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Modelling Potassium Properties in East African Soils Using Infrared Spectroscopy

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ABSTRACT

Potassium (K) is an essential plant nutrient and is often in short supply in the highly weathered soils of East Africa. The development of effective and sustainable fertilisation strategies could be helped by developing rapid and relatively cheap methods that provide initial assessments of inherent nutrient stocks and soil K behaviour. Mid-infrared (MIR) and near-infrared (NIR) models are presented covering a range of soil K properties and K-bearing mineralogy. Initially, 90 soils from Kenya, Tanzania and Uganda were analysed for total K, SrCl₂ exchangeable K, K-release rates (β) and quantitative X-ray diffraction (XRD). Using MIR and NIR scans for each sample, as well as an additional 446 soil samples from the Winam Gulf (WG) in Kenya, key spectral components were identified using a 'Single Mixture Modelling Resolution' analysis, which were used to parameterise models using either stepwise or censored regression techniques for the measured soil K properties and K-bearing minerals in the 90 samples analysed. Stepwise regression models were fitted for K_{Total} ($R^2 = 0.90$), SrCl₂ extractable K ($R^2 = 0.68$), the release constant β ($R^2 = 0.53$), Kaolinite ($R^2 = 0.79$) and the Chemical Index of Alteration ($R^2 = 0.93$), with all models being highly significant ($p < 0.001$). Censored regression models were fitted for the K-containing minerals K-feldspar, mica and illite, along with quartz. The logSigma parameter was highly significant for each ($p < 0.001$). Models were applied to the WG soil samples, and estimates were plotted using different lithologies as variables. Potential exists for these models to act as a toolbox to assess inherent K stocks and likely K dynamics as an initial assessment in developing strategies to improve K sustainability and fertilisation practices. Models could be rerun to include newly generated MIR and NIR scans from soil surveys.

1 | Introduction

Potassium (K) is an essential plant nutrient and is depleted in many African soils due to a lack of volcanic/tectonic rejuvenation and a high degree of weathering over millions of years [1]. Nutrient mining, leaching and erosion contribute to the loss of K, especially in those soils where basement rocks and aeolian

sediments are parent materials [2, 3]. Understanding the mineralogical contribution to a soil's fertility and nutrient reserves is important for its sustainable management [4, 5]. In regions where fertiliser use is low, the potential for nutrient imbalances to occur increases, with crops removing more nutrients than are replaced [6, 7]. Natural sources of K-bearing minerals in soils include those released from parent rocks, such as mica minerals

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(e.g., biotite, muscovite and phlogopite), K-feldspars (e.g., orthoclase and microcline) and clay minerals (e.g., illite and glauconite). Potassium contained in these minerals is described as 'structural K' and generally makes up >90% of the K in soils [8].

Traditionally, four pools of K are described in soils in relation to plant uptake: (1) the water soluble and (2) exchangeable pools that are easily available to plants but make up only ~0.1–0.2% and 1%–2%, respectively, of the total K in soil and (3) the non-exchangeable and (4) structural sites which release K slowly but are important in its long-term supply [8–10]. After release through weathering, K can enter the interlayer space of 2:1 clay minerals such as illite ($(K,H_3O)Al_2(Si_3Al)O_{10}(H_2O,OH)_2$) or smectite (e.g., beidellite $M_{0.33}^{+}Al_2Si_{3.67}Al_{0.33}O_{10}OH_2$, where M^{+} represents exchangeable cations). Potassium can also be sorbed onto the surface of organic matter, where it is available for plant nutrition [11]. The presence of 2:1 clay minerals acts as a potential longer-term K reservoir by fixing and releasing K [12]. Plants may additionally obtain K through enhanced weathering caused by root exudates and K-solubilizing bacteria [13].

Significant work has been undertaken on K fertilisation in tropical regions and on highly weathered soils, with the desired intention of ensuring a sufficient supply of K to crops through manipulation of exchangeable K concentrations [7, 14]. However, without fertiliser application, plants must rely on the inherent reserves of soil nutrients and its mineralogy. Continually improving our knowledge of the K cycle is essential for understanding the productivity and sustainability of agricultural ecosystems [15] and to improve the design of management strategies to ensure efficient use of K and to secure sustainable futures for soil K reserves [9]. Supporting these developments requires a greater degree of understanding of the K-bearing mineralogy of soils. The mineralogical composition of soils is most commonly determined using X-ray diffraction (XRD) analysis [16]. However, XRD is a specialist technique available in relatively few laboratories with a commensurate unit cost that unfortunately limits its use on large datasets or archival collections, particularly in developing countries and where funding is limited.

In recent years, considerable advances have been made in the use of near-infrared (NIR) and mid-infrared (MIR) scanning to predict soil properties, particularly in conjunction with statistical modelling techniques which have included Self Modelling Mixture Resolution (SMMR), Partial Least Square Regressions (PLSRs), Artificial Neural Networks (ANNs) or Random Forest Trees (RFTs) [17–19]. The combination of these techniques provides the opportunity to substantially increase our knowledge of soil K mineralogy on a semiquantitative basis, which may feed into improved management plans for the sustainability of soil K resources. Both NIR and MIR have previously been used to predict various measures of K dynamics in soils including total and exchangeable K [18, 20, 21]. MIR provided improved predictions of exchangeable K^{+} in Brazilian soils compared to NIR [21].

This paper utilises samples from soil archives of eastern Africa from Kenya, Tanzania and Uganda to examine soil K properties and mineralogy in soils. The K-bearing species likely to be naturally encountered in the African soils and identifiable by XRD analysis include the following mineral groups: the

TABLE 1 | K-bearing and clay minerals commonly encountered in African soils.

Mineral group	Mineral subgroup	Example mineral species	General formula	%K
Feldspars	K-feldspar	Orthoclase, microcline, sanidine	$KAlSi_3O_8$	10.7–14.1*
	Plagioclase	Albite, anorthite	$NaAl_3Si_3O_8 \cdot CaAl_2Si_2O_8$	0.5 ¹
Micas	Diocathedral	Muscovite, paragonite	$KAl_2(AlSi_3O_{10})(OH)_2$	7.9–9.8*
	Triocathedral	Biotite, phlogopite, lepidolite	$K(Mg,Fe)_3AlSi_3O_{10}(OH)_2$	9.0–10.1*
Feldspathoid	Nepheline	Leucite, kalsilite	$Na_3(Na,K)[Al_4Si_4O_{16}]$	6.6
Clay minerals	Clay micas	Illite	$(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$	6.0*
	Smectites	Glauconite	$(K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2$	5.5*
	Vermiculite	Montmorillonite, beidellite, saponite	$M_{0.33}^{+}Al_2(Al_{0.33},Si_{3.67})O_{10}(OH)_2$	0.0–1.5 ²
	Kaolinite	Vermiculite	$(Mg,Fe^{2+},Al)_3(Al,Si)_4O_{10}(OH)_2 \cdot 4(H_2O)$	4.0 ³
	Chlorite	Kaolinite, halloysite	$Al_2Si_2O_5(OH)_4$	0.0–0.6 ²
		Clinchlore, chamosite	$(Mg,Fe^{2+})_5Al(Si_3Al)O_{10}(OH)_8$	0.0–0.3 ²

Note: $M_{0.33}^{+}$ in smectite formula represents exchangeable cations.

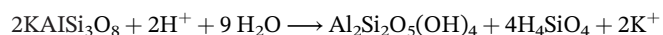
*Stoichiometric values.

¹From [70].

²From [71].

³K in vermiculite is variable, as it reflects relic chemistry formed during weathering of parent mica. Value is from [72].

feldspars, micas and clay minerals (Table 1). Feldspars, including both the K-feldspar (KAlSi_3O_8) and plagioclase ($(\text{Na,Ca})(\text{Si,Al})_4\text{O}_8$) subgroups, form a common, if minor proportion of African soils. They occur as variously sized grains but principally as silt- or sand-grade fragments formed by the weathering of underlying igneous or metamorphic basement rocks. Under prolonged acidic chemical weathering, such fragments typically show decreasing K^+ compositions with decreasing particle size [22] to eventually be replaced by clay minerals such as kaolinite [23]:



K-feldspar + water $\longrightarrow$ kaolinite + silicic acid + potassium.

Similarly, phyllosilicate mica group minerals are also often inherited from various igneous and metamorphic parent rocks. Muscovite ($\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$), biotite ($\text{K}(\text{Mg,Fe})_3\text{AlSi}_3\text{O}_{10}(\text{OH})_2$) and phlogopite ($\text{KMg}_3(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$) are the three most common mica species found in rocks and soils. Although each species has a different composition, each contains K as an interlayer cation between their 2:1 silicate structural sheets. Inherited soil phyllosilicate micas generally form silt- or clay-sized flakes, which like feldspar grains, progressively decrease in grain-size and K-content with increasing chemical weathering. Dioctahedral micas (e.g., muscovite) are more resistant to weathering than trioctahedral micas (e.g., biotite and phlogopite), and for this reason, muscovite tends to be the most common mica mineral in soils [23].

The overall aim of the work was to produce a toolbox of models based on NIR and MIR spectra that could help improve K fertilisation strategies and develop further research directions in soil K dynamics. The work involved the following steps: (i) to produce a database of soil potassium properties including K release rates and a mineralogical database using quantitative XRD in soils from eastern Africa; (ii) to use NIR and MIR scans of samples to develop models of soil K properties and K-mineralogy and (iii) to assess the suitability (potential and limitations) of the models to act as a toolbox to aid K fertilisation strategies and to help develop future research questions. This latter work was undertaken on a larger dataset of soil samples from the Winam Gulf (WG) in Kenya. The use of rapid semi-quantitative assessments of soil K dynamics using NIR and MIR spectra modelling approaches may enable landscape scale trends to be identified [24]. As soil K properties are considered closely linked to mineralogy and hence geology, the nature of these properties and their potential to contribute to improved agriculture fertilisation practices is important to assess.

2 | Material and Methods

2.1 | Sample Archives

Ninety soil samples ($< 2\text{ mm}$) from eastern Africa were obtained from the African Soil Information Service (AFSIS) and British Geological Survey (BGS) archives. These will be referred to as the 'XRD dataset' containing samples (AK1–AK90) and are those where a range of soil properties were measured to use in the parameterisation of IR scan models. The first archive (AK1–AK60) is from the AFSIS Project established in 2008 [20, 25, 26] and collected during the period 2008–14. Information regarding the sampling and preparation of these samples can be found in the AFSIS Technical Specifications Manual [25, 26]. The

second archive (AK61–AK90) was the BGS WG dataset collected in Kenya between 2016 and 19 [27, 28], which consisted of 446 samples, of which a subset of 30 were used as part of the 'XRD dataset.' Information of the WG sampling area (sample locations, lithology, elevation and land use) can be found in SI: Figure 4.

2.2 | Soil Particle Size

Particle size analysis of the soils in the 'XRD dataset' was undertaken at the BGS using a Beckman Coulter LS13320 laser granulometer after removal of organic matter using H_2O_2 . A cutoff for clay particle size was established at $8\text{ }\mu\text{m}$ in line with the suggestion by [29].

2.3 | Soil Mineralogy and XRD Analysis

The mineralogy of the soil samples was determined via a combination of powder and $< 2\text{ }\mu\text{m}$ XRD analysis in the Mineralogy laboratories (BGS) broadly following the methodologies outlined in [30, 31]. To provide a finer and uniform particle size for powder XRD analysis, a 4.5-g portion of milled sample was micronised under distilled water for 10 min with 10% (0.5 g) corundum (American Elements: PN:AL-OX-03-P) and dried at 55°C . The sample was then spray-dried [32] and front-loaded into a standard, stainless steel sample holder for analysis. Fine ($< 2\text{ }\mu\text{m}$) fractions were isolated for clay mineral XRD analysis from organic matter—leached [33], dispersed, crushed soil following gravity separation. Oriented mounts were produced from $\sim 100\text{ mg}$ of the $< 2\text{ }\mu\text{m}$ material resuspended in a minimum of distilled water and pipetted onto a ceramic tile in a vacuum apparatus. Mounts were Ca saturated using $0.1\text{ M CaCl}_2 \cdot 6\text{ H}_2\text{O}$ solution, washed twice to remove excess reagent and allowed to air-dry overnight.

A PANalytical X'Pert Pro series diffractometer equipped with a cobalt-target tube, X'Celerator detector and operated at 45 kV and 40 mA was used for XRD analyses [34]. Micronised powder samples were scanned from 4.5° to $85^\circ 2\theta$ at $2.06^\circ 2\theta/\text{minute}$. Analysis of diffraction data was undertaken using PANalytical X'Pert HighScore Plus Version 4.9 software. This was coupled to the latest version of the International Centre for Diffraction Data (ICDD) database (<https://www.icdd.com>) [34]. After mineral species were identified as being present in the sample, phase quantification was achieved using the Rietveld refinement technique (e.g., [35]) using SiroQuant v4 software. The $< 2\text{ }\mu\text{m}$ oriented mounts were scanned from 2° to $40^\circ 2\theta$ at $1.02^\circ 2\theta/\text{minute}$ after a diagnostic testing program of air-drying, ethylene glycol-solvation and heating to 550°C for 2 h [34]. Clay minerals were principally identified by the position and intensity of their basal spacings and their reaction to the diagnostic testing treatments. Clay minerals were quantified by comparison with individually modelled profiles generated by the program NEWMOD II [36]. The results of $< 2\text{ }\mu\text{m}$ clay mineral analysis were converted to a whole soil basis accounting for the presence of small amounts of nonclay minerals (e.g., quartz). Considerations for analysis include the following: All three mica species present their most diagnostic peaks at $\sim 10\text{ }\text{\AA}$ on powder XRD traces, and species differentiation, where these form only a low proportion of the soil, is usually very difficult/impossible. For this reason, the term 'mica' (undifferentiated mica species) is adopted throughout this paper. An indication of the mica crystallite-size

distribution can be gained by measuring the full width at half maximum height (FWHM, $\Delta 2\theta$) of the $\sim 10 \text{ \AA}$ XRD peak [37].

When phyllosilicate mica species occur in the fine-grained fraction of soils, this 'clay-grade mica' is often termed illite. Illite *senso stricto* has a similar chemistry but contains more Si^{4+} , Mg^{2+} and H_2O but less Al^{3+} and importantly K^+ compared to muscovite [38]. All mica species identified by $< 2 \mu\text{m}$ XRD analyses in this paper are termed 'illite.' Weathering of phyllosilicate mica and illite results in the liberation of K and the development of other clay minerals such as kaolinite under acidic, lateritic conditions and smectites or vermiculites under more humid tropical conditions. Smectites such as beidellite (e.g., $\text{M}_{0.33}\text{Al}_2(\text{Al}_{0.33}\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2)$) and vermiculite (e.g., $(\text{Mg}, \text{Fe}^{2+}, \text{Al})_3(\text{Al}, \text{Si})_4\text{O}_{10}(\text{OH})_2 \cdot 4(\text{H}_2\text{O})$) are groups of swelling 2:1 clay minerals with lower layer charges than the micas, hydrated exchangeable cations and high exchange capacities. Both form in soils by the weathering of micas, and the replacement of interlayer K with hydrated exchangeable cations and, therefore, potentially represent important K sources in African soils. However, it should be noted that the generated 'illite' whole soil concentrations will necessarily also contain indeterminate amounts of $< 2 \mu\text{m}$ phyllosilicate 'mica' species.

2.4 | Total Element Analysis

For samples AK1–AK30, total elements including K (K_{Total}) were determined using XRF and were obtained from the AFSIS database. For samples AK31–AK90, total elements including K_{Total} were determined by digestion using a mixture of nitric, perchloric and hydrofluoric acids and analysed by Inductively Coupled Plasma Mass Spectrometry (Agilent 8900 ICP-MS) in the Inorganic Geochemistry Facility at BGS. The same methodology was used to determine total element concentrations in the WG dataset. Certified Reference Materials used included NIST Montana Soil 2711a, the United States Geological Survey's (USGS) BCR-2, British Geological Survey's BGS 102, the Geological Survey of Japan's JR-2 and the National Research Council Canada's MESS-4.

2.5 | Potassium Release Curves

Potassium release from the soil samples was measured according to the method described by [39]. This method was selected because it is relatively simple, repeatable and allows a focus on K^+ release from the fixed mineral phases that are responsible for buffering K in solution over long periods. Thus, the coefficients obtained from the release curves can be modelled using the IR spectra with relative confidence that most of the exchangeable pool has been removed, thereby allowing focus on the longer-term supply characteristics of the soils. The method involves the removal of the exchangeable K pool by saturation with 0.5-M strontium chloride, followed by sequential extraction using weak (0.0005 M) citric acid to successively remove nonexchangeable K. Duplicate ($1.0 \pm 0.001 \text{ g}$) samples of each soil were weighed into 30-mL HDPE conical based tubes, and 10 mL of 0.5-M SrCl_2 was added and shaken for 30 min at 80 rpm on a flat-bed shaker. The suspensions were centrifuged for 20 min at 2500 rpm with the supernatant filtered through $0.45\text{-}\mu\text{m}$ nylon syringe filters, preserved to 1% with HNO_3 and stored at 4°C prior to analysis. After removal of the exchangeable K with SrCl_2 , the sequential extraction using weak citric acid took place over a 73-day period,

with samples collected after 0.5, 1, 2, 3, 6, 16, 29, 56 and 73 days. At each sampling date the supernatant and residual solid were separated and sampled as above. A fresh 10 mL of 0.0005-M citric acid was added and shaken until the next sampling date. The samples were analysed for their K concentration by ICP-MS in the Inorganic Geochemistry Facility at BGS.

2.5.1 | Modelling of K^+ Release Curves

After analysis, cumulative K (mg kg^{-1}) was plotted against time for each soil. Various models have been used to describe K-release characteristics [39, 40]. In this work, the data were modelled over the whole experimental period of 73 days as a single step model. The model used the Elovich equation as follows:

$$M_t = \alpha + \beta \text{Int}, \quad (1)$$

where α is the intercept (mg kg K) and β is the rate constant ($\text{mg K kg}^{-1} \text{d}^{-1}$) and a rate or release constant (k) can be calculated as the ratio β over α (Simard et al. 1989).

2.6 | NIR and MIR Scanning

A combination of IR scans of soil samples produced by both BGS and AFSIS was used. NIR scans from BGS (Samples AK1 - AK90) were undertaken using an Agri-Spec NIR analyser. A white spectral reference was used for calibration and baseline correction, and each spectra saved was a mean of 25 scans. Duplicate scans were taken for each sample with the second scan taken at a 90° angle to the first. At AFSIS, spectral MIR measurements for samples AK1–AK90 and the 446 WG soil samples were acquired using a Bruker FTIR HTS-xt spectrometer fitted with a high sensitivity liquid nitrogen cooled Mercury–Cadmium–Telluride (MCT) detector. The spectra were recorded in the range $7498\text{--}599 \text{ cm}^{-1}$ which were subsetting further during processing to work with MIR region from 4000 to 600 cm^{-1} . A standard operating procedure is available for the Bruker FTIR HTS-xt spectrometer [41]. Spectral NIR measurements for the 446 WG soil samples were acquired using Bruker FT-NIR Multi-Purpose Analyzer fitted with a TE-InGaAs detector. The spectra were recorded in the range of $12,493.2\text{--}3598.7 \text{ cm}^{-1}$. A standard operating procedure is available [42].

Due to scans originating from a series of instruments, harmonisation was required. Processing was undertaken in the R programming language [43] using the 'prospectr' library [44]. All scans used in this work (the 'XRD dataset' and those from WG) were initially converted from reflectance readings into absorbance data. Further using the 'prospectr' library set all scans to a (i) common spectral range ($\text{NIR} = 350\text{--}2500 \text{ nm}$ and $\text{MIR} = 600\text{--}3998 \text{ cm}^{-1}$), (ii) corrected baselines and (iii) interpolated all spectra to a common wavelength step size. The 'mean difference' technique was used for baseline correction.

2.7 | Modelling Mineral Properties From Spectral Data

The aligned MIR spectra and NIR spectra of the 90 soil samples from the 'XRD dataset' and the WG dataset were subjected to a SMMR process [17, 45]. For each IR spectral range (MIR or NIR), the SMMR algorithm produced a set of underlying spectra and a dataset containing the proportions of each underlying

spectra in each sample. The proportions of underlying spectra data of MIR and NIR spectra were used as predictor variables for measured soil properties. The SMMR selected 14 underlying spectra in the NIR range and 17 underlying spectra from the MIR range for predictor variables. These can be seen in Supporting Information Figures 2 and 3.

Two modelling approaches using the underlying NIR and MIR spectra identified through SMMR were undertaken. These were considered suitable for a relatively small dataset of 90 samples. First, stepwise regression was undertaken in *R* using the 'mass' [46] and 'leaps' [47] packages where the complete dataset existed (K_{Total} , K_{SrCl_2} , K-release rate constants β from the single step K release models). Root mean square error (RMSE) was calculated for each model to assess model fit. Models for minerals associated with K dynamics in soil including 'mica,' illite and K-feldspar, along with others including quartz and kaolinite were complicated by several factors. These were (i) not all minerals appeared in all samples leading to nondetects in the data. For example, different minerals are associated with different rock types and (ii) some minerals were present but were below the limits of detection and where a less than (<) concentration was reported. For these reasons, models were parameterized using 'censored regression' analysis using the censReg package in *R* [48]. This approach is used when the dependent variable is censored, as some of the dependent values are only partially known. Samples which were nondetects or had less than values were typically censored at a value equivalent to half the limits of detection (left censoring). The benefit of applying censored regression is that the model uses all the NIR and MIR scan data within the parameterization of the model, explicitly modelling the censored data. A log transform ($\log_{10}(x+1)$) was performed before modelling. The censored regression models are fitted using log-likelihood, maximised with Newton–Raphson optimisation. The fewer number of optimisation iterations reported indicate quicker model convergence. A return code is provided describing the convergence state (e.g., the message 'gradient close to zero' indicates successful convergence). As in standard linear regression, the censored regression models the parameters and the variance (presented in the form logSigma, the log of the residual standard deviation).

2.8 | Extending the Model to Other Soil Data

The models parametrised using the 'XRD dataset' were applied to the remaining 445 samples from the WG dataset, using total element and IR spectra data. The NIR and MIR spectra in the WG dataset had previously been included in the process to harmonize the spectra properties (Section 2.6). Beyond the models parameterised to predict K properties and dynamics, an additional model was parameterized on this dataset to assess the degree of weathering of these samples using the total element data. The weathering index selected was the Chemical Index of Alteration (CIA) developed by [49] and is defined as in Equation (2). The index is calculated using oxide values in molar units. The authors in [50] describe CIA values between 80 and 100 as being 'highly weathered,' 60–80 as being 'moderately weathered' and < 60 as 'less weathered.'

$$\text{CIA} = 100 \left(\frac{\text{Al}_2\text{O}_3}{\text{Al}_2\text{O}_3 + \text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O}} \right). \quad (2)$$

3 | Results

3.1 | General Soil Characteristics

Data for the properties of the 90 soils used in the training dataset are presented in Tables 2, 3, and 4. Soil textures varied with concentrations of sand ranging from 6% to 85%, silt between 4% and 39% and clay from 8% to 78%. Concentrations of K_{Total} varied between 621 and 52,604 mg kg⁻¹ and SrCl₂ exchangeable K varied between 19 and 8361 mg kg⁻¹.

3.2 | K Mineralogy

Overall, there was considerable variability in the minerals present and their concentration. Tables 5, 6, and 7 summarise the K-bearing mineral components of the soil. Not all samples had detectable concentrations of each mineral, reflecting possible geological and weathering influences. Across the dataset concentrations of K-feldspar reached 48%, 'mica' reached 56%, illite reached 26% and kaolinite reached 74%. Smectite was present in about half of the samples and was detected in concentrations up to 43%.

3.3 | Sequential Extraction of K⁺

SI Figure 1 shows a typical graph showing cumulative desorbed K against time. As demonstrated, the release curves show a rapid desorption rate up to ~10 days followed by a slower phase of release. The data were modelled as a single step model as this allows greater integration of K-bearing mineral and clay-derived K-release processes over a longer period. Obtained values for the constants α , β and the model R^2 can be found in Tables 5, 6, and 7. For the single step model, the values of β ranged from 1.56 to 360 mg K kg⁻¹ day⁻¹. The coefficient β (i.e., identifying the overall K release characteristics of the soils) was modelled using the selected IR spectra.

3.4 | Relationships of K to Mineralogical and Soil Properties

The database of results for the 90 soils was examined for relationships between K_{Total} , K_{Ex} the K-release rate constants (α and β) and the concentrations of K-bearing minerals. There was a reasonable positive correlation between K_{Total} and K-feldspar ($r_s = 0.83$), suggesting that K-feldspar may be the dominant supply mineral. A positive correlation was found between silt and 'mica' ($r_s = 0.50$), suggesting that mica crystals were common to the silt sized fraction. Finally, illite and mica had a positive correlation ($r_s = 0.67$), suggesting their shared origin. However, the overall lack of correlations demonstrates the complexity of K supply in soils in relation to properties such as mineral size, degree of mineral weathering and the combination of K mineralogy found in soils.

3.5 | NIR and MIR Scan Models of K Properties and K-Bearing Minerals

A range of K-related parameters were modelled using NIR and MIR scans from the 'XRD dataset.' Figures 1, 2, and 3 show observed ν predictions of (i) K_{Total} , (ii) SrCl₂ K_{Ex} and (iii) the K-release constant β , with model outputs being shown in Tables 8, 9, and 10 for the 'XRD dataset' of 90 samples. All three models fitted well using stepwise regression with observed ν predicted

TABLE 2 | Measured soil properties of samples AK1 – AK30.

Soil ID	Country	Sand (%)	Silt (%)	Clay (%)	Total K (mg kg ⁻¹)	Mehlich	
						3 ex. K (mg kg ⁻¹)	SrCl ₂ ex K (mg kg ⁻¹)
AK1	Kenya	26.4	25.9	58.7	25,830	529.2	229.8
AK2	Kenya	33.5	23.3	43.1	32,588	610.9	290.8
AK3	Kenya	45.5	25.6	28.7	36,958	344.0	146.1
AK4	Kenya	32.6	11.5	55.8	39,327	1857.2	1033.6
AK5	Kenya	83.2	4.1	12.5	18,032	916.6	440.6
AK6	Kenya	85.0	4.3	10.6	18,983	577.5	291.9
AK7	Kenya	72.6	8.4	18.8	19,522	666.3	413.9
AK8	Kenya	26.1	34.3	39.5	16,026	1645.8	650.2
AK9	Kenya	34.3	20.5	45.0	13,833	NA	280.0
AK10	Kenya	48.1	20.1	31.7	12,219	414.9	281.5
AK11	Uganda	49.8	19.1	31.0	9491	110.7	62.8
AK12	Uganda	55.2	20.0	24.7	14,692	155.6	104.9
AK13	Uganda	48.8	20.9	30.2	9714	560.6	515.2
AK14	Uganda	52.3	18.7	28.9	6715	338.1	237.2
AK15	Uganda	35.5	21.7	42.7	6934	383.0	553.6
AK16	Uganda	37.1	19.7	43.2	6169	484.8	346.1
AK17	Uganda	21.8	15.4	62.7	6126	90.5	65.2
AK18	Uganda	23.4	37.8	38.6	9143	759.1	556.0
AK19	Uganda	45.1	17.4	37.5	6097	115.7	79.4
AK20	Uganda	27.3	20.9	51.7	6675	117.7	221.9
AK21	Tanzania	53.2	16.9	29.8	2312	99.5	59.3
AK22	Tanzania	77.8	9.9	12.2	1903	210.5	216.8
AK23	Tanzania	31.6	32.6	35.7	11,664	538.6	475.8
AK24	Tanzania	24.5	38.6	36.8	14,874	290.3	231.7
AK25	Tanzania	79.5	12.4	8.1	26,354	201.5	145.2
AK26	Tanzania	74.8	14.7	10.3	19,126	118.7	51.3
AK27	Tanzania	65.1	22.0	12.7	40,461	138.6	93.4
AK28	Tanzania	70.7	13.3	15.8	1338	151.6	143.0
AK29	Tanzania	36.1	21.3	42.5	11,855	458.8	392.0
AK30	Tanzania	30.9	27.9	41.0	19,678	460.8	370.6

values close to the 1:1 line. Typically, best fit models for each were produced using data transformed to Log₁₀. For K_{Total}, K_{SrCl2} and the K-release constant β , model R^2 values were 0.91, 0.68 and 0.53, respectively. The RMSE for each model was 0.16, 0.27 and 0.29, respectively.

The mineral models for the K-bearing minerals K-feldspar, 'mica' and illite required left-censoring due to nondetect values or values below the limits of detection. Observed v predicted graphs of the transformed data (see Section 2.7) can be seen in Figures 4, 5, and 6 and model outputs and quantitative performance (R^2 or logSigma) in Tables 11, 12, and 13. For all models, the observed v predicted values were generally close to the 1:1 line. For mica, the logSigma values were greater than for K-feldspar and illite, possibly indicating the varied species of the minerals that are included in the XRD identification (Table 1). In addition, two further models were calibrated for the clay kaolinite (Figure 7 and Table 14) and quartz (Figure 8 and Table 15). These models had RMSE values of 0.22 and 0.18, respectively.

3.6 | Applying Models to the WG Dataset

Scans from the WG were included, along with those from the XRD dataset, in the SMMR analysis to identify the common spectral components. Parameterised models (Tables 8, 9, 10, 11, 12, 13, 14, and 15) were used to predict soil K properties and mineralogy in the WG soils. As the WG dataset had analytical measurements of K_{Total}, the previously parameterised Log₁₀K_{Total} model (Table 8) was used to predict concentrations in the WG data (Figure 9). The modelled outputs had an RMSE of 0.22. Further assessments of models were analysed as box and whisker plots associated with a classification of simple geological lithology based on mapping from the Kenyan Geological Survey [51]. Lithology was used as the current soil descriptions of the area contain over 60 soil types and would require some consolidation to be practical, which would rely on local knowledge. Figure 10 shows the predictions of K_{Total}, K_{SrCl2} and the K-release rate constant β plotted against lithology. On each graph, the highest value of each property, included in the 'XRD dataset'

TABLE 3 | Measured soil properties of samples AK31–60.

Soil ID	Country	Sand (%)	Silt (%)	Clay (%)	Total K (mg kg ⁻¹)	Mehlich	
						3 ex. K (mg kg ⁻¹)	SrCl2 ex K (mg kg ⁻¹)
AK31	Kenya	14.4	10.3	75.3	2268	644.6	129.5
AK32	Kenya	27.8	13.4	58.7	621	597.7	21.6
AK33	Kenya	37.0	11.2	51.7	1819	589.9	57.8
AK34	Kenya	19.3	21.2	59.5	5914	582.3	120.8
AK35	Kenya	17.5	13.0	69.6	2952	551.7	103.9
AK36	Kenya	28.0	13.2	58.8	1494	511.6	89.7
AK37	Kenya	32.7	12.8	54.5	4021	502.5	153.8
AK38	Kenya	51.1	17.7	31.2	10,500	490.5	25.9
AK39	Kenya	26.9	14.6	58.5	3126	477.7	94.6
AK40	Kenya	32.0	8.8	59.2	1615	468.8	59.2
AK41	Kenya	57.8	9.3	32.9	10,120	338.9	195.6
AK42	Kenya	10.7	11.1	78.2	1811	337.8	74.9
AK43	Kenya	20.0	12.2	67.8	2293	328.4	71.8
AK44	Kenya	39.7	9.4	50.9	1805	321.7	71.7
AK45	Kenya	58.2	13.8	28.0	7562	317.3	31.4
AK46	Kenya	23.3	11.6	65.2	3536	303.4	254.5
AK47	Kenya	22.6	10.1	67.3	1027	303.2	158.0
AK48	Kenya	22.9	11.1	66.0	2082	282.5	184.1
AK49	Kenya	21.9	14.1	64.1	2883	280.6	77.1
AK50	Kenya	28.4	9.1	62.5	1904	277.7	119.7
AK51	Kenya	6.4	15.5	78.1	2506	202.8	153.4
AK52	Kenya	23.4	11.1	65.5	1032	201.3	26.3
AK53	Kenya	35.5	17.2	47.4	3720	194.9	121.5
AK54	Kenya	14.1	21.0	64.9	1520	192.9	19.7
AK55	Kenya	28.4	25.4	46.2	2908	190.9	33.1
AK56	Kenya	35.9	9.1	54.9	892	178.3	102.0
AK57	Kenya	17.9	11.7	70.4	1957	171.9	81.7
AK58	Kenya	23.2	12.2	64.7	1973	171.1	29.1
AK59	Kenya	15.2	14.1	70.6	2807	171.0	84.8
AK60	Kenya	20.2	12.2	67.6	2055	168.0	151.2

(Section 2.7), is shown on the graph as a dashed line. For each of the three properties, outliers were identified on the box and whisker plots. The number of outliers were typically < 5% of the total predicted values ($n = 446$). Outliers that are greater than the maximum of the XRD dataset are < 1% of the WG dataset. For K_{Total} , Figure 10 shows these predictions and their associations with lithology. The greatest ranges of K_{Total} concentrations are associated with acid metamorphic rocks and granite. The box and whisker plots for soil extractable K_{SrCl_2} show that igneous rock and Gneiss FM lithologies have the greatest concentration ranges. For the release constant β , the intermediate igneous rocks had the greatest concentration range. A general feature of the K_{SrCl_2} and release constant β populations is that the median value is often towards the low end of the data range for many lithologies, suggesting a greater number of soils had lower K availability or slower release rates.

Predictions of the K-bearing feldspar and mica minerals were made (Figure 11). Again, the outliers associated with certain

lithologies make up a small proportion of the WG dataset, with a few samples above the highest concentration used in the models. For both K-feldspar and K-mica, it was noted that the median value for many lithologies were towards the low end of the concentration ranges. For K-feldspar, highest concentration ranges were found in soils above the acid metamorphic and granite rocks. Greater variation in the median concentration was found in mica across the lithologies. A greater range in concentrations was found in soils above the acid igneous rocks, basalt, igneous rocks and intermediate igneous rocks.

Inherent soil K stocks are linked to the intensity of weathering processes that has occurred. Several weathering related models were produced to explore the potential impact of weathering on mineralogy. As described (Section 2.8), the WG total element data were used to calculate the CIA weathering index. Figure 12 and Table 16 show the observed v predicted values and coefficients of the CIA model parameterised using the IR spectra. The model had an R^2 of 0.92 and a RMSE of 3.9, over a range of

TABLE 4 | Measured soil properties of samples AK61–90.

Soil ID	Country	Sand (%)	Silt (%)	Clay (%)	Total K (mg kg ⁻¹)	Mehlich	
						3 ex. K (mg kg ⁻¹)	SrCl ₂ ex K (mg kg ⁻¹)
AK61	Kenya	27.8	25.2	46.9	16,888	NA	584.3
AK62	Kenya	60.4	16.2	23.3	34,086	NA	126.4
AK63	Kenya	61.6	23.4	14.8	11,782	NA	270.3
AK64	Kenya	70.5	15.3	14.1	36,548	NA	300.3
AK65	Kenya	76.2	13.6	10.1	43,654	NA	362.8
AK66	Kenya	58.5	20.5	20.8	43,164	NA	358.2
AK67	Kenya	78.0	11.2	10.7	51,531	NA	540.9
AK68	Kenya	44.0	29.0	26.9	37,524	NA	453.4
AK69	Kenya	54.5	16.9	28.5	27,203	NA	439.0
AK70	Kenya	26.9	34.7	38.3	32,748	NA	8361.7
AK71	Kenya	73.0	14.4	12.5	37,859	NA	118.0
AK72	Kenya	59.5	20.7	19.6	28,179	NA	351.0
AK73	Kenya	23.4	37.6	38.8	20,106	NA	113.6
AK74	Kenya	10.2	34.7	54.9	19,989	NA	1280.3
AK75	Kenya	17.8	38.6	43.5	21,130	NA	881.7
AK76	Kenya	19.7	28.5	51.7	23,848	NA	538.1
AK77	Kenya	17.7	35.5	46.6	23,685	NA	768.9
AK78	Kenya	70.0	16.6	13.2	25,685	NA	713.2
AK79	Kenya	63.1	20.6	16.2	39,858	NA	229.9
AK80	Kenya	72.4	16.3	11.1	42,132	NA	675.8
AK81	Kenya	32.4	30.9	36.6	32,236	NA	1884.9
AK82	Kenya	29.2	26.9	43.8	31,175	NA	1281.6
AK83	Kenya	36.3	44.3	19.2	42,926	NA	645.0
AK84	Kenya	75.9	13.7	10.3	60,068	NA	356.3
AK85	Kenya	75.6	14.7	9.5	40,201	NA	307.7
AK86	Kenya	75.2	13.2	11.4	30,085	NA	466.6
AK87	Kenya	50.6	25.0	24.2	52,604	NA	525.5
AK88	Kenya	71.6	14.8	13.5	36,838	NA	231.8
AK89	Kenya	19.7	16.0	64.1	12,459	NA	612.0
AK90	Kenya	69.9	19.2	10.8	16,750	NA	3494.5

Note: Melich 3 results for these samples not available (NA).

CIA values from ~15 to 100. Using the parameterised models, concentrations of illite and kaolinite were predicted and plotted as box and whisker plots against lithology (Figure 13). The presence of both these minerals results from weathering processes and hence reflects the potential loss of inherent K from soils. For illite, formed from the weathering of mica, the greatest concentration ranges were found in the basalt, basic and intermediate igneous rocks. Kaolinite forms through the long-term weathering of aluminium silicate minerals such as K-feldspar, in tropical and subtropical climates. High ranges and concentrations of kaolinite were associated with soils above intermediate igneous rocks, igneous rocks and andesites and sandstone, greywackes and arkose lithologies. Low concentrations were evident in soils above the limestone and eolian unconsolidated rocks. To test the kaolinite model, predicted concentrations were plotted against observed CIA values (Figure 14) and show the positive relationship between CIA and % kaolinite, demonstrating the impacts of greater weathering intensity. Lastly, an

assessment of quartz against lithology was undertaken (Figure 15), demonstrating high concentrations in sandstone and other quartz-based rocks, acid metamorphic rock and the erosion based fluvial lithologies. Low concentrations were found in soils above the limestone lithology.

4 | Discussion

The research aimed to parametrise a range of semiquantitative models, based on IR scans, that allow soil K properties, K-bearing minerals and other weathering related minerals to be estimated, initially in the 90 sample XRD dataset. Models were then evaluated on the WG data. On a landscape scale, these models could be used as a toolbox to assess changes in inherent soil fertility and to help develop improved sustainable K fertilisation strategies for highly weathered soils. In addition, models could provide an initial assessment of data and help develop future research

TABLE 5 | K-bearing mineralogical properties of soils AK1–30 used in the NIR and mid-IR scans training dataset to predict K properties in soils.

Soil ID	Whole soil XRD (%)		< 2 μ m XRD measurement converted to whole soil (%)			Elovich single step model constants		
	K-feldspar	'Mica'	Illite	Smectite	Kaolinite	α (mg kg ⁻¹)	β (mg K kg ⁻¹ d ⁻¹)	R ²
AK1	5.1	8.8	6.7	43.6	2.3	24.24	21.50	0.99
AK2	3.2	39.5	23.9	11.7	3.6	23.07	16.81	0.95
AK3	7.6	12.5	9.8	15.8	1.5	11.73	7.43	0.95
AK4	6.5	25.7	26.3	23.6	1.8	62.56	44.96	0.95
AK5	2.7	17.2	7.4	3.1	0.9	27.37	23.07	0.95
AK6	2.3	19.4	6.2	2.6	1.0	17.99	25.80	0.99
AK7	3.9	26.1	13.5	2.2	2.2	31.28	33.62	0.98
AK8	6.7	30.3	21.9	10.8	3.2	48.48	39.49	0.96
AK9	5.3	28.6	10.2	1.6	32.1	13.29	11.34	0.95
AK10	9.8	18.2	6.9	nd	23.6	12.90	9.38	0.98
AK11	nd	23.4	18.4	nd	12.2	3.91	3.52	0.96
AK12	nd	28.5	19.3	nd	5.0	4.30	3.52	0.95
AK13	< 0.5	13.4	3.2	nd	26.1	14.47	8.21	0.97
AK14	nd	9.7	2.5	nd	24.9	9.77	7.82	0.95
AK15	nd	3.6	6.1	nd	30.5	12.12	11.73	0.96
AK16	2.9	3.1	2.3	nd	37.1	14.86	13.68	0.97
AK17	< 0.5	4.1	3.7	nd	52.2	2.74	3.13	0.94
AK18	nd	5.6	5.7	nd	30.9	21.50	17.20	0.98
AK19	nd	6.3	2.0	nd	28.4	4.69	3.52	0.98
AK20	nd	2.8	3.8	nd	43.9	8.60	8.21	0.93
AK21	< 0.5	nd	nd	10.9	18.4	2.35	1.56	0.96
AK22	nd	1.3	0.6	nd	11.1	8.21	4.69	0.94
AK23	7.8	26.6	7.0	nd	28.2	12.90	7.43	0.99
AK24	4.6	32.7	6.5	nd	29.3	11.73	5.08	0.97
AK25	15.3	3.3	3.8	3.3	0.6	15.25	17.59	0.99
AK26	6.3	0.9	4.1	nd	5.9	7.04	3.13	0.93
AK27	16.7	2.4	5.7	1.0	5.6	8.21	6.26	0.98
AK28	nd	2.0	0.7	nd	14.6	6.26	2.74	0.93
AK29	6.4	4.4	1.6	nd	39.9	14.47	10.95	0.96
AK30	7.8	9.9	8.8	12.1	18.9	21.89	12.12	0.97

questions relating to soil K dynamics and fertility and provide a focus for the deployment of more expensive analytical analysis.

4.1 | Soil K Sources and Mineralogy

Potassium properties of soils are subject to several principal drivers including (i) geology (parent material) which provides the initial K mineralogy, (ii) climate and (iii) length of weathering exposure. These all determine the extent of weathering and remaining inherent K stocks. Land-use, in terms of K fertilisation is a more recent influence, with modern day interventions potentially influencing exchangeable concentrations, particularly if fertiliser application has exceeded crop uptake, and where storage may occur in minerals such as illite or smectite. Understanding how these drivers interact is important in understanding soil K status and developing fertilisation and sustainability strategies.

Soil K_{Total} concentrations in the 'XRD dataset' varied by three orders of magnitude and correlation analysis suggests that K-feldspar is a principal mineral source (Section 3.5). The K-bearing minerals found in this study are similar to other reported soil mineral analyses. The authors in [52] examined the weathering products of Precambrian granitic gneiss in Uganda, identifying illite and smectite clay minerals as well as microcline and biotite. The authors in [53] reported the presence of feldspars in the majority (177 out of 184) of topsoil samples analysed during an optical petrographic study. It was suggested that both plagioclase and alkali K-feldspars had been highly altered and decomposed, although in some soils, the crystals remained unaltered. The authors in [54] used XRD to analyse 6 Kenyan soils and identified the presence of mica (muscovite and biotite) in the clay and silt fractions (< 63 μ m), whilst K-feldspar and some mica were found in some sand fractions (> 63 μ m). In the current study, there was

TABLE 6 | K-bearing mineralogical properties of soils AK31–AK60 used in the NIR and mid-IR training dataset to predict K properties in soils.

Soil ID	Whole soil XRD (%)		< 2 μ m XRD measurement converted to whole soil (%)			Elovich single step model constants		
	K-feldspar	'Mica'	Illite	Smectite	Kaolinite	α (mg kg ⁻¹)	β (mg K kg ⁻¹ d ⁻¹)	R ²
AK31	2.4	3.3	1.6	nd	73.5	64.86	27.76	0.97
AK32	2.2	nd	0.3	nd	57.0	6.69	3.09	0.98
AK33	1.9	nd	3.8	nd	46.6	31.98	19.12	0.99
AK34	7.1	8.0	1.2	nd	55.2	106.50	60.52	0.98
AK35	2.5	1.5	0.9	nd	66.0	66.78	41.25	0.99
AK36	6.2	nd	0.7	nd	56.1	40.35	18.73	0.97
AK37	3.6	0.6	nd	nd	51.6	100.33	52.94	0.98
AK38	6.6	nd	0.7	nd	26.4	19.12	13.33	0.99
AK39	5.8	nd	1.1	nd	53.6	58.49	38.04	0.99
AK40	nd	nd	1.2	nd	56.3	24.01	9.11	0.94
AK41	7.3	nd	0.9	nd	30.2	117.96	71.67	0.99
AK42	1.3	nd	2.0	nd	74.1	55.60	28.46	0.98
AK43	2.7	1.9	nd	nd	66.8	44.06	24.91	0.99
AK44	2.9	1.8	0.7	nd	48.4	36.48	17.83	0.97
AK45	5.1	nd	0.7	nd	25.6	18.34	11.03	0.99
AK46	3.2	0.7	nd	nd	62.2	142.08	75.97	0.99
AK47	nd	nd	nd	nd	66.0	58.80	19.74	0.95
AK48	2.00	nd	nd	nd	63.6	85.12	37.53	0.97
AK49	4.3	2.8	1.2	nd	60.6	54.31	31.40	0.99
AK50	2.3	nd	nd	nd	60.8	61.85	29.40	0.98
AK51	2.6	nd	1.4	nd	74.6	73.11	39.45	0.99
AK52	2.4	1.6	nd	nd	50.3	11.38	4.93	0.97
AK53	5.8	5.6	nd	nd	44.0	82.81	40.23	0.96
AK54	3.3	3.9	nd	nd	58.2	12.16	6.57	0.98
AK55	5.0	1.3	1.0	nd	39.3	23.77	15.87	0.99
AK56	nd	nd	nd	nd	54.3	41.37	15.13	0.98
AK57	2.0	1.1	2.5	nd	64.9	35.23	14.47	0.97
AK58	2.6	1.3	0.5	nd	63.5	20.84	16.34	0.99
AK59	2.0	0.9	nd	nd	63.2	50.05	27.29	0.98
AK60	2.4	1.6	nd	nd	66.7	106.15	51.96	0.98

an indication, through a weak correlation (Section 3.5), that 'mica' minerals were associated with silt sized fraction.

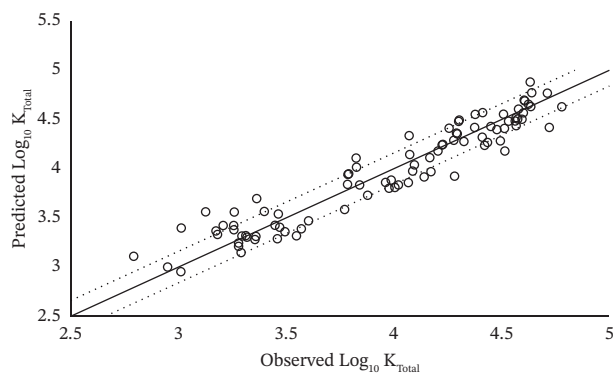
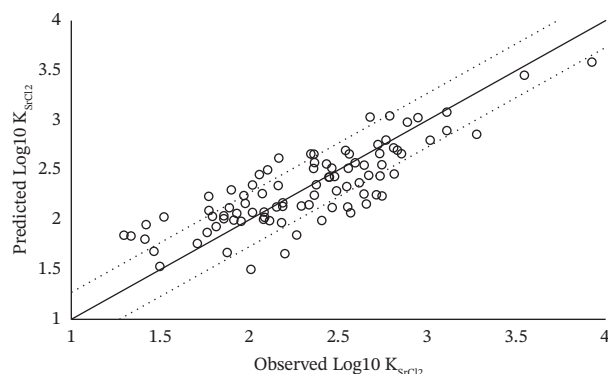
The soil minerals derived from the parent material is of importance due to their differing weathering properties. Whilst K-feldspars weather and release K to soils, it is considered that trioctahedral micas (biotite and phlogopite) weather and release K more rapidly, albeit that they contain smaller proportions of K [8]. Work by [55] used syenite (a silicate rock composed of ~ 90% K-feldspar) and phlogopite mica in plant uptake experiments. They found that the 'mica' treatment supplied similar rates of K as a KCl application, whilst K-feldspar supplied less. In another study [56], the authors again found that biotite rapidly released K, whilst framework silicates such as microcline and nepheline released K more slowly and suggested greater potential to act as longer-term sources of K. The K-release rates obtained from the experimental work, which exist as an integration of minerals present, varied significantly, even when

total and exchangeable K values were similar. Thus, even with knowledge of the K-bearing mineralogy, it was not possible to associate mineralogy to the release rates, likely occurring via ion exchange [54]. This reflects the different K-mineral assemblage, crystal size and degree of weathering.

Of the clay minerals, kaolinite was found to dominate, which is typical of mature, highly weathered soils of the tropics [1]. Smectite was detected in some samples of the XRD dataset. The authors in [57] suggested that smectite clays in soil toposequences from Kenya are typically found in depressions where vertisols persist, whilst kaolinite along with possible illite, were often associated with slopes. They suggested that smectites are the first weathering product and, depending on hydrological conditions, either persist in depressions or undergo further weathering to kaolinite. However, the relatively low occurrence of smectite detected in samples generally concurs with the general concept that they are found in slightly drier climates of

TABLE 7 | K-bearing mineralogical properties of soils AK61–AK90 used in the NIR and mid-IR training dataset to predict K properties in soils.

Soil ID	Whole soil XRD (%)		< 2 μm XRD measurement converted to whole soil (%)			Elovich single step model constants		
	K-Feldspar	'mica'	Illite	Smectite	Kaolinite	α (mg kg ⁻¹)	β (mg K kg ⁻¹ d ⁻¹)	R^2
AK61	14.2	34.0	5.7	nd	38.4	6.26	19.16	0.91
AK62	32.5	2.0	5.2	nd	17.1	−0.39	5.47	0.93
AK63	5.7	nd	6.7	nd	7.2	0.00	19.16	0.88
AK64	20.5	nd	5.9	0.2	7.0	0.39	17.20	0.96
AK65	25.2	5.0	1.1	0.2	8.3	6.65	21.11	0.96
AK66	22.0	30.5	5.7	0.3	13.5	2.74	17.99	0.97
AK67	27.2	12.6	3.0	0.3	6.8	9.77	23.07	0.97
AK68	23.1	18.2	2.6	0.4	22.6	4.69	16.81	0.96
AK69	18.3	20.0	3.1	nd	24.7	4.30	25.80	0.94
AK70	14.8	35.3	19.0	16.1	3.3	220.90	360.48	0.97
AK71	29.5	nd	2.3	nd	9.8	4.69	7.82	394
AK72	26.4	1.0	2.3	nd	16.7	168.90	55.52	0.6
AK73	23.7	51.5	10.8	nd	26.3	3.52	3.13	0.94
AK74	15.9	31.1	24.8	25.4	3.8	17.20	68.81	0.91
AK75	20.0	24.4	10.8	28.0	3.9	3.91	37.93	0.95
AK76	22.5	11.9	22.5	24.1	4.4	20.33	38.32	0.958
AK77	24.1	23.5	18.6	23.9	3.4	11.73	43.01	0.96
AK78	16.2	0.9	4.8	2.2	5.6	16.81	27.37	0.97
AK79	34.2	26.3	4.8	2.0	8.7	20.33	12.90	0.395
AK80	28.8	5.9	2.6	3.0	5.0	54.74	30.50	0.97
AK81	16.4	16.4	9.6	16.8	9.0	−4.30	134.89	0.93
AK82	30.8	55.2	12.2	nd	29.6	5.08	51.61	0.95
AK83	47.9	17.0	1.9	15.6	1.8	53.56	31.67	0.88
AK84	42.4	nd	3.8	nd	5.6	3.91	30.89	0.94
AK85	18.1	5.9	3.8	2.4	2.5	10.56	11.73	0.97
AK86	15.5	3.6	4.4	5.3	1.0	6.65	25.41	0.97
AK87	30.2	41.6	10.2	9.5	3.67	3.52	32.84	0.93
AK88	16.9	19.1	5.8	nd	7.0	7.82	9.77	0.96
AK89	nd	56.4	18.7	12.7	29.0	0.39	45.74	0.93
AK90	3.3	38.8	0.5	10.2	0.1	80.15	208.00	0.96

**FIGURE 1** | Observed vs. predicted graph for Log₁₀ K_{Total} (mg kg⁻¹) for samples AK1–AK90. Solid line represents the 1:1 relationship whilst dashed lines represent ± 1 RMSE.**FIGURE 2** | Observed vs. predicted graph for Log₁₀ K_{SrCl2} (mg kg⁻¹) for samples AK1–AK90. Solid line represents the 1:1 relationship whilst dashed lines represent ± 1 RMSE.

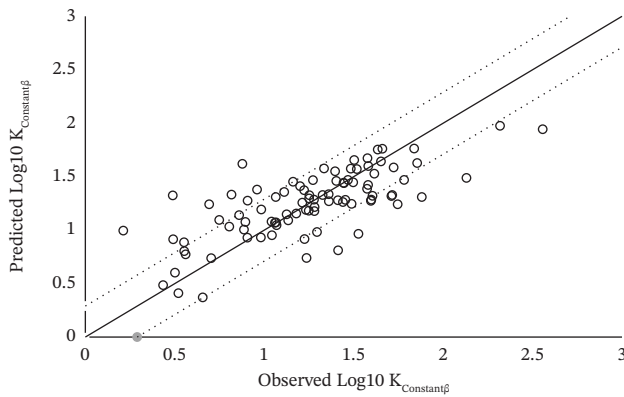


FIGURE 3 | Observed vs. predicted graph for $\text{Log}_{10} K_{\text{Constant } \beta}$ for samples AK1-90. Solid line represents the 1:1 relationship whilst dashed lines represent ± 1 RMSE.

TABLE 8 | Outputs for $\text{Log}_{10} K_{\text{Total}}$ (mg kg^{-1}) regression model for the 'XRD dataset' (AK1-AK90).

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	5.002	0.231	< 2e-16***
MIR3	1.147	0.208	4.73e-07***
MIR4	-0.607	0.193	0.002**
MIR10	-0.612	0.151	0.0001***
MIR11	0.574	0.119	7.53e-06***
MIR12	-0.273	0.136	0.048*
MIR13	-1.074	0.124	5.41e-13***
MIR16	0.353	0.150	0.021*
NIR8	-4.575	2.046	0.028*
NIR10	4.435	1.268	0.0007***
NIR11	-10.88	2.877	0.0003***
NIR14	7.298	0.294	0.002**

Note: Multiple R-squared: 0.901, p value: < 2.2e-16, residual standard error: 0.175 on 78 degrees of freedom.

* $p < 0.05$.
 ** $p < 0.01$.
 *** $p < 0.001$.

TABLE 9 | Outputs for $\text{Log}_{10} K_{\text{SrCl2}}$ (mg kg^{-1}) regression model for the 'XRD dataset' (AK1-90).

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	2.499	0.121	< 2e-16***
MIR3	2.479	0.242	2.49e-16***
MIR5	3.074	0.468	4.07e-09***
MIR10	-0.651	0.195	0.001**
MIR14	-1.310	0.235	2.99e-07***
MIR17	-1.519	0.318	7.42e-06***
NIR1	-1.012	0.368	0.007**

Note: Multiple R-squared: 0.681, p value: < 2.2e-16, residual standard error: 0.284 on 83 degrees of freedom.

* $p < 0.05$.
 ** $p < 0.01$.
 *** $p < 0.001$.

the tropics. The presence of smectite is important as it increases the overall soil CEC due to its 2:1 structure, weaker layer charge and much larger surface area compared to kaolinite. Illite was

TABLE 10 | Outputs for Log_{10} constant β regression ($\text{mg K kg}^{-1} \text{d}^{-1}$) model for the 'XRD dataset' (AK1-90).

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	1.181	0.182	5.71e-09***
MIR1	2.505	0.489	1.94e-06***
MIR3	1.693	0.262	6.87e-09***
MIR9	-0.920	0.331	0.006**
MIR14	-0.998	0.243	9.57e-05***
MIR17	-1.545	0.334	1.34e-05***

Note: Multiple R-squared: 0.532, p value: < 1.257e-12, residual standard error: 0.302 on 84 degrees of freedom.

* $p < 0.05$.
 ** $p < 0.01$.
 *** $p < 0.001$.

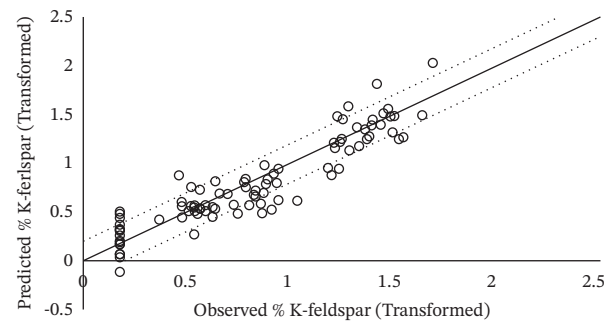


FIGURE 4 | Observed vs. predicted transformed K-feldspar concentrations using censored regression analysis. Solid line represents the 1:1 relationship whilst dashed lines represent ± 1 log residual standard deviation derived from the log Sigma value.

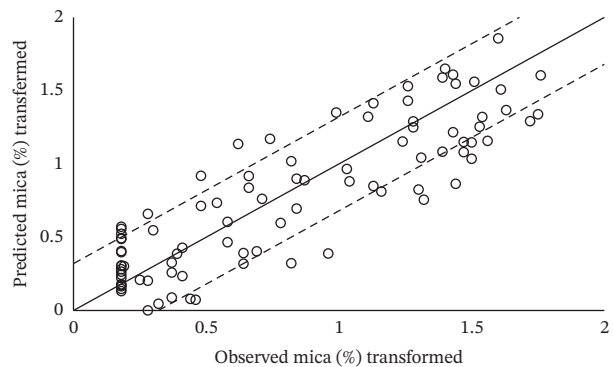


FIGURE 5 | Observed vs. predicted transformed K-mica concentrations produced using censored regression analysis. The solid line represents the 1:1 relationship whilst dashed lines represent ± 1 residual standard deviation derived from the log Sigma value.

present in about 75% of the samples and generally had higher concentrations where higher 'mica' concentrations were present, indicating the continuum that exists between mica and illite crystals [58].

4.2 | Modelling K Properties and Mineralogy

Previous work has demonstrated how soil K properties successfully lend themselves to modelling using IR spectra especially for total and exchangeable phases [59, 60]. This was also found in

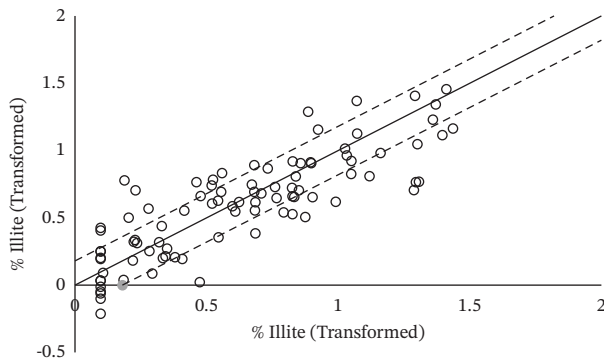


FIGURE 6 | Observed vs. predicted transformed illite concentrations produced using censured regression analysis. The solid line represents the 1:1 relationship whilst dashed lines represent ± 1 log residual standard deviation derived from the logSigma value.

TABLE 11 | Outputs from censreg model for (%) K-feldspar (transformed model) for the 'XRD dataset' (AK1-90).

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	2.194	0.316	4.39e-12***
MIR3	0.865	0.243	0.0003***
MIR4	-0.425	0.247	0.086*
MIR6	-0.973	0.140	3.97e-12***
MIR7	-0.083	0.025	0.0009***
MIR9	-1.393	0.323	1.69e-05***
MIR11	0.535	0.163	0.001**
MIR13	-0.824	0.149	3.65e-08***
MIR15	-0.755	0.235	0.001**
MIR16	0.855	0.171	6.43e-07***
NIR1	-0.788	0.318	0.013*
NIR7	3.514	1.247	0.005**
NIR14	-7.610	1.345	1.55e-08***
logSigma	-1.621	0.085	< 2e-16***

Note: Observations: Total = 90; Left censored = 16; Uncensored = 74, Newton-Raphson maximisation: 8 iterations, Return code 1: gradient close to zero, Log-likelihood: 1.977 on 14 degrees of freedom.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

this study for K_{Total} , K_{SrCl_2} , constant β models and CIA. It was noted that those models using total element concentrations (K_{Total} and CIA) produced improved model fits than those for exchangeable K and the constant β . The improved prediction of K_{Total} and CIA is likely due to NIR and MIR spectroscopy detecting vibrational overtones and combinations of molecular bonds, especially those involving OH, NH, CH and mineral structures, which have distinct spectral features, whereas exchangeable K is more reliant on soil chemistry such as CEC, which is less directly detectable in MIR or NIR spectra [61]. In this work, constant β could be categorised as a long-term exchangeable K prediction.

Models produced can provide information on a semiquantitative basis for the K-bearing minerals K-feldspar and 'mica' (as general groups of minerals) as well as the clay mineral illite that is

TABLE 12 | Outputs from censreg model for (%) mica (transformed model) for the 'XRD dataset' (AK1-90).

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	2.982	0.536	2.78e-08***
MIR2	-6.494	1.160	2.22e-08***
MIR3	2.107	0.313	1.70e-11***
MIR4	-1.481	0.368	5.68e-05***
MIR6	2.452	0.341	6.86e-13***
MIR10	-0.469	0.319	4.34e-06***
NIR4	-2.511	0.414	1.37e-09***
NIR5	-1.325	0.732	0.070*
NIR6	-7.026	1.162	1.50e-09***
NIR7	6.241	1.518	3.95e-05***
logSigma	-1.124	0.087	< 2e-16***

Note: Observations: Total = 90; Left censored = 19; Uncensored = 71, Newton-Raphson maximisation: 7 iterations, Return code 1: gradient close to zero, Log-likelihood: -36.99 on 11 degrees of freedom.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

TABLE 13 | Outputs from censreg model for (%) illite (transformed model) for the 'XRD dataset' (AK1-90).

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	0.208	0.202	0.303
MIR3	1.769	0.208	< 2e-16***
MIR16	-0.371	0.145	0.010*
NIR7	6.379	1.298	8.92e-07***
NIR8	-5.139	1.343	0.0001***
LogSigma	-1.435	0.081	< 2e-16***

Note: Observations: Total = 90; Left censored = 13; Uncensored = 77, Newton-Raphson maximisation: 8 iterations, Return code 1: gradient close to zero, Log-likelihood: -7.899 on 6 degrees of freedom.

* $p < 0.05$.

** $p < 0.01$.

*** $p < 0.001$.

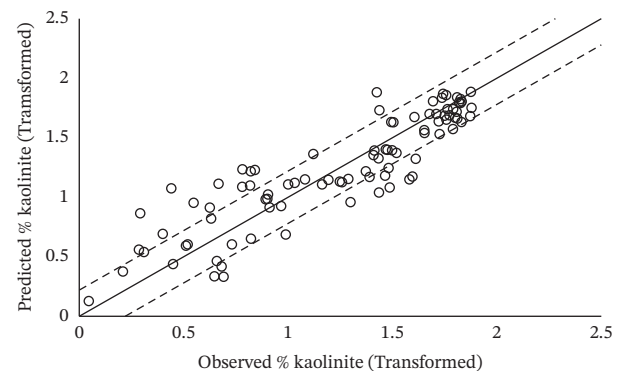


FIGURE 7 | Observed vs. predicted transformed kaolinite concentrations produced using censured regression analysis. The solid line represents the 1:1 relationship whilst dashed lines represent ± 1 log residual standard deviation derived from the logSigma value.

involved in the storage and resupply of K^+ to the soil solution. It is likely that the minerals encompassed a range of weathered

TABLE 14 | Outputs from the stepwise model for (%) kaolinite for the 'XRD dataset' (AK1-90).

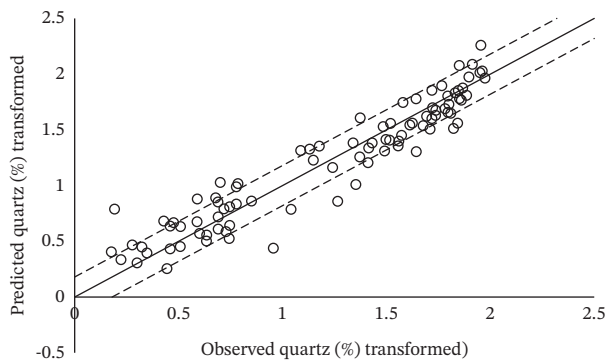
Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	1.341	0.286	1.08e-5***
MIR13	-0.481	0.224	0.034*
MIR14	0.614	0.167	0.0004***
NIR3	3.745	0.419	9.83e-14***
NIR4	1.426	0.328	3.93e-05***
NIR5	-2.913	0.547	8.65e-7***
NIR7	-9.766	1.883	1.53e-06***
NIR12	6.230	1.632	0.0002***

Note: Multiple R-squared: 0.79, p value: < 2.2e-16, Residual standard error: 0.237 on 82 degrees of freedom.

* p < 0.05.

** p < 0.01.

*** p < 0.001.

**FIGURE 8** | Observed vs. predicted transformed quartz concentrations produced using censored regression analysis. The solid line represents the 1:1 relationship whilst dashed lines represent ± 1 log residual standard deviation derived from the logSigma value.**TABLE 15** | Outputs from censreg model for (%) quartz (transformed model) for the 'XRD dataset' (AK1-90).

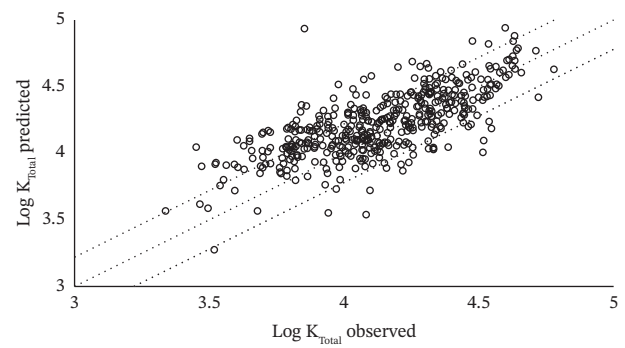
Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	1.695	0.373	5.58e-06***
MIR1	-3.518	0.324	< 2e-16***
MIR2	3.607	0.606	2.69e-09***
MIR13	-0.705	0.138	3.85e-07***
MIR16	-0.561	0.175	0.001**
NIR1	1.957	0.345	1.44e-08***
NIR2	1.881	0.515	0.002***
NIR3	2.022	0.603	0.0008***
NIR4	1.663	0.396	2.71e-05***
NIR11	-11.981	3.207	0.0001***
NIR13	-4.244	2.437	0.081*
NIR14	8.079	3.509	0.0211*
logSigma	-1.707	0.075	< 2e-16***

Note: Observations: Total = 90; Left censored = 1; Uncensored = 89, Newton-Raphson maximisation: 8 iterations, Return code 1: gradient close to zero, Log-likelihood: 24.482 on 13 degrees of freedom.

* p < 0.05.

** p < 0.01.

*** p < 0.001.

**FIGURE 9** | Comparison of observed vs. predicted $\text{Log}_{10} K_{\text{Total}}$ concentrations (mg kg^{-1}). The observed values for the WG dataset were produced by ICP-MS. Model coefficients were obtained from the model parameterised using the 'XRD dataset'.

states and crystal sizes. However, this variability was not found when modelling quartz, suggesting that the weathering state rather than crystal size may be a greater influence on model performance. Overall, the modelling procedure for the minerals worked well despite potential interferences from organic matter and high concentrations of iron oxides (hematite or goethite were found in all samples up to concentrations of 13% and 3.1%, respectively), which have previously been cited as interferences in IR analysis and models [62].

4.3 | WG Model Assessments

The models produced were used to examine the K status of soils from the WG archive. This exercise aimed to assess (i) whether models could reasonably predict K properties, (ii) identify potential issues associated with their use and (iii) their potential to generate future research questions. The opportunity to test previously parameterised models on the WG dataset was limited to ICP-MS measured concentrations of K_{Total} . Reasonable predictions using the parameterised K_{Total} models were produced. Overall, predictions for both soil K properties and mineralogy produced few outliers on the box and whisker plots or concentrations exceeding the highest concentration of the respective property in the 'XRD dataset' used as the modelled variable. Thus, using all the sample scans from the WG dataset in the SMMR selection of NIR and MIR component spectra and including them in model parameterisation appeared to produce reasonable assessments. The instances of overestimation may result from fewer samples being found at the top end of the concentration range for each property. This is a reasonably common issue and would be corrected by the continued inclusion of further samples into models in the future. In addition, the plot between observed CIA and predicted kaolinite concentration (Figure 14) provides confidence that models could provide a basis for understanding inherent soil K status. The calculated values of CIA were also plotted on a WG relief map but no definitive patterns of weathering were identified (SI Figure 4).

The semi-quantitative nature of IR-based soil property models means that they can assess many samples over landscape scales and develop a broad spatial understanding of soil properties. This can help generate research questions. One question that arose from the analysis of lithologies was the role wind and water erosion may play in redistributing K minerals. This

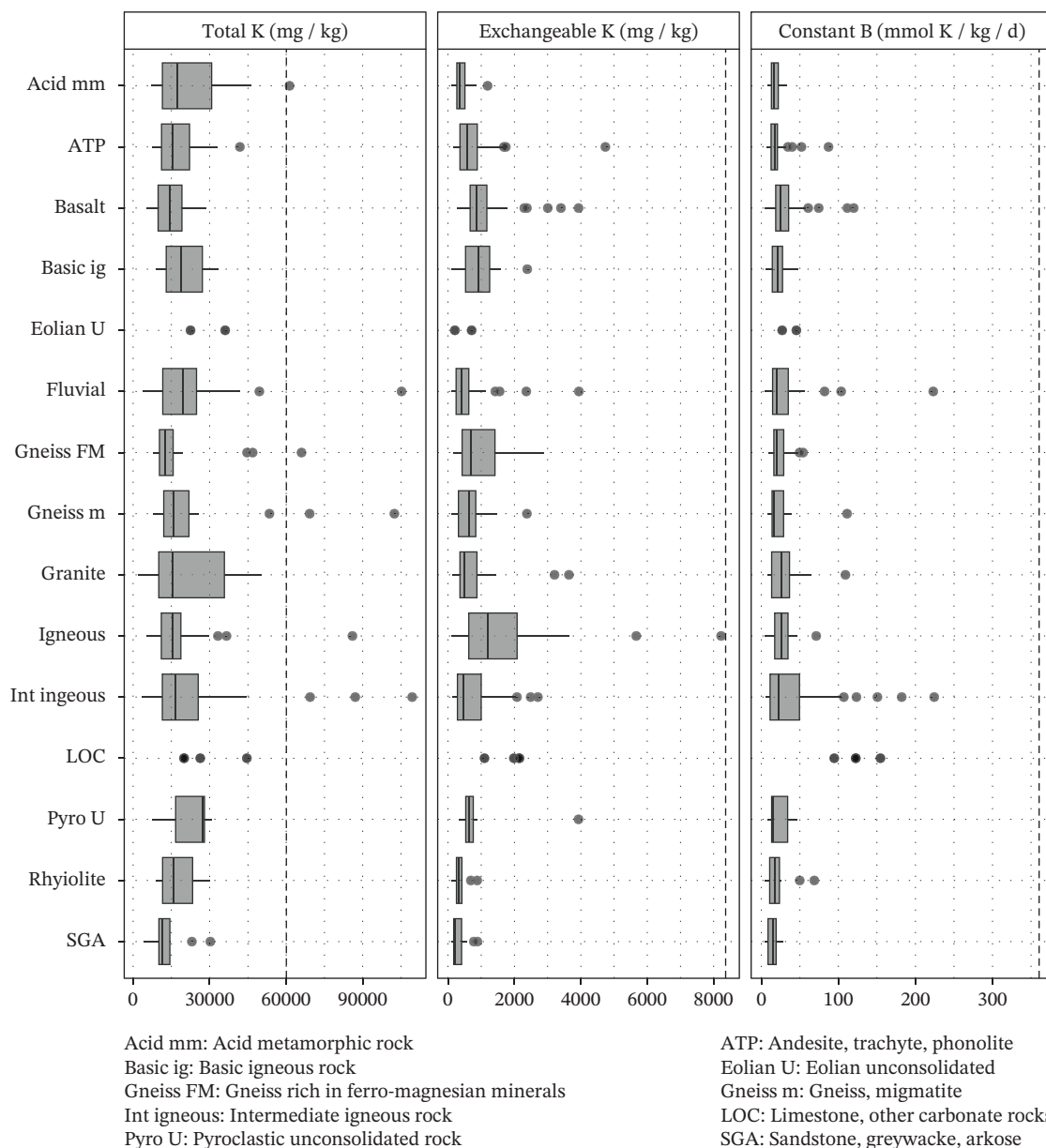


FIGURE 10 | Box and whisker plots of predictions of (i) K_{Total} , (ii) SrCl_2 extractable K and (iii) release constant B for Winam Gulf soils. The vertical dashed line represents the highest value of the property in the XRD dataset used in each model.

question arose from the presence of K-feldspar in soils above basalts, as K-feldspar is not a mineralogical component of basalt. To eliminate the possibility that this was due to models using similar spectral components parts, e.g., the models for total K and K-feldspar share 1 of the identified NIR spectra and 5 of the MIR spectra (Table 17), predictions were compared when the coefficients of the spectra not common to both models were set to '0.' This gave erroneous predictions demonstrating that all selected spectral components were important to predictions. Further possible explanations included the WG geological mapping being low resolution and that within the basalt lithology for instance, secondary rocks such as syenites, nepheline and phonolites exist, which could be a source of K-feldspar and K-mica (biotite). Second, it is highly likely that water and wind erosion in these ancient geological environments may have led to the redistribution of soil particles,

therefore blurring the hypothesised link between soil mineralogy and K-bearing mineralogy. There are reasonably high concentrations of K-feldspar and mica associated with soils above limestone and carbonate rocks (LOC) and eolian unconsolidated sediments (Eolian U), which raise further questions regarding the role of erosion processes. With respect to wind erosion, silt-sized particles are particularly prone to wind erosion and these often contain mineral fragments such as K-feldspar or 'mica' as demonstrated by the relationship found in the XRD dataset between silt and mica (Section 3.5). The influence of water driven erosion in the WG has been examined by [63] using the revised RUSLE equation. However, land degradation across Kenya and eastern Africa enhances the opportunity for erosive redistribution of soils [64]. This suggests that closer examination of the links between inherent K fertility in topsoil, subsoils and lithology is required.

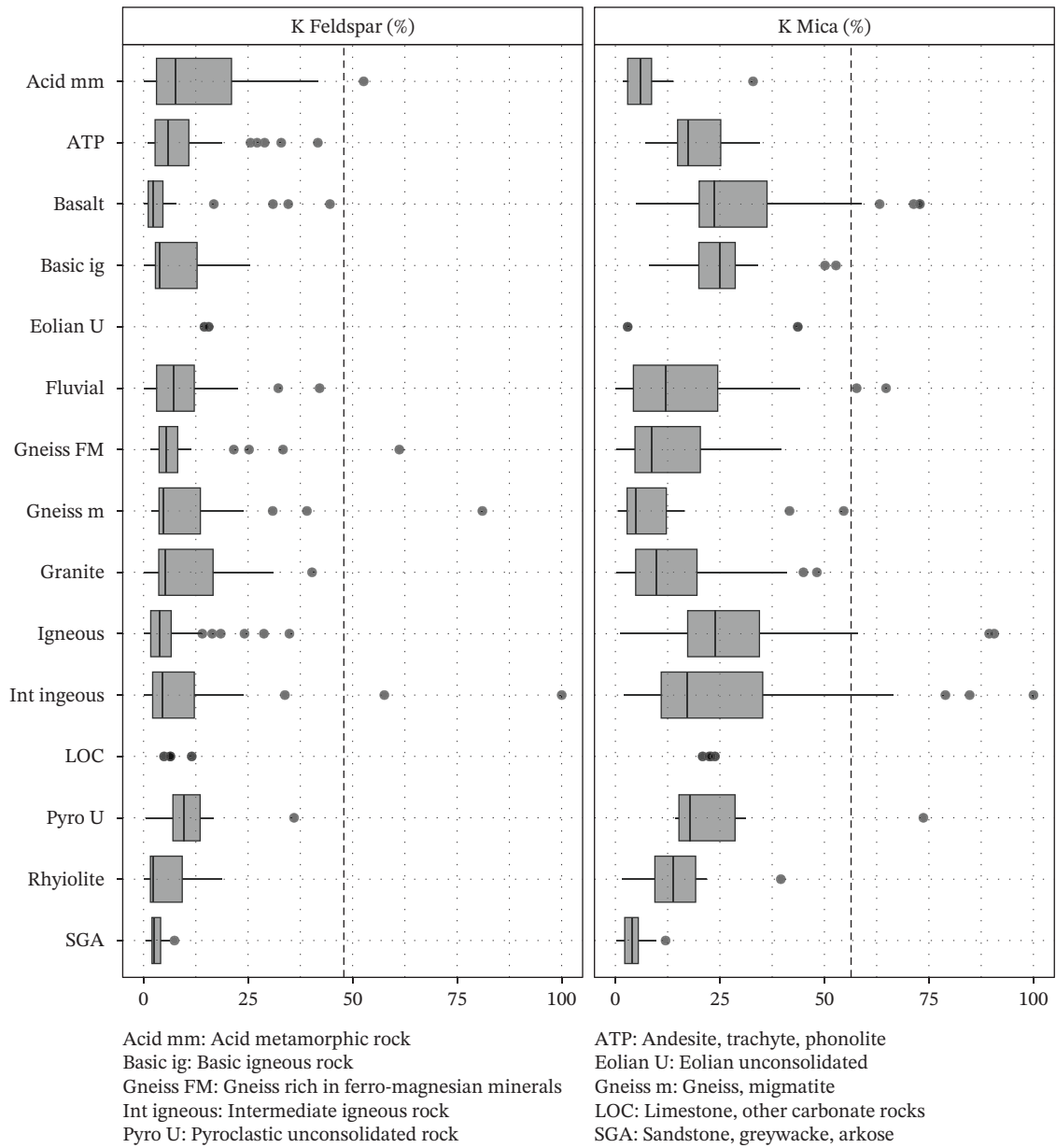


FIGURE 11 | Box and whisker plots of predictions unlogged values of (i) K-feldspar and (ii) mica for Gulf of Winam Gulf soils. The vertical dashed line represents the highest value of the property in the XRD dataset used in each model.

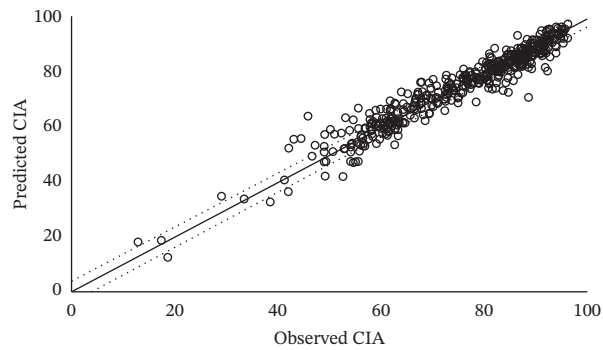


FIGURE 12 | Observed vs. predicted graph for CIA for samples from the WG. Solid line represents the 1:1 relationship whilst dashed lines represent ± 1 RMSE.

TABLE 16 | Outputs from stepwise regression model for the Chemical Index of Alteration (CIA) for the WG soils.

Coefficients	Estimate	Std. Error	Pr (> t)
Intercept	30.012	4.693	4.26e-10***
MIR3	−12.296	4.456	0.006**
MIR4	13.694	1.689	5.60e-15***
MIR5	43.653	4.280	< 2e-16***
MIR7	−3.317	0.397	1.06e-15***
MIR8	67.980	4.016	< 2e-16***
MIR9	24.891	2.718	< 2e-16***
MIR11	−8.623	2.100	4.84e-05***
MIR12	−18.198	2.723	7.38e-11***
MIR15	7.305	2.017	0.0003***
MIR16	−6.661	2.453	0.0068***
NIR1	39.872	4.782	1.06e-15***
NIR2	83.171	9.677	< 2e-16***
NIR3	42.225	11.86	0.0004***
NIR6	−93.373	10.24	< 2e-16***
NIR7	167.76	17.48	< 2e-16***
NIR9	−127.83	18.57	2.10e-11***
NIR12	218.05	28.03	5.58e-14***
NIR14	−230.18	24.52	< 2e-16***

Note: Multiple R-squared: 0.93, *p* value: < 2.2e-16, Residual standard error: 4.021 on 425 degrees of freedom.

**p* < 0.05.

***p* < 0.01.

****p* < 0.001.

4.4 | Extending Use of Models

Soils in sub-Saharan Africa are derived from different lithologies and have undergone potential re-distribution and different degrees of weathering relating to climate and age [65], which may determine their inherent K status. Thus, improving sustainable soil K management requires understanding differences in K properties and the distribution of relevant minerals. The concept of ‘land health surveillance’ [66] has been proposed to help identify problems relating to the degradation of land. Land health surveillance is defined as the ongoing collection of data essential to the planning, implementation and evaluation of land management policy and practice and application of these data to promote, protect and restore land and ecosystem health [67]. Central to this concept are eight factors that combine science with approaches often used in public health. Two of these factors are the ability for (i) repeated measurement of land health and associated risk factors using well defined populations of sample units and (iv) rapid low-cost screening tests to permit detection of cases and non-cases in large numbers of samples. The use of IR-based models, such as those reported in this paper, may enable gaps in soil K knowledge to be filled, to generate baselines and contribute to improved decision-making with respect to K fertiliser use.

Large collections of soil data are progressively seen as a resource to enable increased food production and prevent the degradation of land. For example, the authors in [68] combined XRD patterns with geochemistry and compositional analysis and clustering algorithms to identify mineral–nutrient relationships in African

soils, to aid fertility assessments. However, it is important to understand the levels of data complexity and purpose required by users, who may include small holders, farmers through to policymakers. The value of sample and data archives allows a continuous reassessment of primary soil survey data, especially when combined with new laboratory measurements and modelling approaches. The information produced may complement knowledge obtained through soil classification, geochemical survey and geological mapping, providing policymakers with fundamental knowledge regarding the nature of the inherent soil nutrient status. In addition, these models can be used to identify where further, more expensive analysis could be targeted.

More cost-effective K fertilisation strategies can be formulated for regional areas if first, the presence of those minerals (e.g., illite or smectite) that have the potential to store excess K, either returned via the mineralisation of plant material or from excess fertiliser, is known [58]. Second, it is increasingly important to understand the potential K-bearing mineral reserves that plants can access. New technologies to improve plant K nutrition may be tailored to the differences in release rates of K from minerals [55], using microbial and plant rooting systems [8]. Recent work has focused on those rhizosphere micro-organisms that have the potential to solubilise mineral K [13]. This may lead to scenarios where using IR-based models to understand the K-bearing mineralogy, along with expected release rates, may be used to link new crop varieties, genetically bred to produce greater K efficiencies to soils with known mineralogy. If this involves developing root systems that increase the solubilization of K by exudates and microbes [69], a need exists for knowing K mineralogy over regional areas

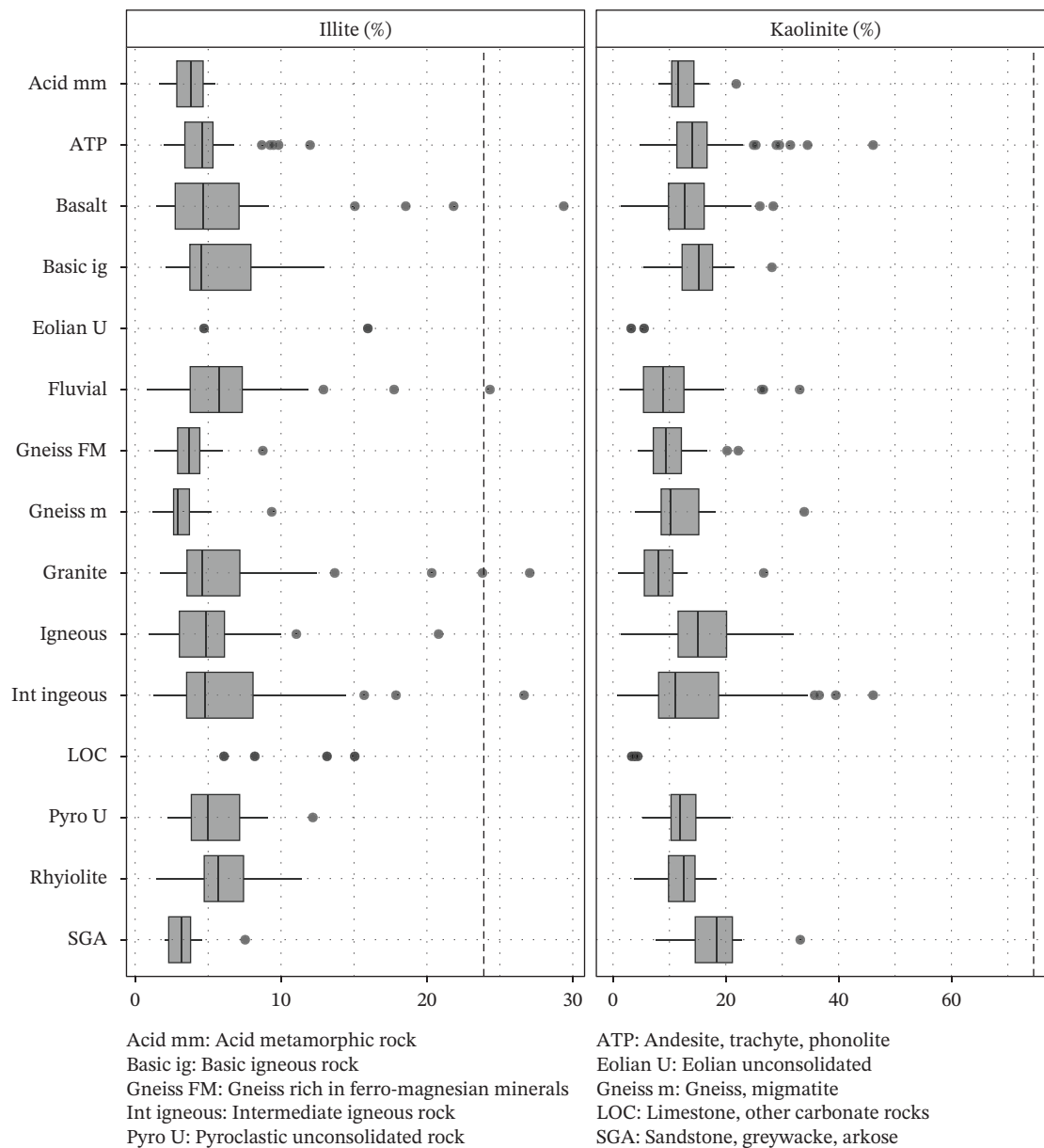


FIGURE 13 | Box and whisker plots of predictions unlogged of (i) illite and (ii) kaolinite for the Winam Gulf soils. The vertical dashed line represents the highest value of the property in the XRD dataset used in each model.

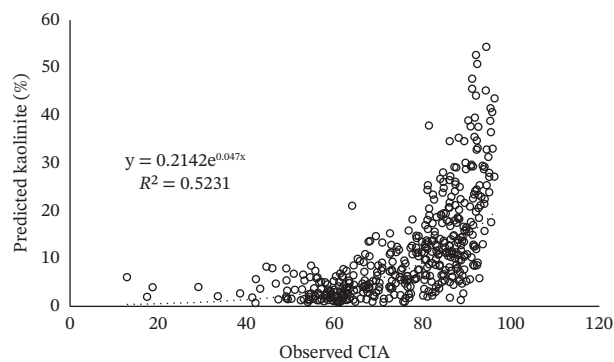


FIGURE 14 | Observed CIA values from the WG calculated from ICP-MS results plotted against predictions of kaolinite using the model outputs from Table 14.

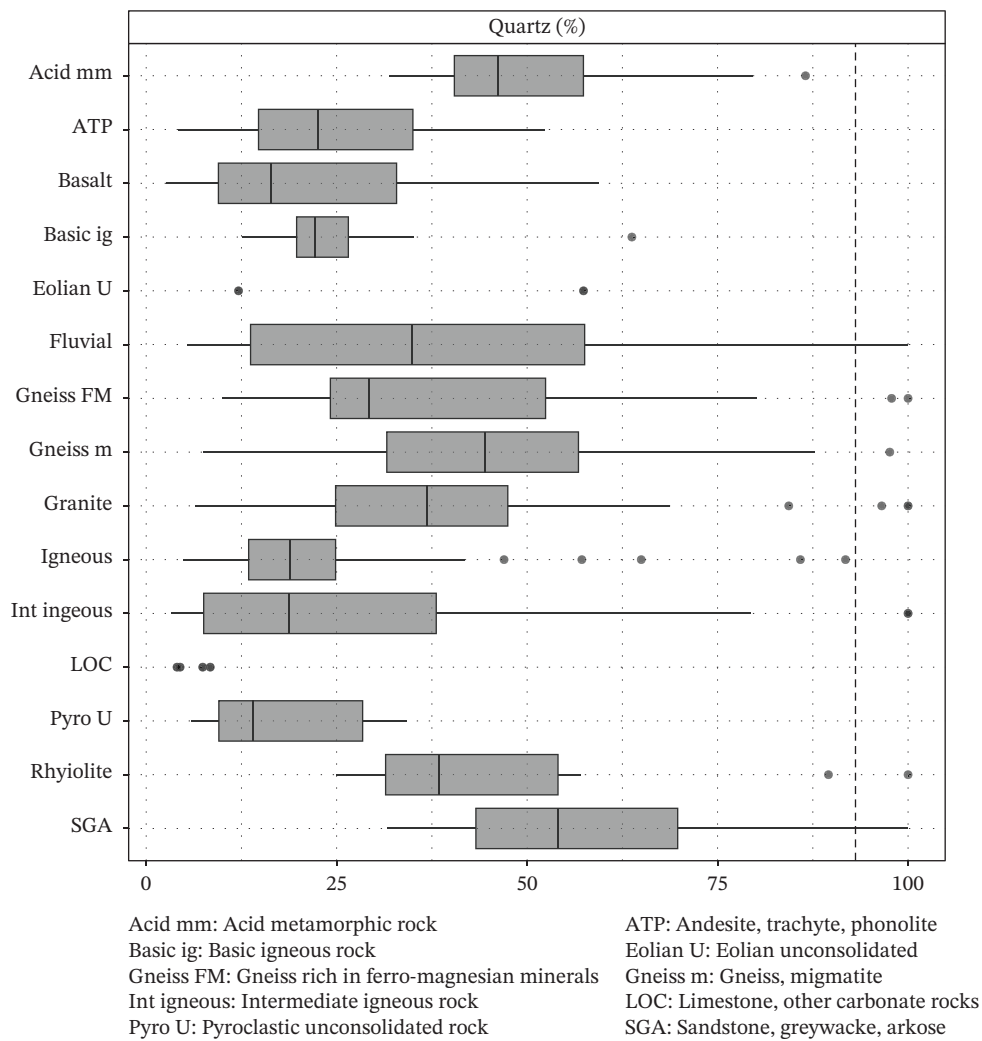


FIGURE 15 | Box and whisker plots of predictions unlogged of quartz for the Winam Gulf soils. The vertical dashed line represents the highest value of the property in the XRD dataset used in each model.

TABLE 17 | Review of spectral components used in parameterized models of soil K properties and mineralogy.

	Mid-IR spectral components																	NIR spectral components													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	1	2	3	4	5	6	7	8	9	10	11	12	13	14
K _{Total}			x	x						x	x	x	x			x									x		x	x			x
K _{SrCl2}			x		x					x				x				x	x												
Constant b	x		x						x					x				x													
K-feldspar			x	x		x	x		x		x		x		x	x		x						x							x
K-mica		x	x	x		x				x											x	x	x	x							
Quartz	x	x	x	x				x		x				x	x	x				x											
Kaolinite	x	x	x	x				x		x			x		x																
Illite			x													x								X	x						
CIA Index			x	x	x		x	x	x		x	x			x	x		x	x	x			x	X		x			x		x

to allow effective wide-spread roll-out. Models based on NIR and MIR spectra, therefore, have a potential role in the long-term monitoring of soils and changes in their K-bearing mineralogy. This application could be used as a guide to monitor nutrient imbalances caused by nutrient mining that often occurs in tropical agriculture. On a more local scale, this type of model could be developed as a cheap way to identify when additional rock fertiliser application may be required and would be highly applicable to the growing interest in the use of milled, K-containing rocks as fertilisers [4].

5 | Conclusions

This work has demonstrated the complexities of soil K properties and mineralogy in soils of Uganda, Kenya and Tanzania. Models were produced, based on NIR and MIR scans for a wide range of soil K properties and minerals using a training dataset and tested on samples from WG. When applied to the soils from the WG, differences in properties with lithology were identified but also questions relating to the role of erosion in maintaining K minerals in topsoils, and that the true lithological relationship to inherent K stocks, may need to be examined through the assessment of subsoil samples. However, the models offer a potential toolbox for developing initial strategies for long-term sustainable management of soil K fertility, across landscapes. These types of rapid IR scanning-based models are ideally placed for future use in decision-making, particularly as soil survey archives increasingly include IR scans. Combined with new lab-based measurements, they have the potential to provide additional tools in developing understanding of the dynamics of nutrient poor soil systems.

Author Contributions

A. M. Tye: conceptualization, methodology, formal analysis, investigation, writing—original draft, writing—review and editing, visualisation, supervision, data curation and funding acquisition.

K. Leeming: methodology, formal analysis, investigation, data curation, writing—review and editing and visualisation.

M. R. Cave: methodology, formal analysis, investigation, writing—review and editing and visualisation.

S. J. Kemp: methodology, formal analysis, investigation, data curation and writing—review and editing.

T. Barlow: investigation and data curation.

O. S. Humphrey: resources, data curation, investigation and writing—review and editing.

M. J. Watts: resources, funding and writing—review and editing.

M. Pearson: investigation, data curation and writing—review and editing.

J. Wragg: investigation, data curation and writing—review and editing.

O. Osano: resources, investigation and writing—review and editing.

E. Weullow: resources, investigation and writing—review and editing.

E. Towett: resources, investigation and writing—review and editing.

K. D. Shepherd: resources, supervision and writing—review and editing.

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collection in the WG. The work is published with the permission of the Director of the British Geological Survey (UKRI).

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Conflicts of Interest

The authors declare no conflicts of Interest.

Data Availability Statement

The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Supporting Information.** SI Figure 1: Example of K release model. SI Figure 2: Spectral components of MIR scans. SI Figure 3: Spectral components of NIR scans. SI Figure 4: Sample locations in the Winam Gulf are shown with those points used in the XRF or model training dataset shown in red. Also shown are maps of elevation, lithology (see Table S1 for legend details) and land use in the study area. Calculated values of the CIA weathering index are shown superimposed on the elevation map. Table S1: Lithology identification code and description for map in SI Figure 4