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Research Paper

An investigation of plant growth by the addition of glauconitic fertilizer

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ABSTRACT

This work investigates the usefulness of glauconite as an alternate fertilizer by field experiments on growing durum wheat. Separate field experiments using glauconitolite and original soil compare the effectiveness of different products for agronomic applications. The addition of glauconitolite to soil increases the grain yield of wheat significantly. Glauconite undergoes noticeable structural and chemical changes in the soil during the growing season of wheat. The addition of glauconite improves the soil physico-chemical properties by enhancing concentrations of organic carbon, nitrates, exchangeable ammonium, K, P, Ca and Mg. The pH of the originally acidic soil increases from 6.0 to 6.7 with the application of glauconitic products. The increased K, P, Ca and Mg contents in the soil are associated with the complex chemical composition and ion-exchange capacity of glauconite. The K_2O content of the original glauconite decreases by about 24% during one growing season. This study, therefore, demonstrates glauconitic rocks as environment-friendly, and slow release fertilizers.

1. Introduction

The application of fertilizers is crucial for meeting the world's current crop demand due to the population growth and decreasing of arable land (Sutton et al., 2011). The K and P fertilizers appear to be the least greenhouse gas emitter especially in comparison to traditional N fertilizer (Wang et al., 2017). Traditional fertilizers release excess nutrients than that can be absorbed by plant roots. This results in the enrichment of chemicals (mainly N) in the soil for environmental pollution (Vitousek et al., 2009; Wang et al., 2017). As plants absorb about 2% potassium from the soil in a season (Shanware et al., 2014), the application of highly concentrated potassium salts contributes to the excessive accumulation of non-exchangeable K in the soil (Basak et al., 2017). The soil releases excess K to the groundwater during the off season. The application of slow release K-fertilizer, on the contrary, serves a dual purpose by providing nutrients for the plant growth and by maintaining the low level of chemicals in the agricultural soils (Liang et al., 2019). A few studies explore mining wastes for the purpose of environment-friendly, alternate fertilizers (Binner et al., 2017; Gurav et al., 2018; Said et al., 2018). The fertilizer potential of glauconite is indicated in recent studies (Shekhar et al., 2017a; Verma, 2018). Recently Franzosi et al. (2014) demonstrated the application of glauconitic rocks for raising the level of potassium in agricultural soil.

Glauconite is a dioctahedral micaceous phyllosilicate mineral with variable chemical composition and a high content of interlayer potassium (up to 8–9%) (Odin and Matter, 1981; Drits, 1997; Meunier and El Albani, 2007). It is widely distributed in ancient coastal marine sedimentary deposits (Baldermann et al., 2015a, 2015b, Baldermann et al., 2017; Banerjee et al., 2012; Banerjee et al., 2016a, 2016b; Bansal et al., 2017). It is used for various purposes like agriculture (Castro and Tourn, 2003; Franzosi et al., 2014; Karimi et al., 2012; Santos et al., 2015), water treatment (Naghipour et al., 2018) and environmental management (Voronina et al., 2015).

The mineral glauconite has several advantages as an alternative potassium fertilizer relative to the widely used potassium salts (example, KCl) (Franzosi et al., 2014). The application of glauconite does not cause salinization of soils and contamination of groundwater with chlorine. Glauconite contains many trace elements including Cu, Zn, Fe, Mn, B, Se, Co, Mo, Cr, Vd, Y which serves as necessary micro-nutrients for the plant growth. Further, glauconite rocks improve soil texture,

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porosity and permeability because of the uniform, pelletal texture. The high sorption capacity of glauconite enhances the moisture retention capacity of agricultural soils. A few studies reported a positive impact of glauconite on growth of agricultural plants, such as olive tree (Karimi et al., 2012), sunflowers (Torqueti et al., 2016), grass (Franzosi et al., 2014), oat (Rudmin et al., 2017b), coffee (Dias et al., 2018), etc. Glauconitic rock may be used directly as fertilizer after crushing (Castro and Tourn, 2003; Karimi et al., 2012; Franzosi et al., 2014; Santos et al., 2016; Rudmin et al., 2017b). Alternately, potassium salts may be produced by the chemical treatment of glauconite for agronomic applications (Shekhar et al., 2017b). As the composition of glauconite varies widely (cf. Baldermann et al., 2017; Banerjee et al., 2016a; Drits, 1997; Meunier and El Albani, 2007), it is necessary to study the physical, chemical and mineralogical characteristics of a particular deposit for agronomic applications. Further, the rate of release of potassium from the glauconite structure is rarely investigated (Santos et al., 2016). The release of potassium from the glauconite structure to soil may be faster than that can be assimilated by plants, causing excess accumulation of nutrients. The application of glauconite as a slow-release fertilizer is an emerging field of research (Franzosi et al., 2014).

This study examines the effectiveness of glauconitic rock by conducting field experiments on wheat plants. The objectives of this investigation are (a) to demonstrate the effectiveness of glauconitic products on the yield of plant and (b) to record modifications of soil fertility before and after the growing season.

2. Materials and methods

2.1. Rock sampling and preparation

Meso-Cenozoic glauconite rocks of the Western Siberia were investigated to assess their fertilizer potential. Rudmin et al. (2017a, 2017b, 2019) provide a detailed geological background of samples. The Bakchar iron deposit in the south-eastern corner of Western Siberia plate (52°01′45″N; 82°07′20″E) (Fig. 1a), belongs to a huge iron ore basin (Belous et al., 1964; Rudmin et al., 2019). The marine-originated Bakchar iron deposit (av. thickness ~80 m) occurs in the subsurface within the Upper Cretaceous and Paleogene sedimentary sequences (Fig. 1b; Belous et al., 1964; Rudmin et al., 2017a, 2019).

The investigated glauconitolite sample occurs at a depth between 201.8 and 205.0 m in the drill hole 627 (Fig. 1c,d). The sample preparation followed standard practice (cf. Rudmin et al., 2017b). Approximately 20 kg core samples were pulverized to < 2 mm with a jaw crusher and a roller crusher. Standard sieves (with mesh openings of 500 and 80 μm) were used to separate lightly crushed samples into three granulometric fractions. The intermediate fraction was further processed using an electromagnetic separator ECM 10/5 (JSC "Mining Machines", Russia). The magnetic concentrate was reprocessed at the same current intensity to enrich the glauconite fraction (hereafter referred to as glauconite concentrate).

2.2. Physical, chemical and mineral characterization

The mineralogical characterization of the studied samples was carried out using a combination of optical microscopy, X-ray diffraction (XRD), X-ray fluorescence (XRF), scanning electron microscopy attached to an energy-dispersive spectrometer (SEM-EDS), and high-resolution transmission electron microscopy (TEM). Bulk mineralogical composition of samples was determined by a Rigaku Ultima IV X-ray diffractometer at the Tomsk Oil and Gas Research and Design Institute, with Cu-Kα radiation at a current of 30 mA and a voltage of 40 kV. < 10 μm fractions of powdered samples were scanned from 3°–70° 2θ, with a step of 0.02° at a scanning rate of 1 s, divergence slit (DS) being 1.2 mm. Each sample was scanned initially after air drying (i.e., untreated), and subsequently by ethylene-glycol solvation by vaporization in a desiccator for 24 h. Glauconitic grains (at least 50 grains of initial and after field plant growth test) were scanned under TESCAN VEGA 3 SBU scanning electron microscope (SEM) and OXFORD X-Max 50 energy-dispersive adapter with 20 kV accelerating voltage, specimen current of 5–12 nA, and spot diameter of approximately 2 μm.

Major element concentrations of the whole-rock, glauconite grains and soil samples were estimated by HORIBA XGT 7200 X-ray fluorescence microscope operated at a tube current of 0.5 or 1 mA, beam diameter of 1.2 mm or 50 μm, respectively, and a voltage of 50 kV.

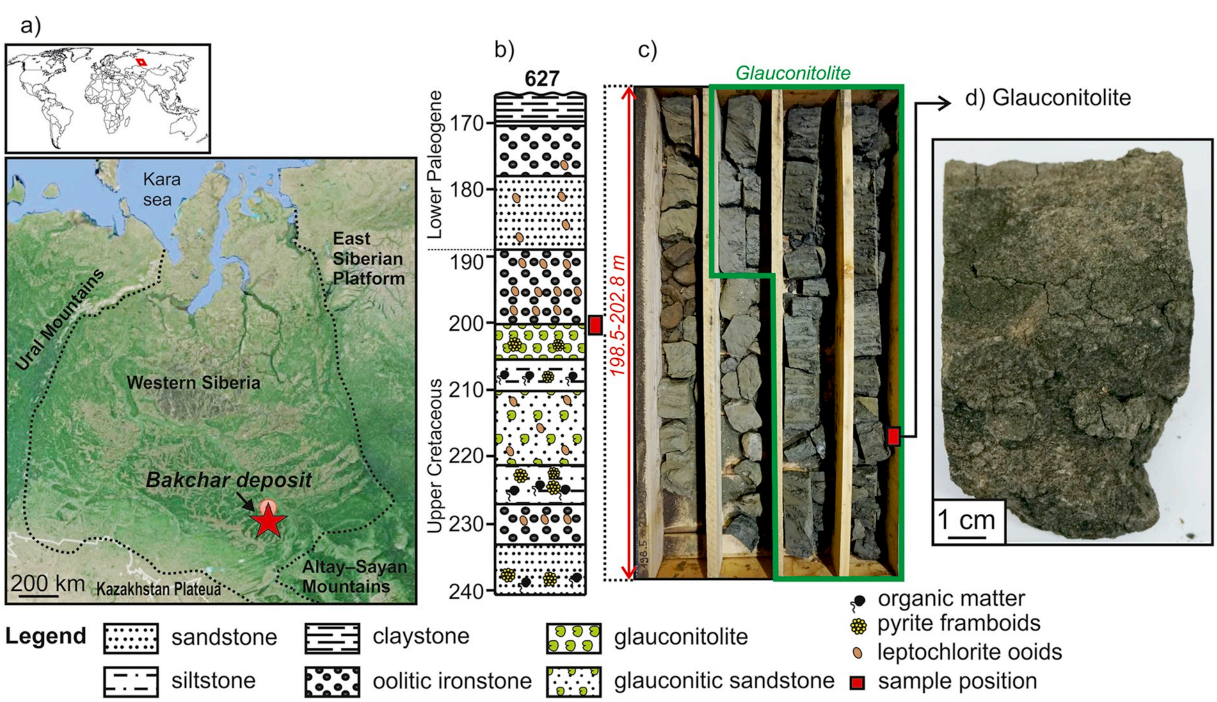

Fig. 1. Location map of Bakchar deposit in the Western Siberia (a), stratigraphic log showing occurrence of glauconitic rocks (b), photos of core (c) and sample glauconitolite (d).

Table 1
Average of major oxides (in wt%) concentrations in initial glauconite and glauconite collected from soil after field plant test according to XRF.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	TiO_2	CaO	Fe_2O_3(total)	L.O.I.	Total
Initial glauconite	0.7	1.7	7.0	51.7	0.1	6.4	0.2	1.5	24.9	5.8	94.2
Glauconite after field test	0.5	2.0	7.8	52.6	0.1	4.9	0.3	1.7	20.4	9.7	90.3

Note: Loss on ignition (L.O.I.) was obtained by heating sample powders to 900 °C for 9 h.

Samples for XRF were prepared by pressing and melting sample powder to discs with diameter of 10 and 3 mm.

The shape and micro-structure of glauconite particles were examined by JEOL JEM-2100F transmission electron microscopy (TEM). TEM images were captured in the transmission mode of the TEM. A drop of clay suspension was allowed to dry on a copper grid (300 mesh, 3.05 mm in diameter) coated with carbon film before examining it with TEM operated at 200 kV. Structural, mineralogical and chemical changes of glauconite were evaluated before and after the growing season. After conducting agrochemical field experiments, glauconite grains were collected from the soil to study their structural and chemical changes. The grains were carefully hand-picked under a binocular microscope and investigated by using SEM.

2.3. Field experiments

A field experiment was conducted with durum wheat (*Triticum turgidum*) in the Tomsk Region (village Zyryanskoe, 56°49′18"N; 86°36′0″E) for 120 days from June 1 to September 28 in the year 2018, with three replications. Experiments were carried out separately by applying glauconitolite and using the original soil. We used dark grey soil, which is the most common variety in S-E Western Siberia.

Results of soil test at a depth of 0–30 cm provide following specifications: total organic carbon–7.05%; pH–6.0, nitrate 12.25 $mg{\cdot}kg^{-1}$, ammonium nitrogen–3.5 $mg{\cdot}kg^{-}1$, P–493 $mg{\cdot}kg^{-1}$ and K–224 $mg{\cdot}kg^{-1}$. Glauconitolite was used as the main plot and a control (soil sample) served as the subplot. Totally, 6 plots were used in the field experiment (1 fertilizer and 1 control × 3 replications). Within a plot of 1 m long and 1 m width 5 lines with 20 seeds were sowed. Spacing between adjacent seeds were kept at 5 cm. Dry glauconitolite was introduced into the soil at 200 $g{\cdot}m^{-2}$ equivalent to 2 $t{\cdot}ha^{-1}$. Glauconitolite was pulverized to < 2 mm with a jaw crusher to introduce into the soil. Grain yield, as well as height and number of plants, were estimated after the field test. Grain yields were estimated as weight of grain (at 12% moisture) after harvest. Wheat grains within each plot were measured by a cereal moisture tester. A ruler (cm) was used to determine plant height. Each parameter was averaged over three plots for a certain fertilizer type and control.

Soil samples were collected on 1st, 60th and 120th day of field experiment for recording agrochemical parameters, including the humus content (by Tyurin's method), the total nitrogen content (Kjeldahl's method), the soil pH (by potentiometric method for pH KCl), exchangeable bases (by the trilonometric method), the exchangeable cation content (in ammonium acetate extract), available phosphorus content (by Kirsanov's method), available potassium content (by flame photometry in the 1 N CH_3COONH_4 extract) (cf. Sokolov, 1975) and total potassium oxide (by XRF).

3. Results

3.1. Mineralogical and chemical characterization of glauconite

Up to 60% of glauconite, 32% of detrital quartz and around 8% of chamosite, goethite, illite are part of glauconitolite. The whole rock chemical composition of the glauconitolite is characterized by 57.3% of SiO_2, 17.5% of Fe_2O_3(total), 11.7% of Al_2O_3, 4.3% of K_2O and 2.3% of MgO. The concentrations of CaO, P_2O_5, TiO_2, Na_2O and MnO are < 2%.

Micro-aggregates of an original glauconite grain exhibits slightly curved, ordered and parallel oriented flakes with sinuous contours, and with domain-like nano-texture (cf. Rychagov et al., 2010). The lengths of the flakes vary from 0.5 to 3 μm. Micro-aggregates of glauconite in the soil modifies after the plantation. The granules show honeycomb to platy nanostructure (Sokolov and Chernov, 2013). These less ordered glauconites exhibit curvier flakes than the original.

XRF and SEM-EDS study reveals that the average chemical composition of the glauconite changes before and after the field experiments (Table 1). The average K_2O content (according to XRF) of the original glauconite is 6.4 wt% (evolved type of Odin and Matter, 1981). The formula of initial glauconite is $K_{0.65–0.69}Ca_{0–0.05}(Fe_{1.46–1.59}Mg_{0.26–0.30}Al_{0.11–0.31})_{1.96–2.06}(Si_{3.48–3.66}Al_{0.34–0.52})_4O_{10}(OH)_2$ according to SEM-EDS data. The average K_2O content of glauconite collected from soil after the field experiment is 4.9 wt%. The formula of this glauconite is $K_{0.46–0.52}Ca_{0.07–0.10}(Fe_{1.00–1.12}Mg_{0.32–0.35}Al_{0.82–1.07})_{2.26–2.41}(Si_{3.96–4.0}Al_{0.03–0.04})_4O_{10}(OH)_2$ according to SEM-EDS.

TEM images of the glauconite grains were compared before and after the plant growth experiments. TEM images show nano-scale spindles of mica crystallites within glauconite pellets (Fig. 3). Mica lamellae consist of 5 or 6 spindles. The spacing between spindles within the lamellae of glauconite grains ranges from 9.4 to 12.5 Å (cf. Amouric, 1985). Glauconite grains rarely reflect poorly crystalline zones (X-phase of Amouric, 1985 and Jimenez-Millan et al., 1998). However, a few zones with 12.5–12.9 Å planes occur within the samples (Fig. 3). The poorly organized lamella with a periodicity of 14 Å, indicate the presence of smectite units (Fig. 3). Mica crystallites of initial glauconite contain up to 10% of poorly crystalline zones and smectite units (Fig. 3a). While lamellae of glauconite include > 10% of X-phases and smectite units after the plant growth test (Fig. 3b).

The XRD-pattern of the air-dried glauconite sample exhibits a (001) reflection at 10.03–10.05 Å, a weak (002) reflection at 5.03 Å and a strong (003) reflection at 3.43 Å (Fig. 4). The (001) reflection shifts slightly from 10.47 Å to 10.13 Å on glycolation (Fig. 4), indicating the high maturity of glauconite (or "evolved variety" of Odin and Matter, 1981; Amorosi, 1995) with 90–94 wt% glauconite layers and up to 10% smectite layers.

3.2. Influence of glauconite on plant growth and soil

Rainfall and temperature of the growing season in south-eastern Western Siberia (Tomsk Region) remain near-normal. Grain yield, as well as height and number for durum wheat plants, vary considerably with an application of different fertilizers (Fig. 5). With application of glauconitolite into the soil (at a concentration equivalent to 2 $t{\cdot}ha^{-1}$) grain yield, plant height and the number of plants increase by 18.4%, 32.3%, 5.9%, respectively. While the application of the glauconitolite produces to soil yields 1613 $kg{\cdot}ha^{-1}$. The yield of the control sample, on the contrary, is far less (1362 $kg{\cdot}ha^{-1}$).

Basic soil physico-chemical properties at the beginning, middle and end of the growing season of wheat vary considerably (Fig. 6, Table 2). The pH of original soil treated with glauconitolite increases steadily, exceeding 6.7. Whereas the pH of the control sample increases slowly after 60 days, but remain within 6.5. The average concentrations of available potassium within the soil increases to 542 and 376 $mg{\cdot}kg^{-1}$ (Fig. 6b) for plots with glauconitolite and without fertilizers, respectively. While the total K_2O content decreases marginally (from 0.01 to

Table 2
Agrochemical characteristics of soil during plant growth test.

Time[a]	Soil sample	pH	Available K, $mg \cdot kg^{-1}$	Available P, $mg \cdot kg^{-1}$	Ammonium nitrogen, $mg \cdot kg^{-1}$	Nitrate, $mg \cdot kg^{-1}$	Organic carbon, %	Available Ca, $mg \cdot kg^{-1}$	Available Mg, $mg \cdot kg^{-1}$	Total K_2O, wt%
1st	Control	6.0	224	493	4	12.3	7.1	15.9	2.0	2.00
60th	Glauconi-tolite	6.3	338	523	2.3	16.5	7.6	16.7	3.7	2.01
	Control	6.4	265	552	2	13.8	7.2	16.1	3.5	1.99
120th	Glauconi-tolite	6.7	542	838	1.3	18.7	7.9	17.2	2.5	2.00
	Control	6.5	376	835	2	19.2	7.5	16.6	3.1	1.95

[a] Duration days after plant seeding.

0.05%) during the growing season (Table 2). The glauconitolite and the control sample exhibit a similar increase in the concentrations of available phosphorus (Fig. 6c, 838 and 835 $mg \cdot kg^{-1}$). All plots record a consistent decrease in ammonium nitrogen; the glauconitolite sample records the maximum decrease to 1.28 $mg \cdot kg^{-1}$ (Fig. 6d). Further, concentrations of nitrates, organic carbon, calcium and magnesium within soil records a general increase during the growing season (Table 2). The soil treated with glauconite records the highest concentrations of organic carbon and calcium (7.9% and 17.2 $mg \cdot kg^{-1}$, respectively). This sample also exhibits the least concentration of nitrate.

4. Discussion

SEM-EDS, XRF, and TEM studies of glauconite grains before and after the field experiments reveal that the structure and composition of glauconite changes favorably for fertilizer applications during 120 days of the growing season of wheat. Glauconite structure records an increase in the sinuosity of micro-aggregates after the growing season (Fig. 2). A decrease of interlayer potassium due to its diffusion into the soil possibly results in the collapsing of the glauconite structure (Castro and Tourn, 2003; Meunier and El Albani, 2007; Baldermann et al., 2012, 2013). The CaO content of the glauconite increases marginally from 0.2 wt% to 0.3 wt% after the experiment (Table 1). The increase in CaO content of glauconite possibly relates to the substitution of K^+ by Ca^{2+} content of the soil within the interlayer structure. The Fe_2O_3(total) concentration in glauconite decreases from 24.9 wt% to 20.4 wt%. Since Fe occurs in both bivalent and trivalent form in glauconite, its diffusion from the mineral as Fe^{2+} proceeds more intensively than other cations (Baldermann et al., 2015a, 2015b; Baldermann et al., 2017). TEM data reveals an increase in the amount of smectite and poorly crystalline spindles in glauconite after the field test (Fig. 3). The interaction between glauconite and soil transforms the original glauconite to glauconite-smectite and smectite (Loveland, 1981; Chang et al., 2008; Skiba et al., 2014). The conversion of glauconite to smectite facilitates the moisture retaining capacity of the soil, especially during the growing season. Further, smectite acts as the micro-sorption barrier to downward migrating excessive nutrients (like nitrogen). The K_2O content of the glauconite decreases from initial 6.4 wt% to 4.9 wt% after the field experiment. As the K_2O content of glauconite depletes by ~24% of the original, the same fertilizer is expected to release remaining potassium in the next two or three seasons. The introduction of glauconitolite within a weakly acidic soil has a stimulating effect on the seeding and growth of durum wheat. The direct application of initial glauconite rocks (especially glauconitolites) is a cost-effective option as it can be used after simple grinding. On the contrary, beneficiation of potassium salts from glauconite requires many steps and huge investment treatment (Rudmin et al., 2018). Silicate minerals are being explored in recent years for alternate sources of K, especially in the situation where conventional potash salts are economically inaccessible (Manning, 2010, 2018). Powdered granite is found to be a less efficient fertilizer as it increases wheat plant biomass < 10% relative to the control (Hinsinger et al., 1995). While the introduction of powdered syenite or phlogopite mica to soil increases plant diameter (leek, *Allium ampeloprasum* L. var.) by 60% (Manning et al., 2017). The application of zeolite (separated from coal ash) to soil increases the yield by around 26% (Flores et al., 2017). However, because of the low cost and easy availability of glauconite rock of the Bakchar deposit is a highly promising alternate potash fertilizer candidate.

The application of glauconitolite improves the physico-chemical properties of soil for the agronomic application (Fig. 6, Table 2). The soil pH increases to 6.7, corresponding to near neutral behavior when added with glauconite. Usually, the soils in the Tomsk region are acidic (Sorokin et al., 2018). The concentration of available K in the soil increases relative to the control by 45% when added with glauconitolite. Total potassium decreases slightly in the soils mixed with

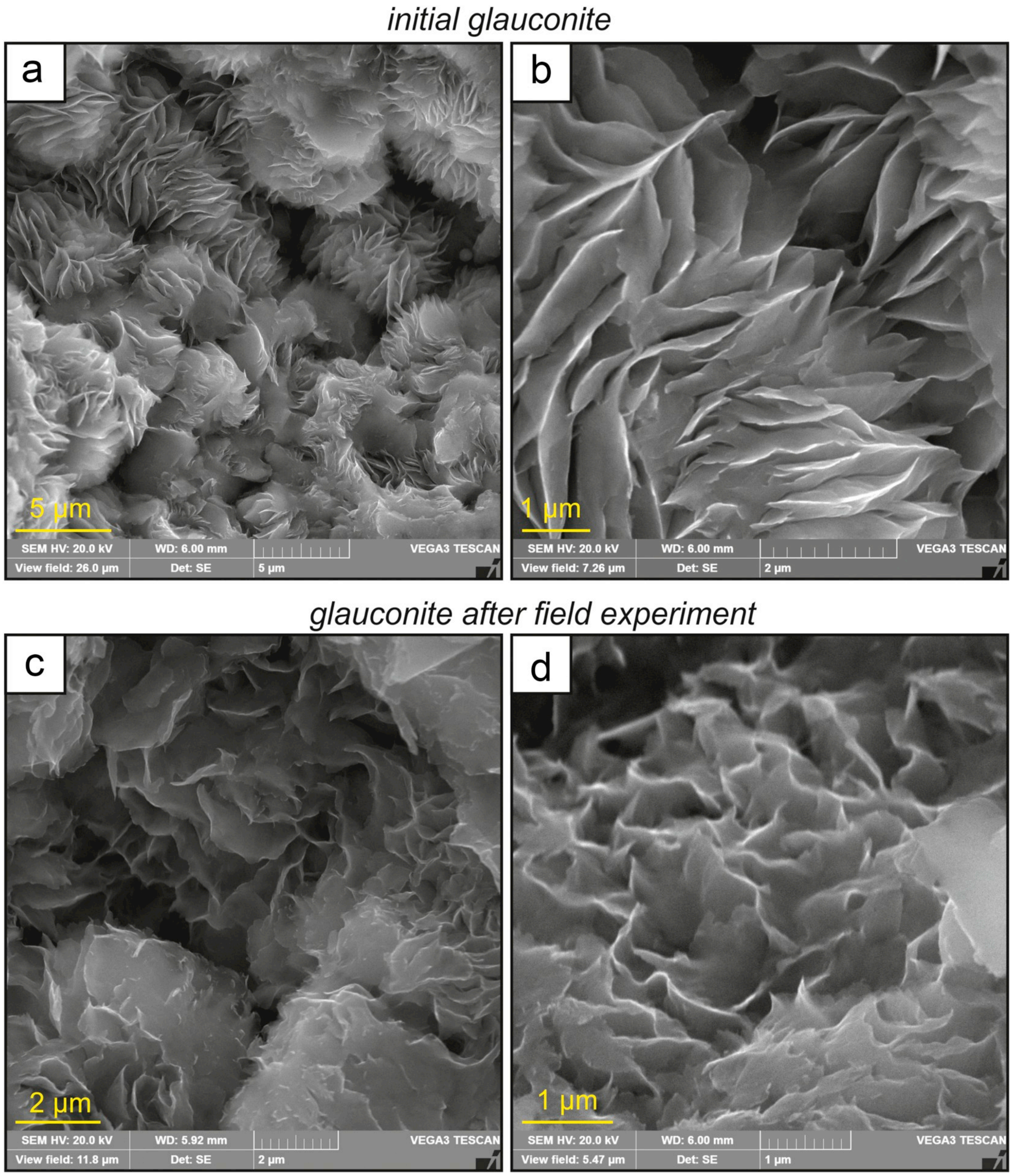

Fig. 2. SEM-images of initial glauconite (a,b) and final glauconite after field experiment (c,d).

glauconitolite. This confirms the slow-release ability of potassium from glauconite. In addition to potassium, this product releases nutrients such as Ca and Mg. The available phosphorus appears to increase in all plots including the control sample. It is associated with its accumulation due to low consumption of phosphorus by plants compared to potassium from the same volume of soil. Alternately, organic acid excretion from plant root due to increasing soil pH contributes to the decomposition of phosphate-bearing minerals present in the soil such as Al and Fe oxides (Jones and Darrah, 1994; Shen et al., 2011) and, therefore, elevates the P content in soils. The relatively high content of organic carbon (Table 2) and the low content of nitrate provides a good moisture retention capacity to the soil. The gradual increase in exchangeable K in soil with the addition of glauconitolite and subsequent gradual depletion of K_2O by 24% of the original product qualifies it as a slow-release fertilizer. Slow-release fertilizers are environmentally friendly and equally effective like conventional fertilizers (Trenkel, 1997; Chen et al., 2017; Fu et al., 2018). The Cl-anion, present in KCl, after the absorption of potassium to plants remains in the soil or diffuses downward in the groundwater, which leads to environmental pollution (Griffioen, 2001). Excessive N fertilization leads to environmental problems because of groundwater, soil, and atmospheric pollution with reactive N (Wang et al., 2017). A similar slow-release fertilizer has already been reported by Franzosi et al. (2014). Franzosi et al. (2014) revealed an increase in grass biomass ashes of 109% with the introduction of the greensands of Salamanca Formation, which was 10% higher than the test with KCl. The introduction of glauconite and glauconite rocks (especially verdete) into agricultural soils showed stimulating effects on the growth of other plants as well. Fine-grained glauconite with 7.5 wt% K_2O content increased the diameter, height and postharvest commercial durability of sunflowers (Torqueti et al., 2016). Addition of glauconite rocks to the soil (with an equivalent dose of K_2O 0.168 t·ha^{-1}) in the state of Minas Gerais (Brazil) resulted in a 50% increase in coffee yield and also to better sensory analysis of the resultant beverage (Dias et al., 2018).

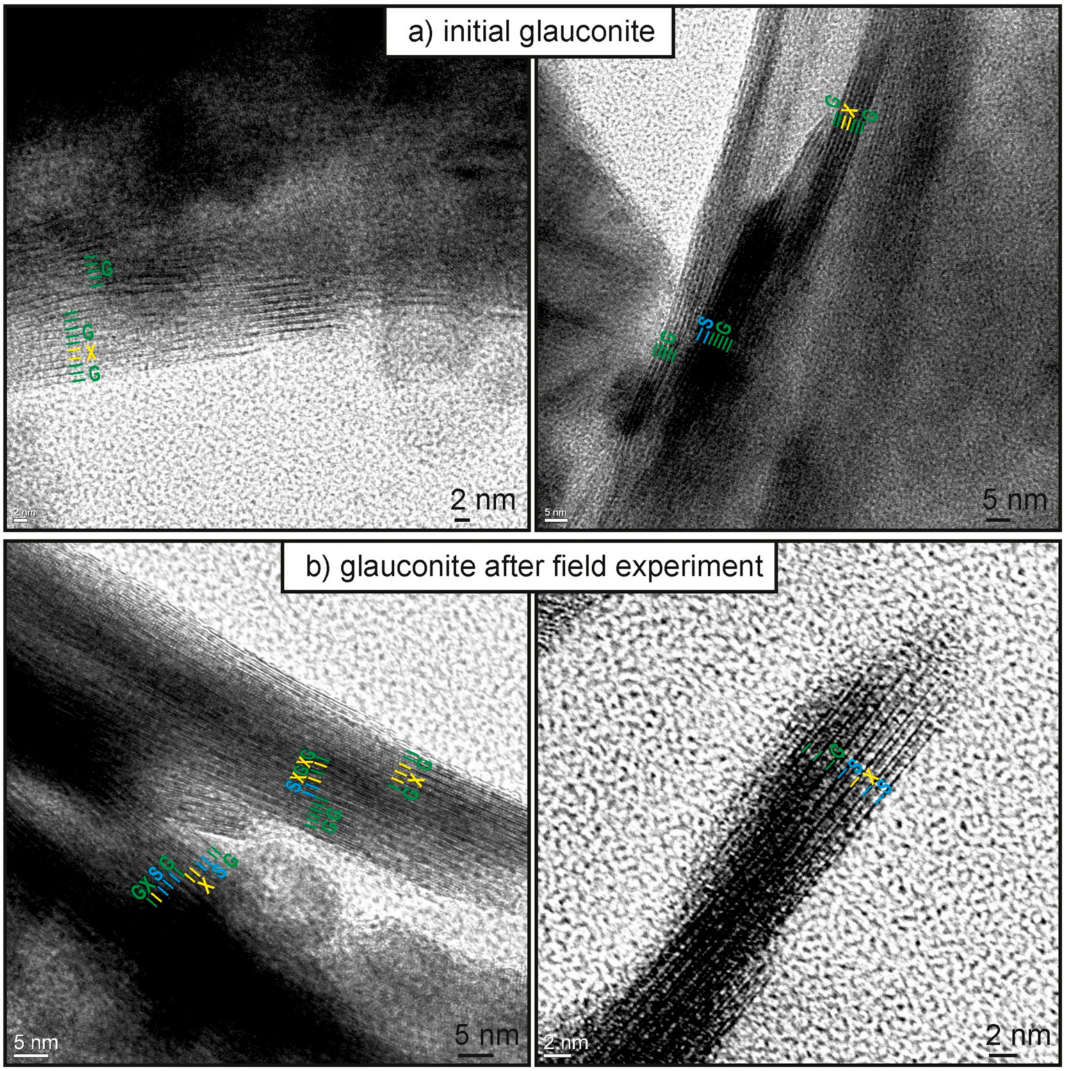

Fig. 3. High resolution TEM lattice fringe images of initial glauconite (a) and final glauconite after field experiment (b). G – glauconite layers (d_{001} ~ 10 Å); X – X-phase (d_{001} ~ 12.5 Å) according to Amouric (1985), S – smectite layers (d_{001} ~ 14 Å).

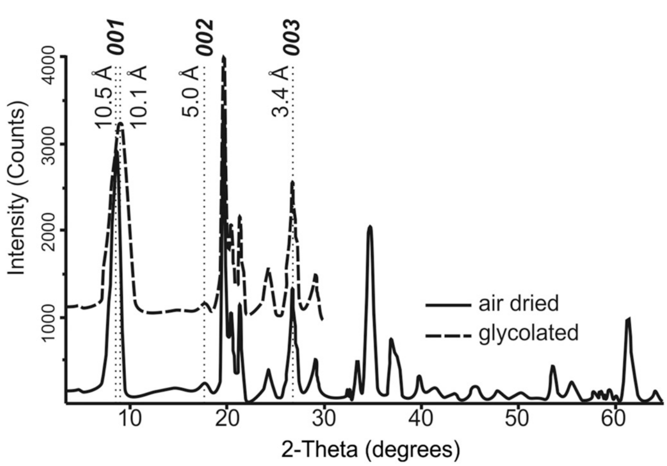

Fig. 4. X-Ray diffractograms of the randomly oriented and ethylene glycol-treated glauconite sample.

5. Conclusions

The conclusions of this study on alternate potassium fertilizer potential of glauconite are as follows.

(1) Glauconite undergoes distinct structural and chemical changes in soil conditions within 120 days of the growing season of wheat. The glauconite develops an increasing sinuosity of flakes, and a decreasing content of K_2O with time.
(2) Glauconite reduces its original K_2O content by 24% during one growing season of durum wheat, indicating its effectiveness as a fertilizer for the next 2 or 3 cycles.
(3) Glauconitic rock, simple grinding of glauconitolite to < 2 mm fraction makes it suitable as an alternative fertilizer.
(4) The introduction of glauconite improves the physico-chemical properties of soil by increasing the concentrations of K, P, Ca, Mg. The soil pH changes from acidic to near neutral after using a glauconite rock in 120 days. The increased concentrations of K, P, Ca, Mg in the soil is marked by the complex interactions of

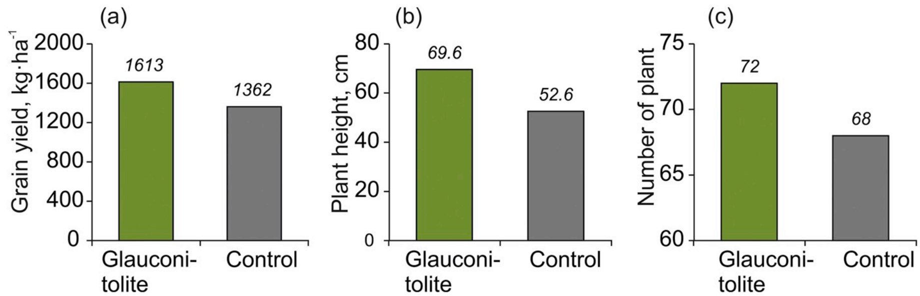

Fig. 5. Effect of glauconitolite as fertilizers on grain yield (a), plant height (b) and number of plant (c) of durum wheat for 120 days in Tomsk region (S-E Western Siberia).

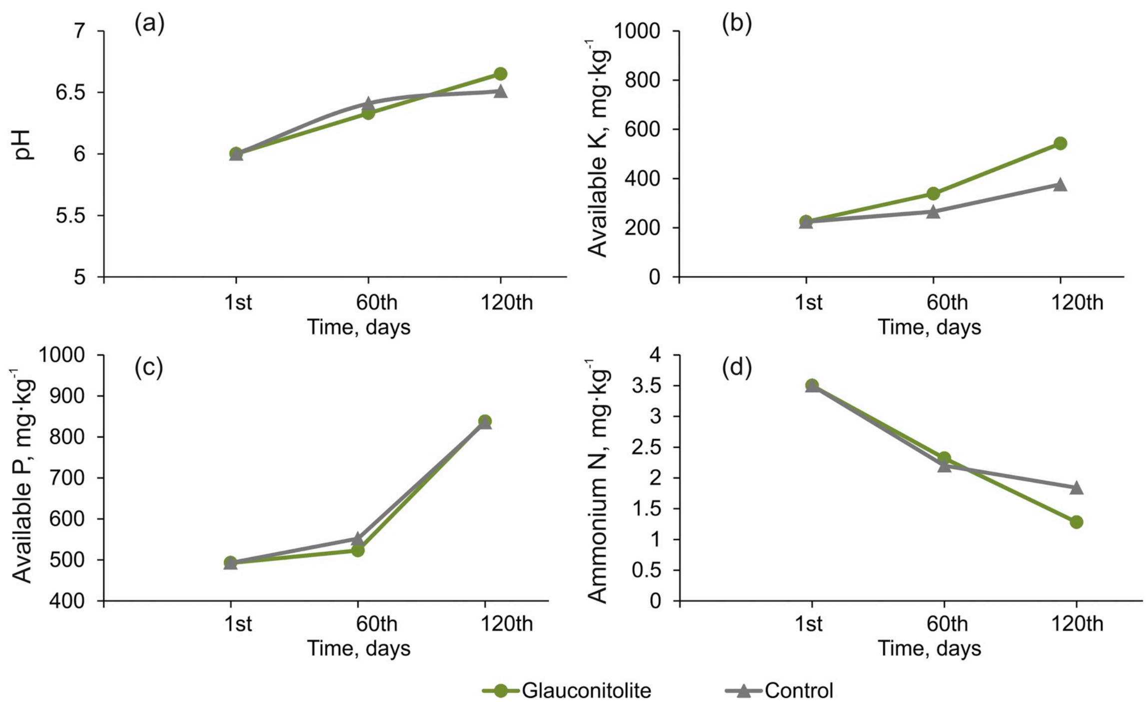

Fig. 6. Effect of glauconitolite on pH (a), available potassium (b), available phosphorus (c) and ammonium nitrogen (d) of soil versus time of plant cultivation.

glauconite with soil.

(5) The addition of glauconitolite results in an increase in grain yield and also improve physico-chemical properties of the soil. Further, the incomplete leaching of potassium and enhanced moisture saturation makes glauconite of Bakchar deposit as an environment-friendly and slow release fertilizer.

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