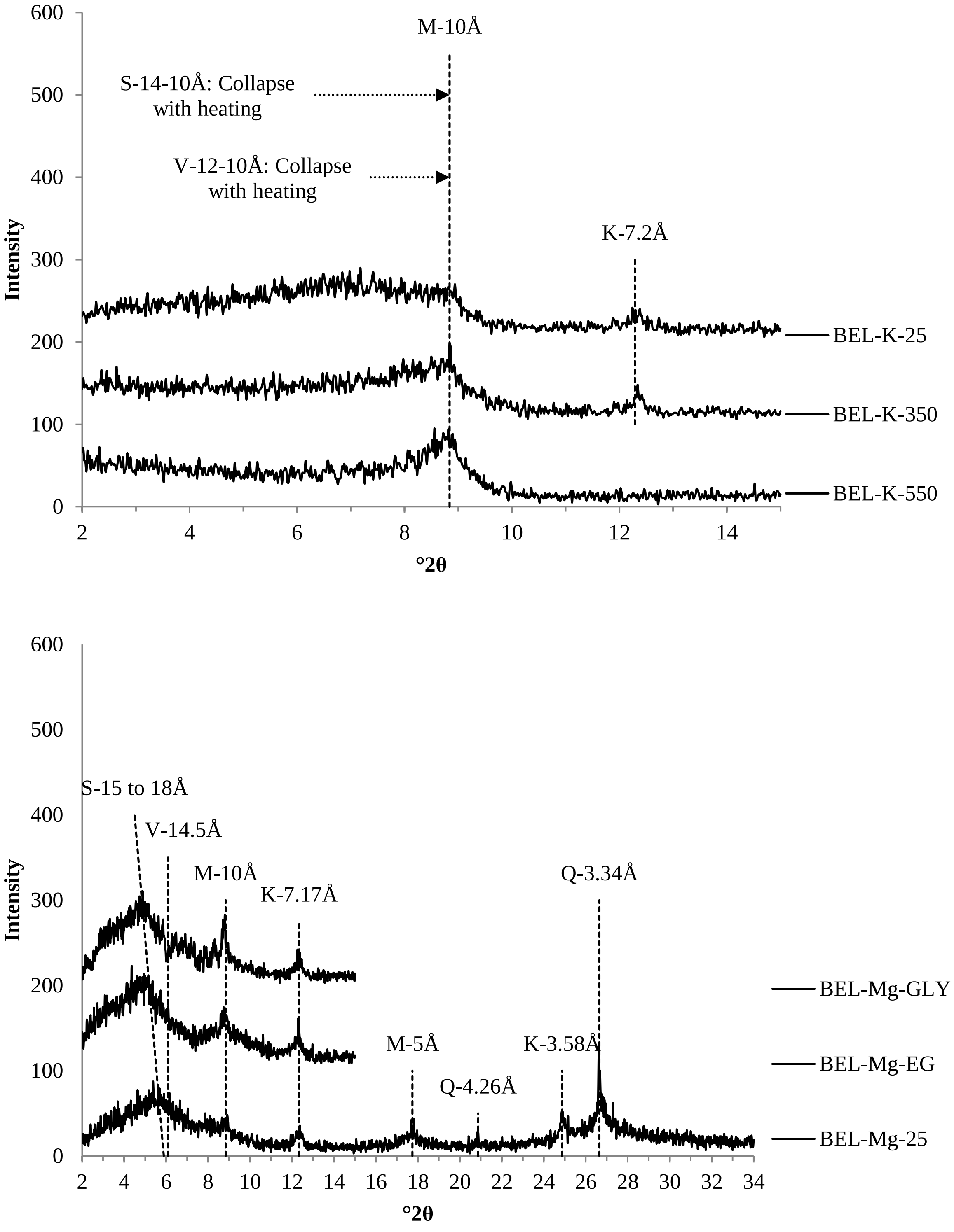
BEL and CHE have similar mineralogy in that they both contain kaolinite, mica, smectite, and quartz. BEL may contain small amounts of vermiculite. BEL has relatively more mica and smectite, whereas CHE has relatively more kaolinite and quartz (Figures 5-6, 5-7, and 5-8). While this may be due to the Cherokee soil being more highly weathered, being in southeast versus northeast Kansas, it couldalso simply be a function of different parent materials. However, the presence of different feldspars in addition to quartz in the Belvue silt fraction compared to the purely quartz Cherokee silt fraction supports the notion that the Belvue soil is less weathered (Figure 5-9).

Figure 5-6 Comparison of semi-quantitative clay mineralogy for BEL and CHE.



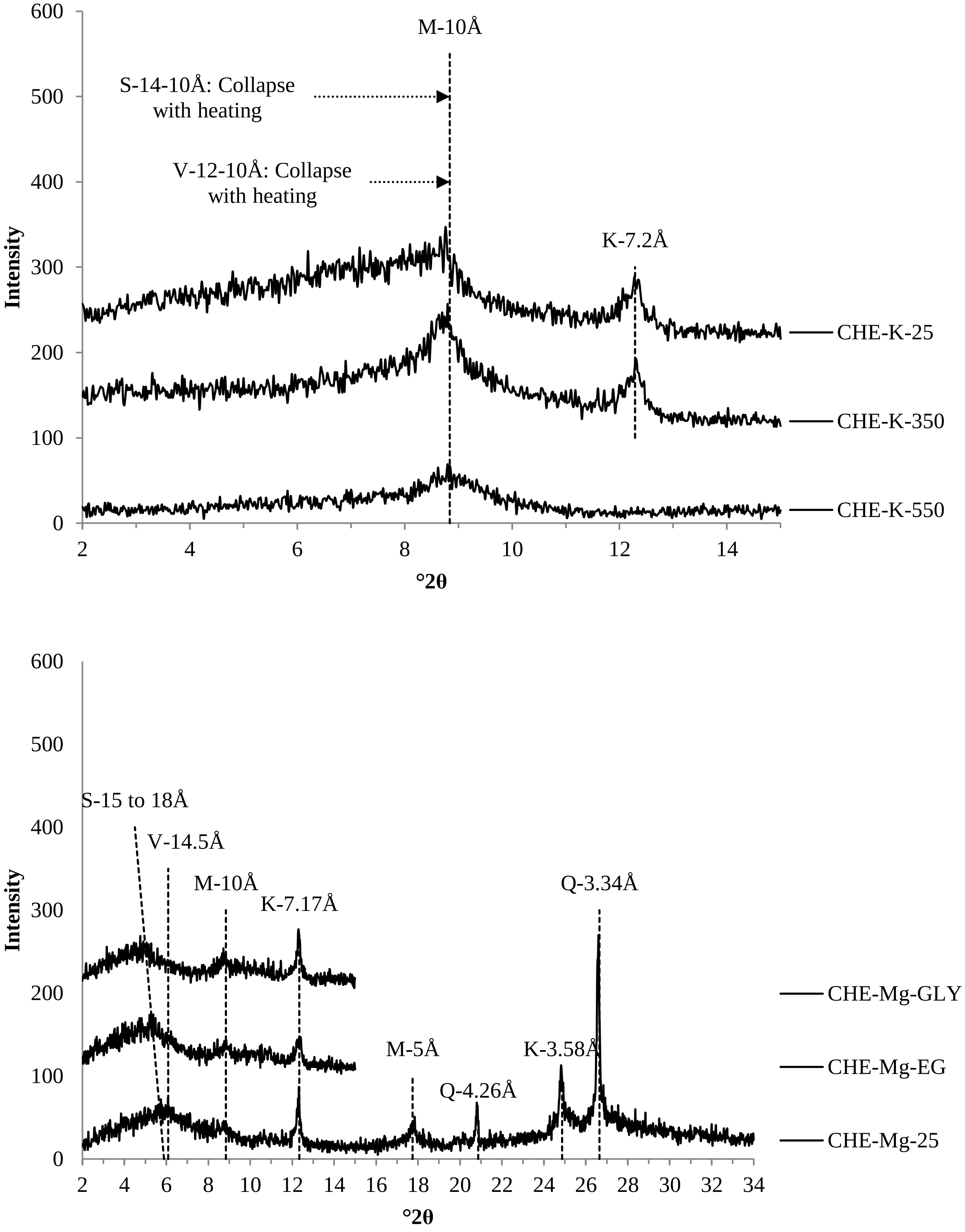
K = kaolinite. M = mica. S = smectite. Q = quartz.

Figure 5-7 XRD patterns for BEL total clay.



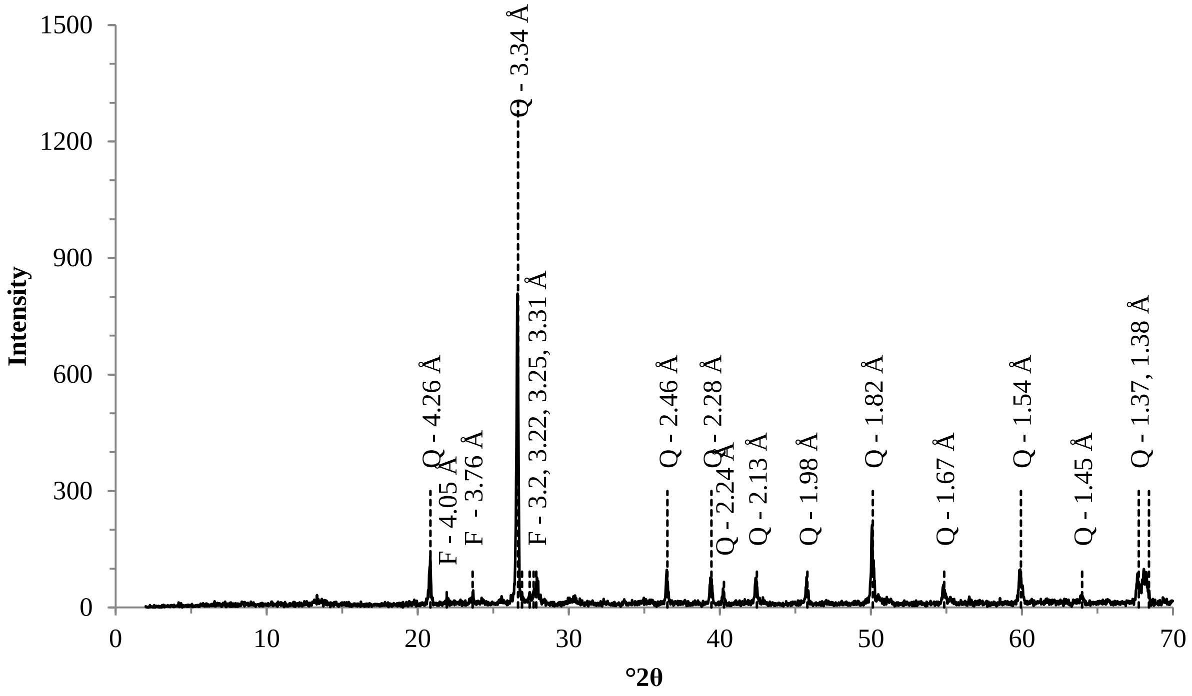
K = kaolinite. M = mica. S = smectite. V = vermiculite.

Figure 5-8 XRD patterns for CHE total clay.



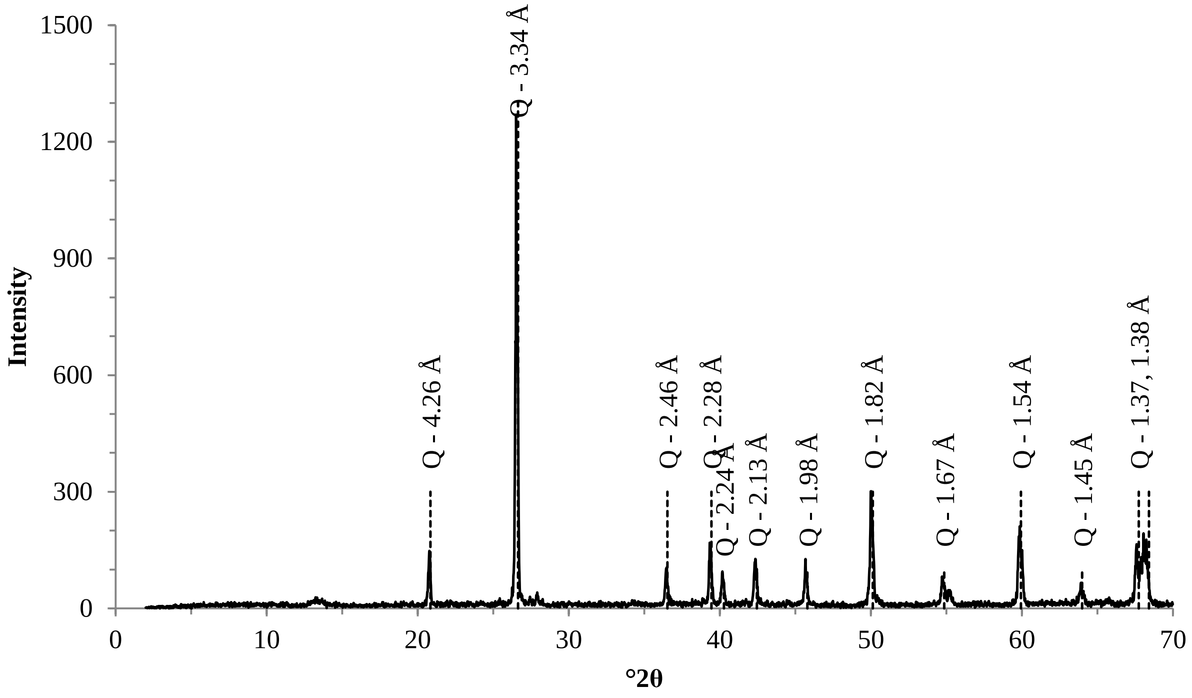
K = kaolinite. M = mica. S = smectite. V = vermiculite.

Figure 5-9 XRD patterns of BEL total silt.



F = feldspar. Q = quartz.

Figure 5-10 XRD patterns of CHE total silt.



Q = quartz.

Unaltered and reduced iron contents of soil and reference clays

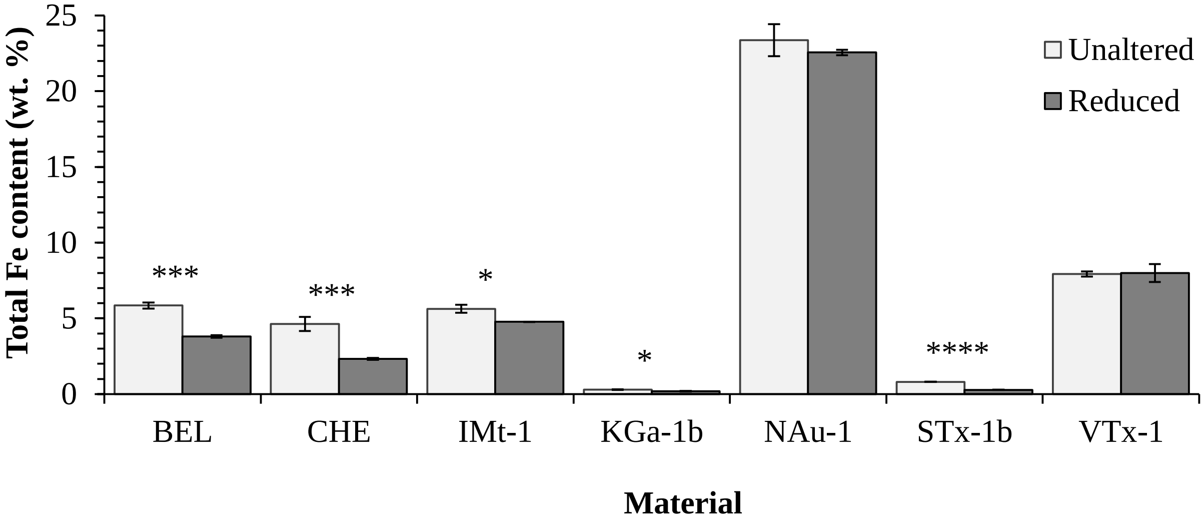
Total structural iron present in the clay minerals ranged, as a weight percent, from less than 1% for KGa-1b and STx-1b to a high of approximately 23% for NAu-1. Initial amounts of ferrous iron were low for all clay minerals, ranging from 0% for KGa-1b to a high of 1.17% for IMt-1. This was to be expected as many of the pretreatments steps used prior to iron assay were oxidizing—e.g., air drying, dry grinding, treatment with hydrogen peroxide, suspension in solutions containing dissolved oxygen, freeze drying, etc. Additionally, many of the reference minerals started in a fairly if not completely oxidized form. After reduction, ferrous iron contents ranged from 0.15% for KGa-1b to a high of 15.40% for NAu-2 (Table 5.1).

Table 5.1 Unaltered and reduced iron contents of soil and reference clays as weight percents. Data are means. N=3. Standard deviations are in parentheses.

Material	Unaltered			Reduced		
	Fe^{2+} (%)	Total Fe (%)	Fe(II)/Total Fe	Fe^{2+} (%)	Total Fe (%)	Fe(II)/Total Fe
BEL	0.61 (0.12)	5.85 (0.34)	0.11 (0.02)	1.46 (0.08)	3.81 (0.15)	0.38 (0.01)
CHE	0.55 (0.05)	4.63 (0.82)	0.12 (0.01)	1.23 (0.08)	2.32 (0.10)	0.53 (0.01)
IMt-1	1.17 (0.16)	5.63 (0.46)	0.21 (0.02)	1.69 (0.21)	4.77 (0.02)	0.35 (0.04)
KGa-1b	0.00 (0.01)	0.29 (0.05)	0.01 (0.02)	0.15 (0.03)	0.19 (0.03)	0.77 (0.14)
NAu-1	0.12 (0.01)	23.37 (1.85)	0.01 (0.00)	15.40 (0.16)	22.56 (0.32)	0.68 (0.01)
STx-1b	0.04 (0.01)	0.81 (0.01)	0.05 (0.02)	0.24 (0.05)	0.28 (0.02)	0.85 (0.13)
VTx-1	0.77 (0.61)	7.93 (0.28)	0.10 (0.07)	1.65 (0.03)	7.99 (1.03)	0.21 0.01)

Generally, reduction was associated with a loss in total structural iron; however this loss was not significant for NAu-1 and VTx-1 (Figure 5-11). Iron loss was most likely due to phyllosilicate dissolution as a result of the chemical reduction process (Stucki, 2006). In the soil clays, which experienced the most total loss in iron, there was also likely some loss in iron associated with iron oxide dissolution. While the x-ray diffraction patterns did not indicate the presence of iron oxides in either sample, it is almost impossible to detect poorly crystalline iron oxides, especially amongst crystalline materials, using conventional x-ray diffractometry techniques (Bigham et al, 2002).

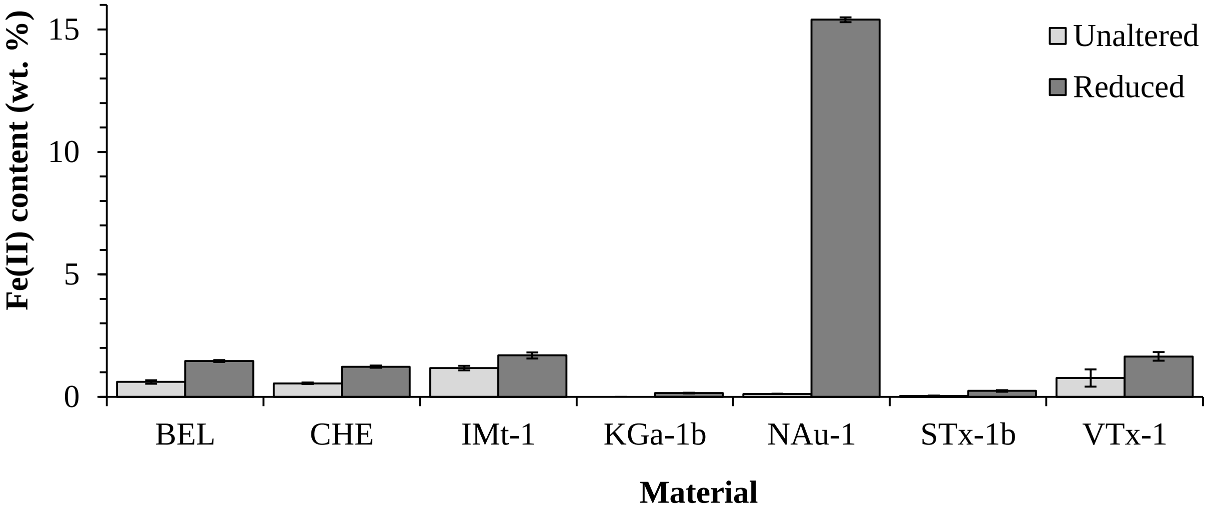
Figure 5-11 Mean total structural iron content (± SEM) for different clay minerals both unaltered and reduced. N=3.



Significances are indicated as follows: * P < 0.05; ** P <0.01; *** P<0.001; **** P<0.0001.

Upon reduction, ferrous iron increased by about 1.5-fold for IMt-1 to about 130-fold for NAu-2. BEL, CHE, and VTx-1 upon reduction, all roughly doubled their ferrous iron contents. Since STx-1b and KGa-1b had relatively small amounts of ferrous iron to begin with, their modest increases were actually 6 and 15-fold increases in ferrous, respectively (Figure 5-12).

Figure 5-12 Mean ferrous iron content (± SEM) as a weight percent for different clay minerals both unaltered and reduced. N=3.



The information that can be gleaned comparing the unaltered and reduced ratios of ferrous iron to total iron is limited due to the fact that some of the total structural iron was lost during reduction. Nonetheless, it merits noting that IMt-1 seemed particularly resistant to the reduction process. The relative unresponsiveness of IMt-1 to reduction may be attributable to the relative inaccessibility of ferrous octahedral iron due to the non-expansibility of micaceous minerals—collapsed clay layers make electron transfer more difficult. Others have also noticed the difficulty with which micaceous minerals are reduced (e.g., Gilkes et al., 1972; Douglas, 1967; Ross and Rich, 1974).

One caveat, however, when comparing the relative abilities of different phyllosilicates to be reduced is that reduction rates are as much a function of particle size and surface area as clay mineralogy (Ernsten et al., 1998; Kostka et al., 2002). The smaller the particle size, the more rapid and greater the extent of reduction is due to the increased surface area. Thus, what might appear to be one type of clay mineral being more responsive to reduction than another may really be a finer material being more responsive to reduction than a coarser material.

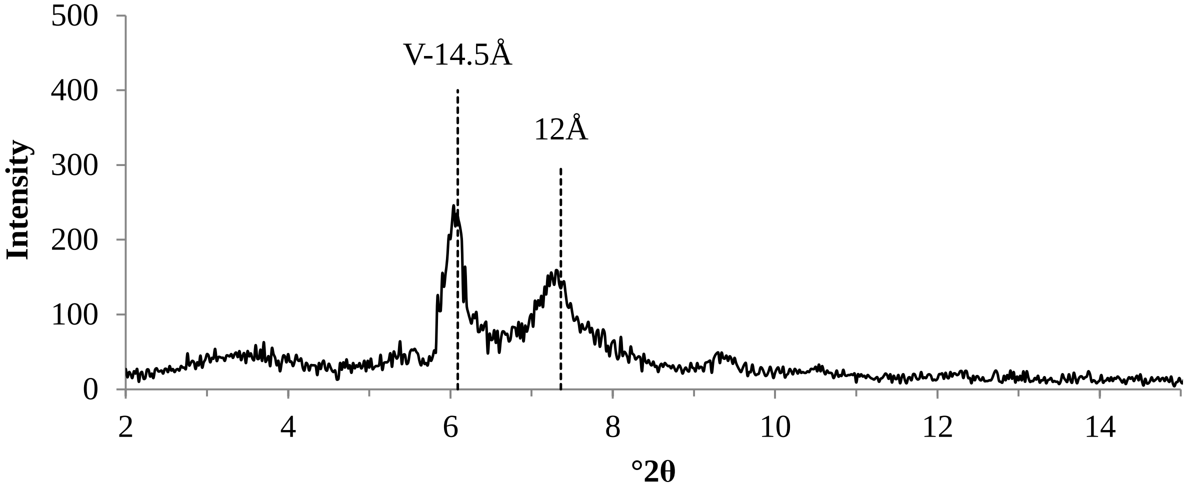
Potassium fixation of clay minerals in unaltered and reduced state

Prior to evaluation of clay mineral fixation capacity, baseline potassium values were evaluated for each of the clay minerals being studied (Table 5.2). The results confirmed high amounts of potassium in IMt-1 and negligible amounts of potassium in KGa-1b, NAu-2, and STx-1b. These results were to be expected on the basis of characterization data from the Clay Minerals Society (van Olphen and Fripiat, 1979). VTx-1, however, was 20 mg K g clay^{-1} which far exceeded the trace amounts of potassium it was supposed to have according to source clay characterization data. This high potassium likely explains the unusual x-ray diffraction patterns obtained for VTx-1 (Figure 5-13**).** Magnesium saturated and air-dried vermiculites should have a strong 14.5 Å d-spacing, which this particular sample of VTx-1 has. However, it also has a strong 12 Å d-spacing which is indicative of a vermiculite that has been potassium saturated and air dried. The vermiculite sample, unlike the rest of the reference clays, was not obtained directly from the Clay Minerals Society, but rather through an intermediate, uncertain whether or not the sample had been previously processed in any manner other than grinding. Thus, it may have been that the particular sample of VTx-1 used had been previously treated with potassium.

Table 5.2 Potassium contents of clay minerals prior to potassium treatment and after potassium treatment for both unaltered and reduced samples. Standard deviations are in parentheses.

ID	Potassium contents (mg K*g clay^{-1})		
	Prior to K treatment. N = 2.	After K treatment. Unaltered samples. N = 4.	After K treatment. Reduced samples. N = 4.
BEL	20 (2)	17 (1)	17 (3)
CHE	13 (2)	12.1 (0.6)	13 (1)
IMt-1	56.7 (0.3)	60 (3)	59 (3)
KGa-1b	0.0 (0.3)	1 (1)	0.2 (0.4)
NAu-2	0.2 (0.3)	1 (1)	7 (3)
STx-1b	0.2 (0.2)	3 (3)	3 (2)
VTx-1	20 (1.3)	21 (3)	31 (2)

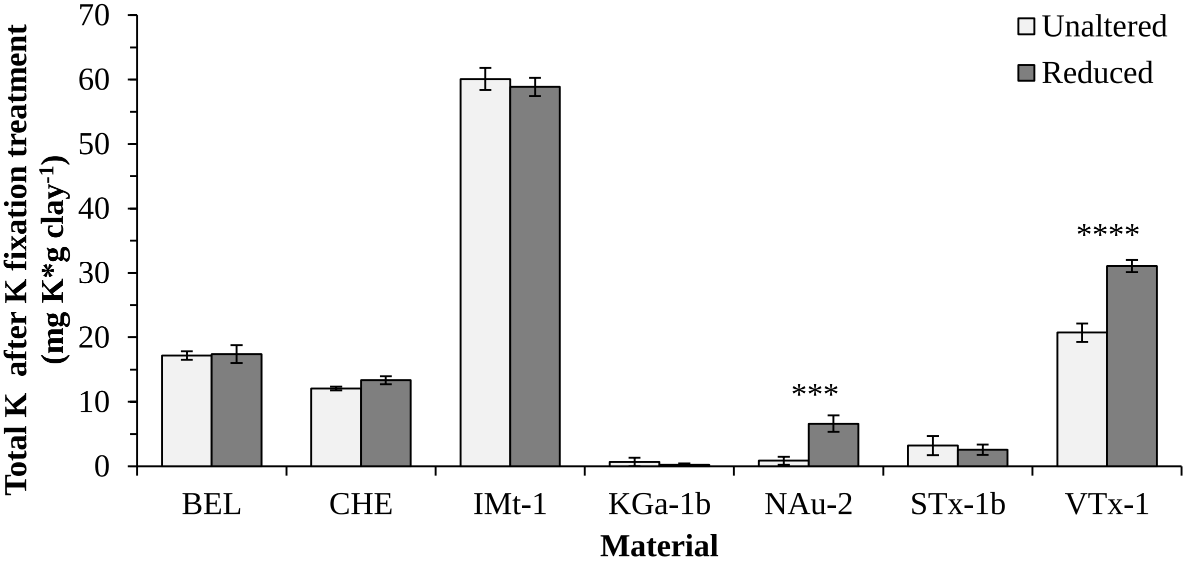
Figure 5-13 Expanded XRD pattern of VTx-1. Mg-25 treatment. V=vermiculite.



Baseline results also indicated that BEL contained more potassium than CHE which is consistent with the conclusion that BEL contained more mica than CHE. These results also supported the idea that the Cherokee site is more highly weathered than the Belvue site as CHE had less reserve potassium than BEL.

There was no effect on the amount of potassium fixed as a result of reduction for all of the clay samples containing less than six percent iron (Figure 5-14). There was however a highly significant effect for the clay samples containing more than six percent iron—NAu-2 and VTx-1.

Figure 5-14 Mean total potassium content (± SEM) in different clay mineral samples unaltered and reduced after potassium fixation treatment. N = 4.



Significances are indicated as follows: * P < 0.05; ** P <0.01; *** P<0.001; **** P<0.0001.

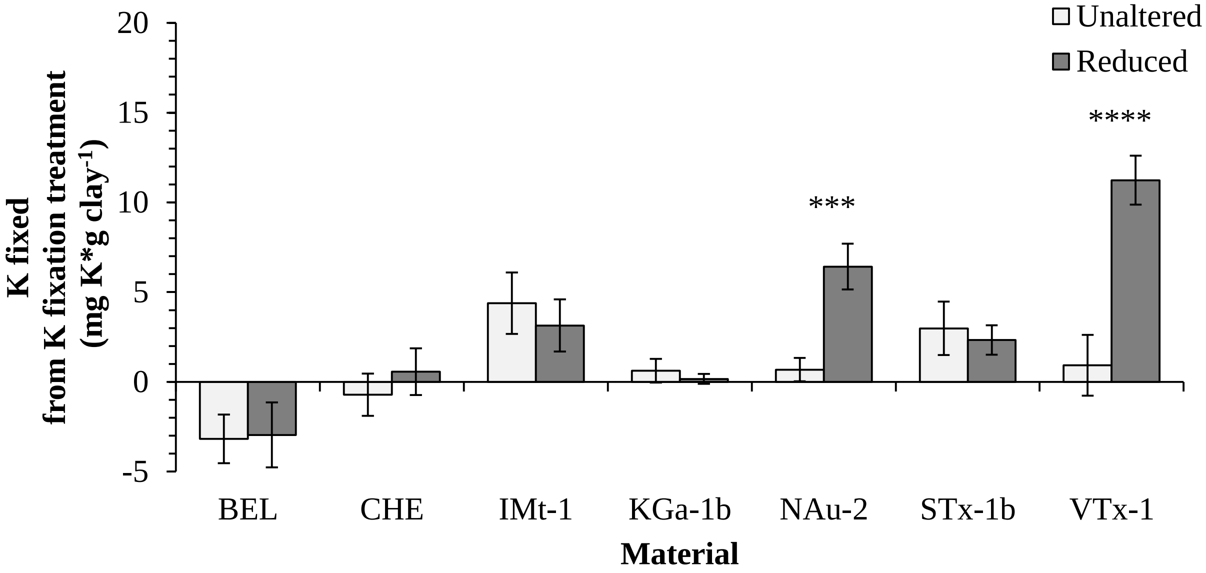
In order to better understand these data, it is helpful to subtract off the baseline amount of potassium—i.e., the amount of potassium that was in the sample prior to any treatment. This allows a distinction to be made between the potassium that was already in the sample and the potassium that was fixed by the fixation treatment (Figure 5-15). For example, referring to Figure 5-14 alone, we might infer that IMt-1 is capable of fixing the most potassium of any of the clays tested. While IMt-1 certainly contained the most fixed potassium, it did not fix the most potassium. Most of the fixed potassium being measured in IMt-1 was there prior to the addition of any potassium.

The clay that actually fixed the most potassium under this particular experimental setup was VTx-1 in the reduced form, followed by NAu-2 in the reduced form. Even though neither of these minerals fixed much potassium in the unaltered form, they fixed the most potassium of any clay mineral in the reduced form. The amount of potassium fixed increased by nine-fold for

NAu-2 with reduction and twelve-fold for VTx-1 with reduction. Of the other reference minerals, KGa-1b fixed the least, fixing essentially no potassium, and STx-1b and IMt-1 fixed intermediate amounts of potassium.

Of the soil clays, BEL consistently released potassium rather than fixed it, and CHE sometimes released small amounts of potassium and sometimes fixed small amounts of potassium. There was no statistically significant effect of iron reduction on potassium fixation for either of the soil clays under this particular experimental setup.

Figure 5-15 Potassium fixed (± SEM) from potassium fixation treatment for different clay minerals unaltered and reduced.



Significances are indicated as follows: * P < 0.05; ** P <0.01; *** P<0.001; **** P<0.0001.

While the potassium concentrations of the magnesium chloride washes were saved and measured for the purpose of confirming that all solution and exchangeable potassium had been removed, their values lend some unanticipated insight into the relationship between iron oxidation state and potassium fixation and release (Table 5.3). While in most situations, the large bulk of potassium removed was removed after three washes with magnesium chloride, this appeared to be generally less true for the reduced samples as compared to the unaltered samples. This was especially pronounced for NAu-2. In the unaltered sample, the fourth and fifth wash yielded an average of 5 and 1 mg K g clay^{-1} whereas in the reduced sample, they yielded an average of 18 and 6 mg K g clay^{-1}, respectively.

Table 5.3 Mean amount of potassium removed by five successive washes with 50 mL of 0.5 M $MgCl_2$. N=4. Standard deviations are in parentheses.

ID	Unaltered, wash number (mg K*g clay^{-1})					Reduced, wash number (mg K*g clay^{-1})				
	1	2	3	4	5	1	2	3	4	5
BEL	203 (37)	5 (1)	0.28 (0.06)	0.04 (0.03)	0 (0)	228 (26)	17 (7)	3 (1)	1.4 (0.5)	1.2 (0.4)
CHE	234 (26)	7.0 (0.9)	0.8 (0.9)	0.2 (0.2)	0.06 (0.07)	285 (11)	23 (6)	3 (2)	2 (1)	2 (1)
IMt-1	239 (5)	9.7 (0.8)	2.3 (0.3)	2.6 (1.3)	0.4 (0.3)	182 (51)	15.7 (0.5)	1.5 (0.1)	0.7 (0.1)	0.66 (0.08)
KGa-1b	229 (14)	4 (3)	0.8 (0.6)	0.02 (0.03)	0 (0)	181 (61)	4 (2)	0.5 (0.2)	0.2 (0.4)	0.37 (0.03)
NAu-2	330 (49) [a]	26 (2)	5 (3)	1 (2)	0.92 (0.09)	452 (29)	98 (26)	19 (8)	18 (9)	6 (4)
STx-1b	285 (12)	7 (5)	0.7 (0.1)	0.3 (0.2)	0.08 (0.08)	285 (32)	50 (21)	5 (2)	3 (1)	1.7 (0.9)
VTx-1	221 (19)[b]	7 (1)	1 (0.3)	0.5 (0.1)	0.28 (0.04)	273 (46)	42 (3)	4.8 (0.4)	2.9 (0.2)	1.6 (0.2)

[a] N=2. Outliers due to mechanical error omitted.

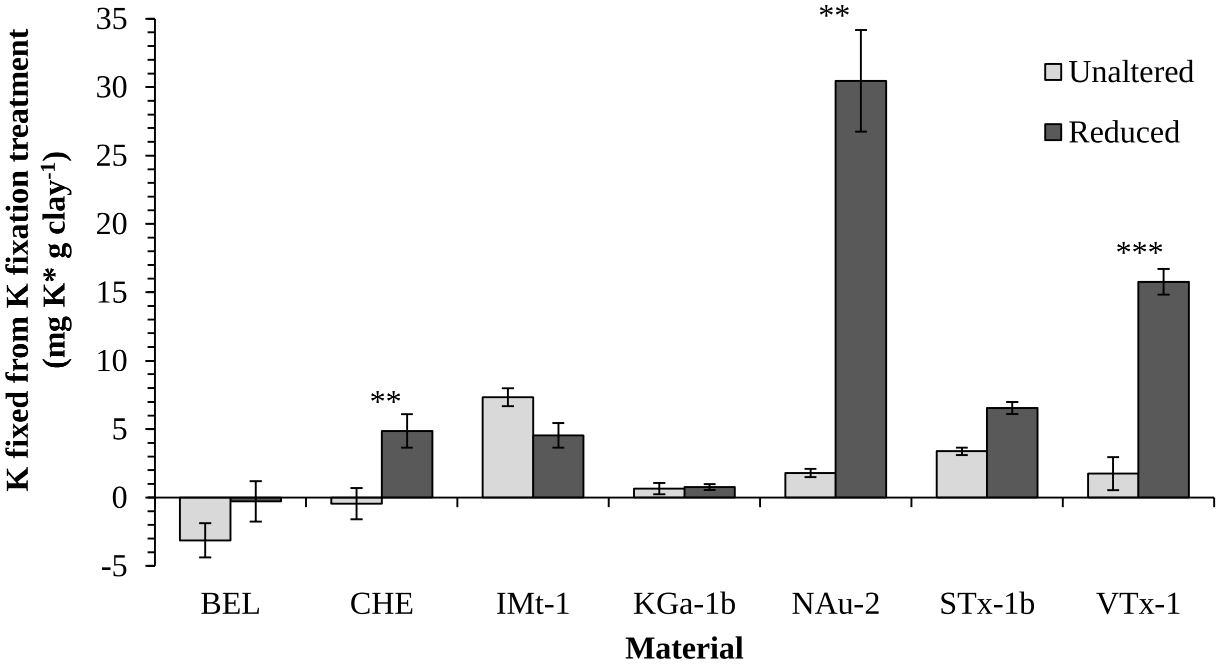
[b] N=3. Outlier due to mechanical error omitted.

One interpretation might be that the five magnesium chloride washes were too weak to effectively remove all the exchangeable and solution potassium. However, five washes with magnesium chloride were more than sufficient in removing this fraction in the unaltered samples. Another interpretation might be that reduction increased negative layer charge which increased either the tenacity with which potassium was held or the amount of potassium that could be held, which would lead to more potassium appearing in the later wash solutions and more potassium appearing in the wash solutions in general.

Yet another intriguing interpretation is that the washing process is oxidizing reduced iron, reversing the effects of reduction and causing the clay minerals to yield up their recently fixed potassium. If this last interpretation is the case, it may be that this study missed possible differences caused by iron redox changes on potassium fixation. If for example, only three washes were made, there might have been more significant differences between the amounts of potassium fixed by the unaltered and reduced versions of different clay minerals.

In order to see if this might have been the case, the amounts of potassium in the fourth and fifth washes were added to the amounts of fixed potassium calculated for each sample (Figure 5-16). Interestingly, stopping at the third magnesium chloride wash would have made the effect of reduction significant for CHE—increasing the amount fixed from about 0 to 5 mg K g clay^{-1}. Additionally, in this hypothetical scenario NAu-2, not VTx-1, fixed the most potassium. While all the clays appear to fix more when subjected to three washes instead of five, the relative rankings of different unaltered and reduced clay minerals in terms of potassium fixation remains roughly the same, with the exception of reduced NAu-2 and VTx-1.

Figure 5-16 Amount of potassium that would have been fixed (± SEM) from potassium fixation treatment for different clay minerals unaltered and reduced if there had only been three washes with magnesium chloride solution.



Significances are indicated as follows: * P < 0.05; ** P <0.01; *** P<0.001; **** P<0.0001.

Synopsis

The results obtained are highly consistent with study expectations. NAu-2 and VTx-1 were the most responsive to structural iron reduction in terms of potassium fixation, which is consistent with the fact that they had the most iron to reduce and subsequently the greatest increases in ferrous iron with reduction.

Despite VTx-1 having the lesser increase in ferrous iron, each unit gain in ferrous iron resulted in much larger increases in potassium fixation than it did for NAu-2. Since VTx-1 had all of its structural iron in the tetrahedral sheet and NAu-2 had almost all of its iron in the octahedral sheet, this observation is consistent with the fact that interlayer cations are more strongly attracted to negative charge derived from the tetrahedral sheet than the octahedral sheet.

IMt-1, KGa-1b, and STx-1b were not significantly affected by reduction in terms of their potassium fixation. This was not unexpected as these three clay minerals experienced the smallest gains in ferrous iron of all the soil clays tested.

KGa-1b fixed essentially no potassium which was appropriate because KGa-1b has an inaccessible interlayer due to hydrogen bonding. While IMt-1 and STx-1b fixed comparable, intermediate amounts of potassium, they probably did so for different reasons. IMt-1 has a relatively large negative layer charge but much of this negative charge is already satisfied by existing fixed potassium, which suggests that not as many fixation sites are available as would be expected on the basis of layer charge alone. STx-1b also has a relatively large negative layer charge but no existing fixed potassium. Thus it might be expected that it would fix much more than IMt-1. However STx-1's charge is derived entirely from the octahedral sheet and therefore is not as effective at attracting interlayer cations as charge derived from the tetrahedral sheet.

In the unaltered form IMt-1 and STx-1b fixed more than NAu-2 and VTx-1. Comparing their theoretical layer charges based on structural formulas, IMt-1 and STx-1b have much greater negative layer charges than NAu-2 and VTx-1, which could explain their greater potassium fixation capacity in the unaltered form (Table 5.4). Additionally, not only did NAu-2 and VTx-1 fix less than IMt-1 and STx-1b in the unaltered form, they essentially fixed no potassium. Accounting for the pre-existing interlayer potassium in VTx-1, NAu-2 and VTx-1 both actually had positive layer charges, which may have been the reason they fixed virtually no potassium in the unaltered form. There was no negative charge to attract them.

Table 5.4 Theoretical charge magnitudes and distributions of 2:1 reference phyllosilicates based on structural formulas.

ID	Charge per formula unit		
	Octahedral	Tetrahedral	Total
IMt-1	-0.43	-1.23	-1.66
IMt-1 (with initial interlayer K)	-0.43	-0.07	-0.50
NAu-2	+0.92	-0.43	+0.49
STx-1b	-2.96	-0.00	-2.96
VTx-1	+0.02	-0.29	-0.27
VTx-1 (with initial interlayer K)	+0.02	+0.12	+0.14

Charges calculated off of structural formulas minus exchangeable and fixed cations. Adjustments were additionally made for IMt-1 and VTx-1 to account for the large amounts of potassium in the structures neutralizing the negative charge of the tetrahedral sheet.

As for the soil clays, it was expected that CHE would fix more than BEL, having the more unpredictable potassium behavior in the field. In the initial design of the experiment it was hypothesized that if there was an effect of reduction on the potassium fixation of the soil clays, the effect would be more pronounced for CHE because of the extreme temporal fluctuations in soil extractable potassium observed in the field from which the CHE sample was taken.

While CHE did not appear to fix all that much potassium, BEL released much more potassium than CHE, indicating that BEL had more readily available fixed potassium—an observation consistent with the mineralogical observation that BEL was less weathered and the total potassium results indicating that BEL contained more reserve potassium than CHE. While after five washes with $MgCl_2$ there was no appreciable effect of reduction on either of the soil clays, if the number of washes would have been confined to three, there would have been a significant effect of reduction on the potassium fixation of CHE. In the scenario where only three washes with $MgCl_2$ were used, CHE fixed no potassium in the unaltered form and an average of 5 mg K g clay^{-1}in the reduced form.

Chapter 6 - Discussion

Experimental limitations

There are quite a few limitations associated with this study in terms of interpreting the data. The greatest limitation exists in the difficulty of extrapolating lab measurements to predict field behavior. The source of this limitation is many-fold and includes the following aspects:

Grinding of specimen clays. It was necessary to grind some of the reference clay minerals in order to obtain particles less than two microns in diameter. Ground particle edges, however, behave different from naturally weathered edges—e.g., compared to naturally weathered particles, ground particles weather more rapidly (Scott and Amonette, 1988).

Use of specimen clays to draw conclusions about mixtures of soil clays. While the specimen clays used were selected for their similarities to the clays present in temperate soils, soil clays do not behave exactly in the same way as specimen minerals of the same type (Richards and McLean, 1963; Robert, 1986)). Different clays of the same general type can vary widely in terms of their cationic composition, which brings about variations in layer charge and bond geometry which in turn affect the energy with which potassium is held between collapsed clay layers (Rich, 1968). Nonetheless, it is reasonable to assume that there is generally less variation within clay mineral classification groups than between them in terms of potassium fixation.

Use of chemical reduction instead of biological reduction. In field situations, structural iron is never naturally going to be reduced by sodium dithionite. Rather, in soil environments, microorganisms are the agents of structural iron reduction. While chemical reduction and biological reduction alter clay physical properties in similar ways, their effects on clay properties are not entirely equivalent. For example, bacterial reduction occurs preferentially around the edges of each clay layer, whereas chemical reduction—specifically reduction by dithionite—occurs evenly throughout the octahedral layer (Ribeiro et al., 2009). Additionally, while microbial reduction of structural iron can be extensive under optimum conditions and given sufficient time, chemical reduction is much more aggressive in terms of reaction rate and extent (Ernsten et al., 1998; Kostka et al., 1999b). Thus, chemical reduction is not wholly analogous to bioreduction and care should be taken to not over-analogize the effect of chemical reduction in the laboratory onto the effect of biological reduction in the field on potassium fixation.

Use of a single reduction event rather than exploring the effect of redox cycles. The study fails to capture that in field situations structural iron in phyllosilicates will cycle between the ferrous and ferric form. Though the effect of reduction on potassium fixation can be somewhat reversed through re-oxidation the reversals documented are not perfect, likely because re-oxidized phyllosilicates are not precisely the same as their unaltered counterparts (Khaled and Stucki, 1991; Shen and Stucki, 1994; Stucki, 2011). During structural iron reduction, there can be extensive octahedral sheet dehydroxylation as well as cationic rearrangements in the octahedral sheets to form trioctahedral domains. Many of these changes are irreversible with the degree of irreversibility proportional to the initial extent of reduction (e.g., Fialips et al., 2002a or b; Lee, 2007; Lee et al., 2006; Neumann et al., 2010; Ribeiro et al., 2009; Stucki et al., 2002; Vodyanitskii, 2007). Thus, while it may be tempting to use the potassium behavior of the unaltered samples as proxies for the potassium behavior of reduced and then re-oxidized samples, there are enough differences between the two to make drawing this analogy inappropriate.

Re-oxidation during magnesium chloride extractions. Since there was no effort to deoxygenate the magnesium chloride wash solutions and minimal attempt to protect the samples from exposure to the air during these washes, this process undoubtedly re-oxidized some of the reduced iron in the phyllosilicates. A hypothetical scenario was calculated in which only three washes were used and the conclusions drawn from that scenario were different than the ones drawn from the five wash scenario—a discrepancy most likely caused by differing levels of re-oxidation. In hindsight it would have been useful to determine the extent to which the $MgCl_2$ washing procedure re-oxidized reduced iron and perhaps better to have stopped at three washes to minimize re-oxidation while still removing the bulk of solution and exchangeable potassium.

Much of the recommended future research in this area would be to address these limitations as to better comment on the effects of clay mineralogy and structural iron oxidation state on potassium behavior in field settings. For example, it would be valuable to do a similar study to this one but to use microorganisms as the reducing agents rather than sodium dithionite. It would also be of interest to investigate the effect of several redox cycles on potassium fixation, which would require an oxidation step, preferably one mimicking natural oxidation processes that would occur in field settings.

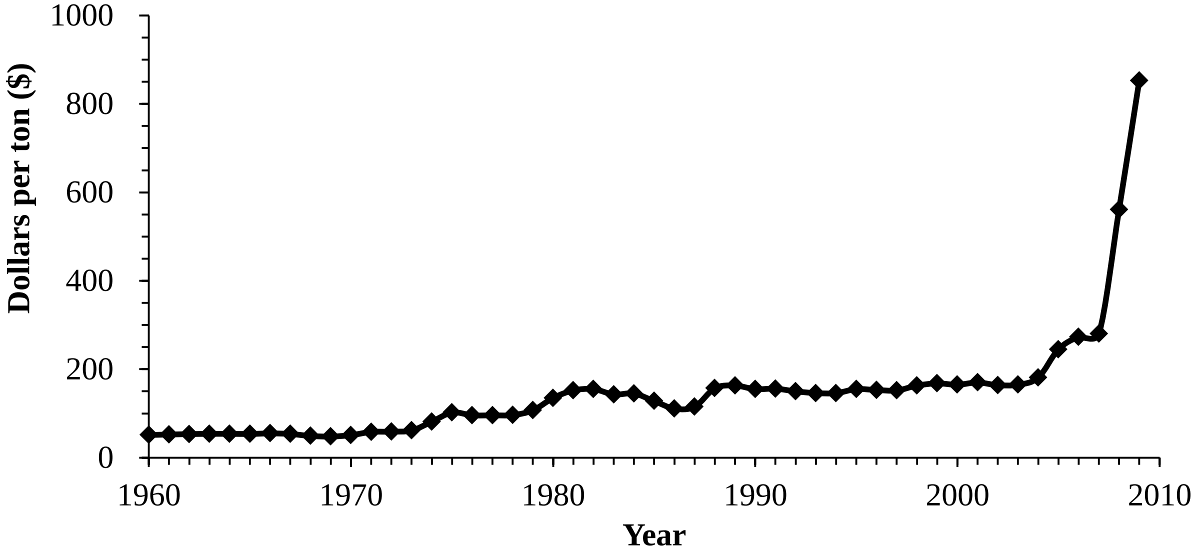
Broader impacts

Understanding how soils fix and release potassium will become increasingly crucial to advances in soil potassium fertility as soil potassium reserves are mined down and potassium fertilizer prices rise. However, the factors governing potassium fixation and release inform more than simply soil potassium dynamics. Potassium fixation is in many ways analogous to both ammonium and cesium fixation. Subsequently understanding of the factors governing potassium fixation and release can be used to inform understanding of ammonium availability and mobility in agricultural systems and radioactive cesium mobility and retention in nuclear waste storage facilities. Additionally, the factors governing potassium fixation and release are virtually the same as the factors governing layer silicate collapse and expansion and the decontamination or degradation of various hazardous materials by clays is largely a function of the accessibility of interlayer spaces to these compounds. Thus, not only can an understanding of the factors governing potassium fixation guide nutrient management decisions, it can also guide the engineering of waste barriers and the remediation of contaminated sites.

Nutrient dynamics

Potassium is an essential nutrient for plant development, and in recent years, an increasingly expensive fertilizer input (Figure 6-1).

Figure 6-1 Average U.S. farm prices for KCl.



Source data from USDA-ERS.

Across the United States, soil extractable potassium values have been observed to fluctuate throughout the year and from year to year without apparent cause. The inability of agricultural producers to understand and anticipate these fluctuations poses a significant nutrient management issue in some regions. Potassium fertilizer recommendations are based on soil extractable potassium values and inexplicable, sudden variations in soil extractable potassium can make it difficult to accurately make fertilizer recommendations.

This project was initiated because of dramatic and perplexing fluctuations in soil extractable potassium observed specifically in southeast Kansas. While fluctuations in soil extractable potassium are often generally attributed to potassium fixation and release phenomena, no attempt has been made to specifically explain how fixation and release could drive temporal fluctuations in soil extractable potassium. For example, it is unclear as to why some soils demonstrate these mysterious swings in extractable potassium and others do not.

The two research sites used in this study were selected on the basis that they were very similar in terms of physical, chemical, and mineralogical properties, but varied markedly in terms of their potassium behavior. The characterization of the two soil clays fractionated from these sites offer insight into some of the possible mechanisms behind their different extractable potassium behaviors.

BEL consistently released rather than fixed potassium while CHE tended to release potassium in the unaltered form and fix potassium in the reduced form. This seems consistent with the Belvue site exhibiting relatively stable extractable potassium behavior and the Cherokee site exhibiting puzzling fluctuations in soil extractable potassium.

It seems highly likely on the basis of a variety of pieces of evidence that the Cherokee site is more highly weathered than the Belvue site. While the Belvue sample had some feldspar minerals in its silt fraction, the Cherokee only had quartz. While their clay fractions were similar, BEL had more mica and smectite in its clay fraction while CHE had more kaolinite and quartz. BEL also contained more potassium than CHE—presumably in the form of native, interlayer potassium.

Thus, it seems that the relatively less weathered Belvue soil is more able to buffer losses in extractable potassium by potassium release than the more highly weathered Cherokee soil. Not only does the Belvue clay fraction contain more potassium and more readily yield its potassium, the silt fraction also likely contains reserve potassium in the form of potassium feldspars. The

Cherokee soil is not only less able to buffer extractable potassium losses due to its relatively low amounts of reserve potassium, the clay fraction of the soil seems to additionally be inclined to fix substantial amounts of potassium in the reduced condition. Furthermore, this fixed potassium can be released upon re-oxidation. This ability to alternately fix and release potassium depending on oxidation-reduction conditions seems like a feasible driver of temporal fluctuations in soil extractable potassium.

Structural iron reduction in field settings is almost always biotically induced. Subsequently, reduction can only occur if the following parameters are met: presence of organic matter and anaerobic microorganisms, and absence of oxygen, nitrate ions, and manganese oxides (Stucki, 1988). The Cherokee soil certainly has organic matter. Being poorly drained, the Cherokee soil also regularly experiences anaerobic conditions. While the Cherokee site most likely has nitrate ions and manganese oxides, which are preferentially reduced before structural iron, it seems likely that their quantities would be much less than the quantites of iron in the soil. While anaerobic iron bioreducing microorganisms have not been specifically cultivated from the Cherokee site, they have been cultivated from such a wide range of sources including agricultural fields that it seems likely that these organisms do exist at the Cherokee site (Dong et al., 2009).

Bioreduction is optimized between a pH of 5 and 6 and by the addition of carbon sources (Bishop et al., 2010; Kostka et al., 1996; Kostka et al., 1999a). The upper 15 cm of the Cherokee site had a pH of 5.5 in calcium chloride and 6.3 in water, and according to word of mouth, there may have been a historical application of poultry litter to the Cherokee site. Furthermore, the fact that soil extractable potassium levels vary inexplicably over time in only some regions suggests that the factors driving these fluctuations need to vary regionally and temporally. Clay mineralogy ranges significantly regionally and soil redox conditions can vary signficantly temporally. While none of these coincidences indicate any relationship between structural iron oxidation state changes and fluctuations in soil extractable potassium, they certainly indicate the feasibility of such a relationship.

In order to test the actuality of iron redox changes driving extractable potassium fluctuations in the field, it would be useful to take regular redox potential readings along with regular soil samples at a large group of sites to see if potassium behavior moves in concert with changes in soil redox conditions. In addition to testing the soil samples for extractable potassium, it would be advantageous to also evaluate their potassium fixation capacity to see how that changes in reference to soil extractable potassium changes. The expectation would be that in an isolated system, as fixed potassium goes up, extractable potassium should go down and vice versa.

Pollutant dynamics

Different clay minerals are capable of both trapping and transforming different pollutants—e.g., radioactive cesium. The factors affecting potassium fixation also affect the ability of different clay minerals to trap and/or transform different pollutants. The ability of clay minerals to transform pollutants is a function of both their iron content and expandability. The more expansive a clay mineral is, the easier it is for pollutants to become adjacent to structural iron which can transform the pollutant through coupled oxidation-reduction reactions.

Cesium fixation and potassium fixation are quite analogous in terms of mechanism and effects, and thus the factors governing potassium fixation and release may also govern cesium fixation and release[5]. Cesium-137 composes much of the activity of nuclear waste. Nuclear waste is often stored in such a way that it is surrounded by 2:1 clay minerals with the intention that the 2:1 clay minerals will either slow or stop the movement of radioactive cesium from the disposal site. One method to store nuclear waste is to place it in canisters in excavated rock formations and backfill both the canisters and bore hole with expandable 2:1 clay minerals (Anastácio et al., 2007). Another method is to discharge the waste into rock formations containing large amounts of 2:1 clay minerals. For example, at Oak Ridge National Laboratory, intermediate-level waste was discharged into a formation of shale composed of predominately illite (Jacobs and Tamura, 1960).

It is not clear whether a particular type of clay mineral would be better than others as a nuclear waste storage barrier. Currently, smectites are used the most widely because of their large CEC and their swelling properties which allow for the swelling and filling of fractures when hydrated by field leakages. However illite, despite its lower CEC, is more highly selective for cesium and has been argued to be potentially the superior barrier mineral (Tamura and Jacobs, 1960; Meunier and Velde, 2004). Though vermiculite is considered widely to fix cations

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[5] Though cesium fixation and potassium fixation have been shown to be analogous in many ways, there is also evidence that their fixation release rules vary in some significant ways (Coleman et al., 1963b).

in the greatest quantities, it has been little considered as a barrier material for nuclear waste. The efficacy of using vermiculite to retain radioactive cesium should be further investigated. While all of these clay minerals have some sort of retention capacity for cesium, it is uncertain that this retention would be sufficiently long in duration for the decay of the radioactivity. Thus, understanding the factors governing release is as important as understanding the factors governing fixation.

Under natural storage conditions, the 2:1 clay minerals surrounding nuclear waste are subjected to redox cycles. It is unknown how redox cycles affect the long-term stability of the clay minerals as a barrier material (Anastácio et al., 2007). Thus, in addition to the need for more research pertaining to the cation fixation and release behavior of different clay minerals, more needs to be understood about the effects of redox cycles on cesium fixation and release behavior. While what has been learned about potassium fixation of different clay minerals in different redox conditions should not be used in lieu of independent study about cesium fixation, it can be used as a framework with which to begin to understand cesium fixation by different materials in different conditions.

To understand the factors governing potassium fixation and release is also to understand in large part the factors governing phyllosilicate collapse and expansion. The expansibility of phyllosilicates determines the accessibility of various pollutants to phyllosilicate structural iron. Structural iron in phyllosilicates is capable of transforming a variety of environmentally hazardous materials—e.g., hexavalent chromium, radioactive elements such as technetium and plutonium, and a wide array of chlorinated organics—into immobile forms, less hazardous forms, and non-hazardous forms via coupled iron redox transformations (e.g., Cervini-Silva et al., 2000; Hixon et al., 2010; Kocherginsky and Stucki, 2000; Lee, 2004; Lee and Batchelor, 2003; Neumann et al., 2009; Sorenson et al., 2004; Tor et al., 2000; Yan and Bailey, 2001). The more expansible the phyllosilicate is, the greater the surface area and the greater the rate and extent of coupled redox transformations (e.g., Bishop et al., 2011; Kostka et al., 1999). Thus understanding of the factors governing phyllosilicate expansion and collapse can be used to help understand the factors governing the kinetics of these coupled redox transformations.

Coherent theory of potassium fixation

While potassium fixation has been variously defined, most authors agree that the fixation of potassium is associated with the entrapment of potassium in dehydrated, collapsed interlayer spaces in 2:1 phyllosilicates (Rich, 1968). While there are numerous documented factors affecting potassium fixation, at its core, potassium fixation is the result of forces of contraction exceeding expansion forces in 2:1 phyllosilicates.

Expansive forces include the presence of hydroxy-interlayers, interlayer water molecules, interlayer large organic cations, et cetera. One way to facilitate fixation is to decrease or remove these forces of expansion. For example, by dehydrating the interlayer via drying, the expansive force of interlayer water molecules can be removed from the system.

Alternatively, fixation can be facilitated by increasing the forces of contraction. Clay layers collapse either due to the lack of expansion forces or due to van der Waal's forces of attraction exceeding the force of expansion. The strength of van der Waal's forces lies in the proximity of clay layers to each other and the proximity is controlled by the coulombic force of attraction of interlayer cations for interlayer surfaces. The greater the attraction, the closer the cation is held to the interlayer surface. The closer the cation is held, the closer an adjacent clay layer can approach. The closer adjacent clay layers become, the stronger van der Waal's force becomes. If van der Waal's force can exceed the forces of expansion, then the clay layers will collapse. This is why cations with high energies of hydration and large hydrated ionic radii are not appreciably fixed. It is difficult to overcome the distance that these large hydrated cations place between clay layers and the energy with which they hold onto their surrounding water molecules.

The coulombic force of attraction of interlayer cations for interlayer surfaces is in turn a function of layer charge, charge location, and bond geometries in the phyllosilicate. Increased layer charge equates increased attraction between interlayer cations and interlayer surfaces. Tetrahedrally-derived negative charge is more effective than octahedrally-derived negative charge at attracting interlayer cations as a result of its proximity to the interlayer surface. Similarly, bond geometries—particularly the hydroxyl group orientations of the octahedral sheet, which are largely a function of cationic occupancies in the octahedral sheet—affect the attraction of interlayer cations for interlayer surfaces by controlling the nearness with which interlayer cations can approach negative layer charge.

Variation observed in the potassium fixation capacities of the clays in this study can be largely explained by variations in layer charge and charge location. Greater negative charges were associated with greater levels of fixation because greater negative charges meant increased attraction for interlayer cations. NAu-2 and VTx-1 fixed little potassium in the unaltered form when they had little to no excess negative charge, but great amounts in the reduced form when electronic gains presumably lead to increases in negative charge. The gains in fixation were greater for VTx-1 per unit increase in ferrous iron than for NAu-2. This was presumably partially due to the tetrahedral location of iron in VTx-1 as compared to the octahedral location of iron in NAu-2.

Tetrahedrally derived charge was associated with greater fixation than octahedrally derived charge. This was evidenced by STx-1b which had the most excess negative charge of all the reference clays and yet only fixed moderate amounts of potassium. This was likely due to all the negative charge in STx-1b being derived from the octahedral layer. While IMt-1 had substantial amounts of negative charge in the tetrahedral layer, it most likely only fixed moderate amounts of potassium because much of its negative charge was already satisfied by fixed interlayer potassium.

Potassium fixation can be thought of most simply as the forces of lattice contraction exceeding the forces of lattice expansion with potassium ions in the interlayer space. Most of the documented factors affecting potassium fixation and release can be understood entirely through their effect on those three aspects: (1) contraction force, (2) expansion force, and (3) potassium presence.

Potassium fixation and release phenomena are often used to explain fluctuations in soil exchangeable potassium. While it is possible that redox driven changes in potassium fixation are partly responsible for temporal fluctuations in soil exchangeable potassium, more work needs to be done to further test that possibility. However, it seems clear that certain sites are less susceptible to fluctuations in soil exchangeable potassium than others due to their high potassium buffering capacity. The BEL soil most likely did not experience dramatic oscillations in soil exchangeable potassium due to its relatively large amounts of reserve potassium in the form of potassium feldspars and micas, which would have rapidly buffered losses in soil exchangeable potassium. Contrast this to the CHE soil, which had relatively low amounts of reserve potassium, and would have not been able to rapidly buffer losses in soil exchangeable potassium.

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Appendix A - Compilations of geochemical data

Table A.1 Average elemental abundances of potassium in the continental crust and in soils of the USA.

Element	Continental Crust [a] (μg g^{-1})	Soil [b] (μg g^{-1})
O	$4.55 * 10^5$	$4.90 * 10^5$
Na	$2.3 * 10^4$	$1.2 * 10^4$
Mg	$3.2 * 10^4$	$9.0 * 10^3$
Al	$8.4 * 10^4$	$7.2 * 10^4$
Si	$26.8 * 10^4$	$3.1 * 10^5$
K	$9.0 * 10^3$	$1.5 * 10^4$
Ca	$5.3 * 10^4$	$2.4 * 10^4$

[a] From Faure (1991)

[b] From Shacklette and Boerngen (1984)

Table A.2 Ionic radii and enthalpies of hydration for Group I and Group II elements.

Ion	Ionic radius (Å) [a]	Hydration enthalpy (kJ*mol^{-1}) [b]	Hydrated ionic radius (Å)[c]
H^+	v. small	-1091	2.80
Li^+	0.82	-515	3.82
Be^{2+}	0.45[b]	-2487	4.59
Na^+	1.10	-405	3.58
Mg^{2+}	0.80	-1922	4.28
K^+	1.46	-321	3.31
Ca^{2+}	1.08	-1592	4.12
Rb^+	1.57	-296	3.29
Sr^{2+}	1.21	-1445	n.d.
Cs^+	1.78	-263	3.29
Ba^{2+}	1.44	-1304	n.d.

[a] From Faure (1991); C.N. = VI

[b] From Burgess (1978)

[c] From Volkov et al. (1997)

Appendix B - Alternative usages of the term potassium fixation

While the term “potassium fixation” is now generally used to indicate the entrapment of potassium ions in between collapsed clay layers, the term has been and still is occasionally used to refer more broadly to simply the removal of potassium from solution. For the sake of comprehensiveness, different mechanisms by which potassium has been documented to be removed from solutions simulating soil environments have been summarized in Table B.1.

Table B.1 Summary of alternative usages of the term potassium fixation.

Material	Phenomenon	Author(s), Year
Aluminosilicates		
Zeolites	Potassium ions occupying channel sites on the interior of zeolite structure.	Volk, 1938
Allophane	Potassium ions migrating into pores between allophanic spheres too small for larger hydrated cations to replace them.	e.g., Schuffelen and van der Marel, 1955 Moss and Coulter, 1964 Barber, 1979 Yamada and Shoji, 1982
Phosphates		
	Drying with aluminum and iron phosphates rendering aqueous potassium insoluble to extraction.	Joffe and Kolodny, 1936
	Precipitation of $K_3Al_5H_6(PO_4)_8{\bullet}18H_2O$ (taranakite) from a solution of calcium phosphates, aluminum hydroxides, and aqueous potassium.	Taylor and Gurney, 1965
	Precipitation of taranakite from a solution containing aluminum resin and potassium phosphate.	Kim et al., 1983
Sulfates		
	Formation of $KAl_3(SO_4)_2(OH)_6$ (alunite) by combining $Al_4(SO_4)(OH)_{10}{\bullet}5(H_2O)$ (basaluminite) with potassium.	Adams and Rawajfih, 1977[6]

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[6] Authors do not refer to this specific laboratory phenomenon as potassium fixation, rather Sparks and Huang (1985) in a later review of the literature do.

Appendix C - Reduction of structural iron: method development

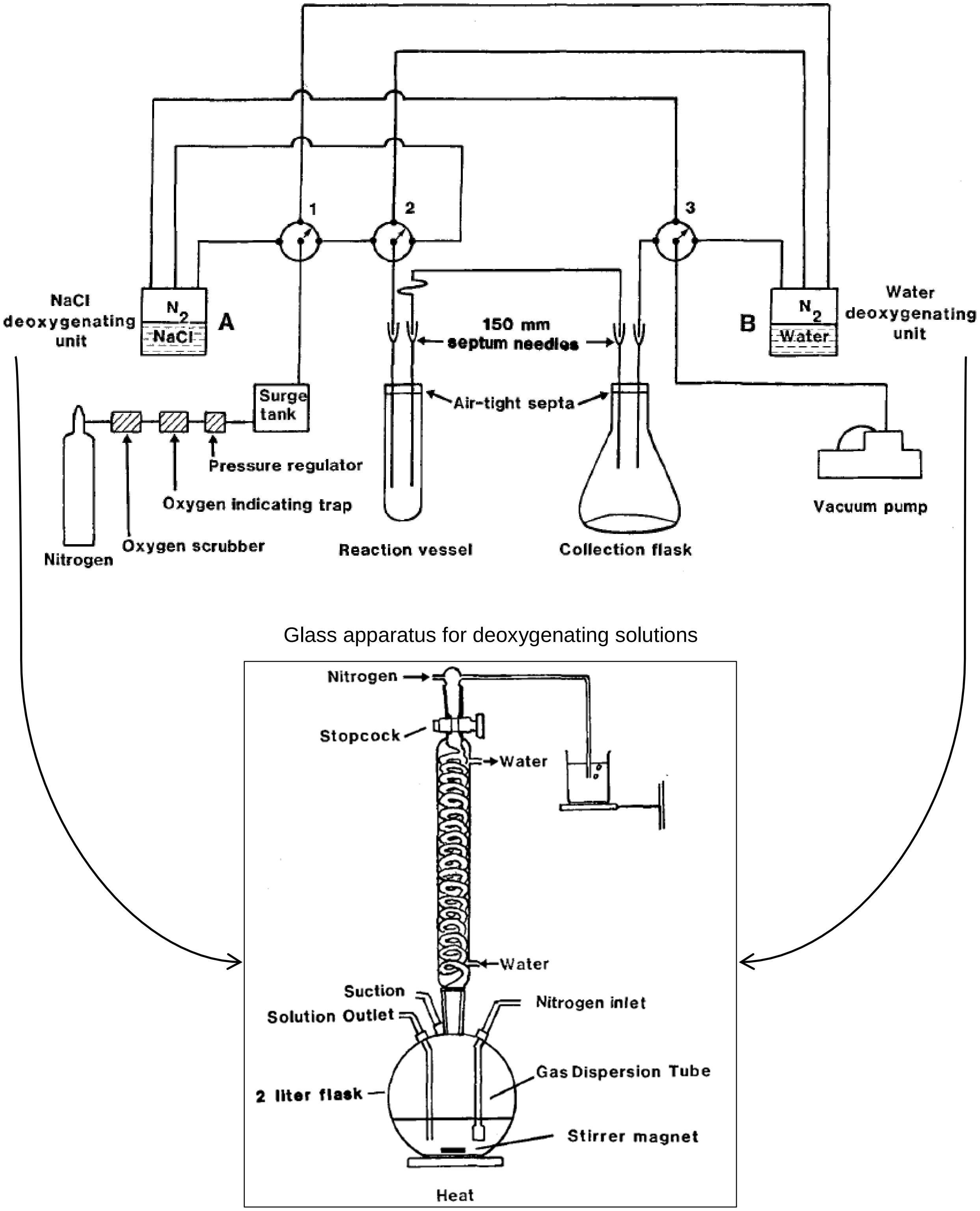
Structural iron in phyllosilicates can be reduced in a variety of ways. One of the most effective approaches and subsequently one of the most popular approaches is to chemically reduce the iron using sodium dithionite as the reducing agent (e.g., Amonette et al, 1985; Komadel et al., 1990; Komadel et al., 2006; Lerf et al., 2001; Gan et al., 1992; Rozenson and Heller-Kallai, 1976a; Rozenson and Heller-Kallai, 1976b; Stucki et al., 1984a; Stucki et al., 1996; Stucki et al., 2002).

While dithionite reduction procedures for phyllosilicates vary slightly, generally the method involves suspending the clay in a buffered solution, adding an amount of sodium dithionite, simultaneously heating the suspension and purging the suspension of oxygen with nitrogen gas, and allowing the reduction procedure to react for a set amount of time. Afterward the suspension is washed of excess sodium dithionite with deoxygenated dilute salt wash solutions under highly deoxygenated conditions.

This general procedure relies heavily on an experimental setup referred to as the Controlled Atmosphere Liquid Exchanger (CALE) which is a setup where solutions can be deoxygenated, exchanged, and collected all under inert atmosphere conditions (Figure C-1). This setup was unavailable for the experiment and thus an alternative procedure was developed. In developing an alternative procedure for structural iron reduction, it was desirable that cost and convenience be balanced with extent reduction and preservation of the phyllosilicate structure.

Since reaction temperature, reaction time, and dithionite quantity are considered the main factors controlling extent reduction (Stucki, 2006), a preliminary experiment testing the effects of each of these parameters on extent reduction was carried out. NAu-1 was selected as the reference clay to use to develop an iron reduction procedure for its high ferric iron content and lack of ferrous iron. Most reduction procedures use anywhere from 30 to 200 mg samples of freeze-dried clay. For this procedure, 50 mg samples were used to maximize sample size without using more sample than could be handled by the iron assay procedure.

Figure C-1 Schematic drawing of the apparatus for exchanging and collecting supernatant solutions under an inert atmosphere.



Modified from Stucki et al. (1984b).

Freeze-dried, Na-saturated clay samples were placed in 50 mL centrifuge tubes along with 50 mL of citrate-bicarbonate buffer, which left just a small amount of air space at the top of the vessel. The citrate-bicarbonate buffer was made in the style of Stucki (1984b). The tubes were capped and shaken gently overnight to disperse the sample, thereby maximizing reactive surfaces[7]. After dispersion, many studies directly incorporate sodium dithionite into the tube, however measuring out and transferring such small volumes of sodium dithionite accurately is difficult, so the sodium dithionite was made into solution and five milliliter aliquots of the dithionite solution were added to the vessels, filling the void in the vessel almost completely, minimizing re-oxidation. Since sodium dithionite in solution degrades over time, losing its reduction power, it is advisable to make the sodium dithionite solution immediately prior to its addition to the sample.

The amount of sodium dithionite contained in the five milliliter aliquot was varied to evaluate the effect of sodium dithionite quantity on extent reduction. In the first experiment, 100 and 600 mg were used, roughly reflecting the minimum and maximum amounts of sodium dithionite used in past iron reduction literature. In the second experiment, after determining the effect of sodium dithionite amount on extent reduction to be significant, 1200, 1800, and 2400 mg of sodium dithionite were added to the samples.

After capping the samples with the added sodium dithionite, the tubes were placed into a water bath. The temperatures used were 70°C and 90°C—reflecting the most commonly used temperature and an elevated temperature, respectively. The systems were allowed to react for either four or eight hours. In past studies, reaction times as short as thirty minutes and as long as a week have been used. It has been made clear that increasing the time from thirty minutes to four hours significantly increases the extent of reduction. Eight hours was selected as a reaction time to see if the extent of reduction associated with a four hour reaction time could be significantly improved by doubling the reaction time. A longer time period was not evaluated as it would have been prohibitive to being able to accomplish a reduction cycle in a work day.

After reduction, the samples were centrifuged at 1500 rpm for five minutes. If the supernatants were clear, they were decanted off and if they were not clear, the sample was centrifuged for 5 minutes periods at 1800 rpm until supernatants were clear and could be

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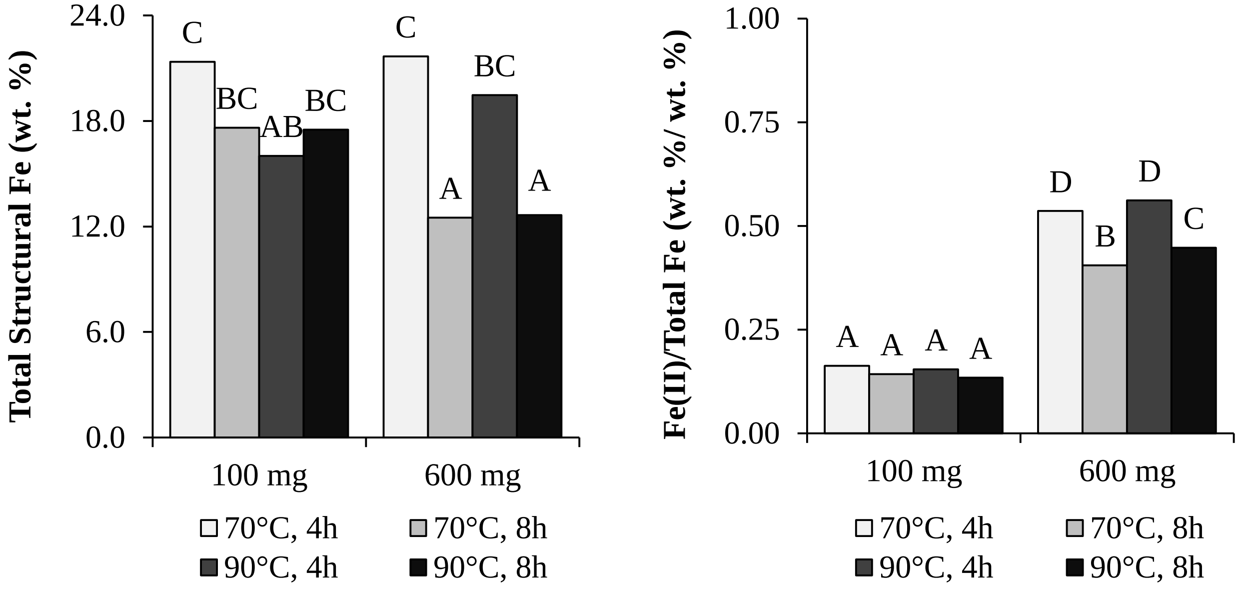
[7] In an informal side study to evaluate the effect of reducing the dispersion time to one hour, it was found that this decreased the extent of reduction.

decanted off. The samples were then transferred with a little deionized water into 125 mL amber HDPE bottles for ferrous iron and total iron analysis.

A few things stand out about the effects of sodium dithionite quantity, temperature, and reaction time on the extent of reduction on NAu-1 (Figure C-2). Before evaluating the effect of these factors on the ratio of ferrous iron to total iron, it is necessary to evaluate the effect of these factors on total structural iron preserved.

Figure C-2 Effect of sodium dithionite quantity, temperature, and reaction time on total structural iron preserved and ratio of ferrous iron to total iron. N=3. Means with different letters are significantly different (p<0.05).

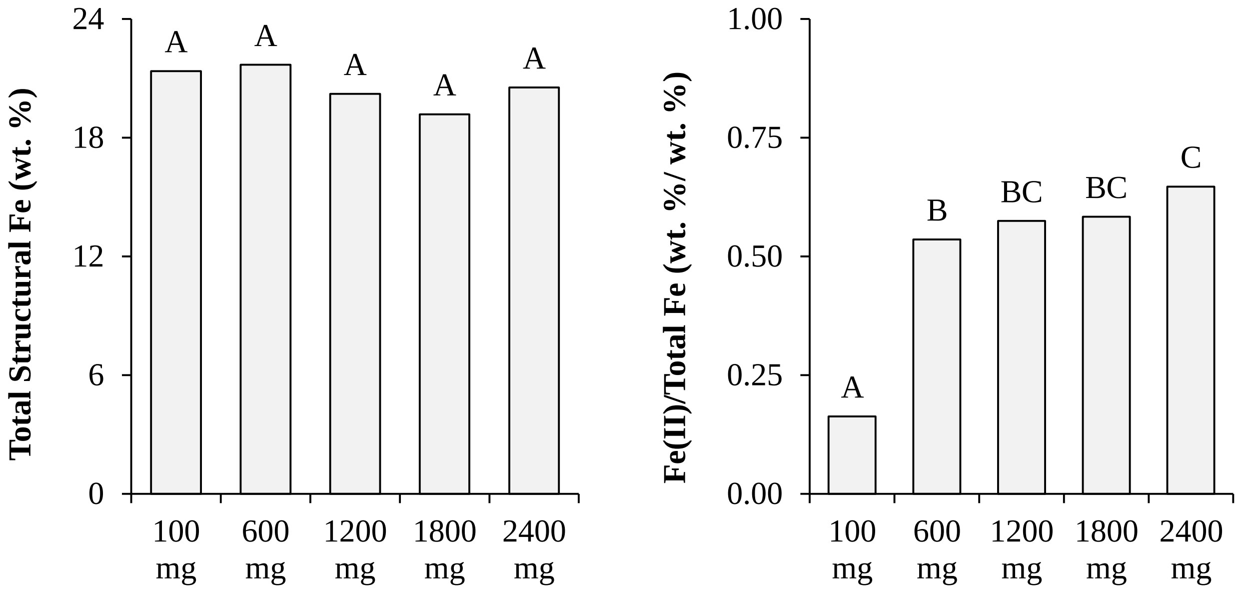


The only treatments that retained most of the initial structural iron were the treatments where the reaction temperature was kept at 70°C and the reaction time was kept at four hours. Increasing reaction time and temperature, which would have been expected to increase reduction levels, generally lead to losses in total structural iron. This could be because at greater levels of reduction, there are also greater levels of phyllosilicate dissolution.

Because it was undesirable to have significant levels of phyllosilicate reduction, a four hour reaction time and 70°C reaction temperature were chosen to be used for the project. In deciding the amount of dithionite to be used, it was helpful to compare the ratio of ferrous iron to total iron obtained by each iron weight. Increasing the sodium dithionite amount from 100 mg to

600 mg more than doubled the amount of ferrous iron in the sample without compromising the structural integrity of the sample. Since the results seemed highly sensitive to dithionite amount, greater amounts of sodium dithionite were evaluated for their effect on the amount of structural iron preserved as well as extent reduction (Figure C-3).

Figure C-3 Effect of sodium dithionite quantity on extent of reduction and total structural Fe preserved when subjected to a 4 hour reaction time in a 70°C water bath. N=3. Means with different letters are significantly different ($p<0.05$).



While, increasing the amount of sodium dithionite used all the way to 2400 mg did not appear to compromise the structural integrity of the clay sample, and it did increase the amount of ferrous iron in the sample, the gains were modest compared to the initial gains associated with increasing the amount of sodium dithionite from 100 mg to 600mg. Thus, it was decided to use 600 mg of sodium dithionite to reduce samples for the project.

It could have been that four hours was an insufficient time period for the larger sodium dithionite quantities to fully react. However, it is likely that if the time period was extended, there would have been significant levels of phyllosilicate dissolution and iron loss. Phyllosilicate dissolution was an undesirable outcome as it would have interfered with the comparison of potassium fixation of phyllosilicates in the oxidized and reduced form.