



# Haloalkalitolerant plants drive alkaline mineral weathering and dealkalization of seawater-treated bauxite residue

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## Abstract

**Background** Ecological engineering of tailings into soil-like growth media (i.e., technosol) has emerged as a nature-based solution for soilless rehabilitation of alkaline bauxite residue. However, field applications often result in spatial heterogeneity, where uneven amendment leaves behind highly alkaline and saline BR pockets that limit sustainable rehabilitation. It is hypothesized that haloalkalitolerant plants with roots partially grown in the improved niches render their strong tolerance of BR matrix to form extensive roots-mineral interfaces, generate physical and biochemical modification, and irreversibly neutralize the extremely alkaline pH in BR niches.

**Methods** In this study, seawater-treated BR was used to simulate these residual alkaline matrices. Four plant species, including two halophytes, one haloalkalitolerant native acacia and one glycophytic sorghum grass were cultured in a sand-BR compartment system to simulate field heterogeneity.

**Results** Massive roots-BR interfaces were formed. Root activities at the interfaces accelerated the weathering of alkaline minerals and neutralized alkaline pH to circumneutral. Halophytes (*Atriplex nummularia* and *Chloris gayana*) were found to be the most effective in weathering and neutralizing BR, due to their higher capacity to exude low-molecular-weight organic acids rich in carboxyl groups in roots-BR interfaces. The LMWOAs facilitated  $\text{Na}^+\text{-H}^+$  exchange with sodalite and disrupted its structure.

**Conclusion** These interactions stimulated the formation of nanosized amorphous Al-Si-Fe minerals on root surfaces. Plant uptake of liberated Na led to Na depletion in the rhizosphere. Therefore, halophytic

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species should be included in the field application to eliminate substrate heterogeneity of eco-engineering soil formation for soilless BR rehabilitation.

**Keywords** Bauxite residue · Haloalkalitolerant plants · Roots-mineral interfaces · Weathering · Dissolved organic matter · Carboxyl-rich organic acids

## Introduction

Toxic bauxite residue (BR) is the largest environmental problem facing the aluminum industry worldwide. BR has biologically inhibitory properties, because it contains large amounts of alkaline minerals (e.g., sodalites) and finely textured clay particles, exhibiting extremely alkaline (pH 9.2–13) and saline (EC: up to 40 mS cm<sup>-1</sup>) conditions and physical compaction (Gräfe and Klauber 2011; Gräfe et al. 2011). Ecological engineering of BR into soil-like growth media (i.e., technosol) has emerged as a nature-based approach to rehabilitate BR (Huang et al. 2012, 2014; Wu et al. 2019). This process involves incorporating abiotic and biotic inputs (organic matter, functional microorganisms, and pioneer plants) to accelerate mineral weathering and geochemical improvements and physical alteration (Huang et al. 2012; Wu et al. 2019). Research findings have so far demonstrated that these eco-engineering inputs can enhance microbial activity, thereby accelerating the initial stages of mineral weathering, pH neutralization, and formation of early technosols that are capable of supporting pioneer plant species in field trials (Huang et al. 2014; Huang and You 2018; Li et al. 2024; Wu et al. 2021).

However, field operation to amend BR with OM for the initial microbial driven process has inherent spatial heterogeneity at industry scale, in which remnant BR matrix and profiles cannot be dealkalized and neutralized by microbial mechanism alone without further mechanical disturbances and admixing. The co-existence of improved habitats and patches or pockets of unweathered and unimproved BR matrix profile can cause the resurgence of alkaline and saline conditions and limiting the colonization of glycophytic plant species. Therefore, it is proposed to utilize haloalkalitolerant plant species (such as halophytes) as a proactive biological driver to weather alkaline minerals of these unimproved BR profiles for achieving irreversible neutralization as a

whole, thus advancing the development of BR early technosols for colonization of diverse plant species at later stage. It is hypothesized that haloalkalitolerant plants' roots that are partially established in improved habitats of organic matter (OM) amended BR, can grow their roots towards the unimproved BR pockets or profiles to form extensive root-mineral interfaces. Roots-driven processes, such as exudation of acidic metabolites may weather alkaline minerals and neutralize alkaline pH conditions in BR matrix.

Haloalkalitolerant plants, including halophytes, are common pioneers in disturbed and degraded lands, thriving in highly saline and alkaline environments (Lopez and Bacilio 2020; Sun et al. 2018). Through the secretion of acidic root exudates, particularly low molecular weight organic acids (LMWOAs), these plants drive mineral weathering by acidifying the rhizosphere, chelating metal ions, and enabling ion exchange reactions (Adeleke et al. 2012, 2017). These processes not only dissolve primary minerals, but also facilitate the formation of amorphous minerals, favouring soil aggregation and further development of technosols. Various haloalkalitolerant pioneer plants have been identified in the peripheral areas of BR storage dams, such as halophytes with strong salt tolerance: Rhodes grass (*Chloris* spp.) and *Atriplex* spp.; salt-tolerant native leguminous species: *Acacia* spp.; and drought tolerant pasture species *Sorghum* spp. (Wehr et al. 2006; Huang and You 2018). Plant species with fibrous root system possess large root surface areas, such as Rhodes grass, generating extensive interactions with tailings minerals (Blum et al. 1977; Cheng et al. 2009; Loades et al. 2010). Salt-tolerant *Atriplex* spp. can colonize highly saline and alkaline soils (pH up to 9.5) by root-exudation and shoot-accumulation of salt (Bui 2013; Noshad et al. 2022). Haloalkalitolerant leguminous plants like *Acacia* spp. tolerate salinity while fixing atmospheric nitrogen through Rhizobium nodulation, releasing protons into the rhizosphere to promote mineral interactions (Bordeleau and Prévost 1994; Zahran 1999). These haloalkalitolerant plant roots can exudate acidic metabolites rich in organic ligands, enhancing alkaline mineral weathering and driving dealkalization of BR.

Therefore, these plant species have been used as test species to advance the weathering and dealkalization of unimproved BR matrix profiles in large scale field operations. The present study aims to investigate whether haloalkalitolerant plants form extensive roots-mineral interactions to modify BR matrix through accelerating

the weathering of alkaline minerals and neutralizing alkaline pH in BR. It is hypothesized that: (1) the root activities of plants can stimulate the weathering of alkaline minerals in BR, leading to pH neutralization and the formation of secondary minerals; and (2) plants with different root systems and salinity tolerance have varying capacities for weathering alkaline minerals in BR. It is expected that halophytic plant species with extensive fibrous and dense lateral roots, such as Rhodes grass and salt bush, would be more effective in generating rhizosphere modification in roots-mineral interfaces to dealkalize BR, than woody species of tap root system. To simulate the spatial heterogeneity of improved and unimproved habitats in the initially OM-amended BR, a compartmentalized cultivation system (Figure S1) consisting of a sand chamber and BR chamber, was used, in which plants were initially established in the sand chamber simulating the improved habitats. To characterize mineralogical changes in roots-modified BR, we employed a complementary suite of advanced micro-spectroscopic techniques, including synchrotron-based X-ray diffraction (XRD), X-ray absorption fine structure (XAFS) spectroscopy, and scanning transmission electron microscopy with selected area electron diffraction (STEM-SAED).

## Material and methods

### Materials

The alkaline seawater treated BR used in this study was from a BR dam at Queensland Alumina Limited, which was strongly alkaline (pH 9.89), highly saline (EC 17.49 mS/cm) and low in organic carbon (0.03% w/w) and nitrogen (0.04% w/w) (Table S1). Elemental analysis showed that the BR mainly contained Fe (17.84%), Si (8.03%), Al (9.79%), and Na (9.34%), with hematite, sodalite, and calcite identified as the dominant mineral phases (Table S2). These characteristics underscore the challenging conditions for plant establishment and highlight the need for haloalkalitolerant species.

The plant species used in this experiment are Rhodes grass (*Chloris gayana*, Cg), saltbush (*Atriplex nummularia*, An), legumes (*Acacia auriculiformis*, Aa), and *Sorghum* spp. hybrid cv. Silk (SHS), of which the former two are halophytes and the latter non-halophytes. These plants were chosen for their respective ecological roles of pioneer colonizers,

understory species of productive primary producers, and biological nitrogen fixation. Plant seeds were germinated in sterilized Petri dishes moistened with distilled water, from which germinated seeds with vigorous radicle emergence were selected and transplanted into a two-compartmentalized cultivation system (river sand and seawater-treated BR, Figure S1) for the formal experiments.

### Experimental design

The compartmentalized cultivation system was designed with two chambers to facilitate direct root-mineral interactions: (1) a large chamber filled with river sand, serving as the primary growth substrate, and (2) a smaller chamber containing BR. Plants were initially cultured in the sand chamber, with their roots extending toward the BR chamber to establish a rhizosphere zone with intense root-mineral interactions (Figure S1). The river sand used was primarily composed of quartz, thoroughly rinsed with distilled water until a neutral pH was achieved, ensuring no background alkalinity and salinity (Figure S2). The BR chamber consisted of a Petri dish (4 cm in diameter) filled with 30 g of BR, covered with a nylon mesh (2 mm pore size) to allow root penetration while minimizing BR loss. These dishes were placed vertically within the sand, enabling the gradual extension of plant roots into the BR chamber (Figures S1 and S3). Four different types of Australian native pioneer plants were selected for the experiment, including *Hybrid* cv. Silk (SHS), *Chloris gayana* (Cg), *Atriplex nummularia* (An), and *Acacia auriculiformis* (Aa). The treatments were named “BR + SHS,” “BR + Cg,” “BR + An,” and “BR + Aa,” respectively.

To assess the specific effects of BR and plants, two control treatments were established (Table 1, Figure S4): (a) a control for assessing the effects of plants, consisting of Petri dishes with BR placed in river sand without plant growth, and (b) a control for assessing the effects of the BR chamber on plant growth and Na uptake, consisting of river sand only without the BR chamber.

Each treatment consisted of four replicates, with four seedlings in each pot. The pots were randomly positioned in a glasshouse and watered daily to maintain a water content of 15% w/w. A nutrient solution (Table S3) without the use of elements Na, Si, and Fe was applied to plants every two weeks to support plant

**Table 1** Description of the experimental design and the abbreviation of different treatments

|             |                                                                                              |
|-------------|----------------------------------------------------------------------------------------------|
| SHS Control | <i>Sorghum</i> spp. Hybrid cv. Silk (SHS) grown in river sand without BR-filled Petri dishes |
| Cg Control  | <i>Chloris gayana</i> (Cg) grown in river sand without BR-filled Petri dishes                |
| An Control  | <i>Atriplex nummularia</i> (An) grown in river sand without BR-filled Petri dishes           |
| Aa Control  | <i>Acacia auriculiformis</i> (Aa) grown in river sand without BR-filled Petri dishes         |
| BR Control  | No plant grown in river sand with BR-filled Petri dishes                                     |
| BR + SHS    | <i>Sorghum</i> spp. Hybrid cv. Silk (SHS) grown in river sand with BR-filled Petri dishes    |
| BR + Cg     | <i>Chloris gayana</i> (Cg) grown in river sand with BR-filled Petri dishes                   |
| BR + An     | <i>Atriplex nummularia</i> (An) grown in river sand with BR-filled Petri dishes              |
| BR + Aa     | <i>Acacia auriculiformis</i> (Aa) grown in river sand with BR-filled Petri dishes            |

growth, as BR could be the sole source for these elements. The plants were cultivated in a controlled glass-house at 25 °C with 14/10 h (light/dark) and the light intensity in the range of 600–1200  $\mu\text{mol m}^{-2} \text{s}^{-1}$ . The plants and BR were harvested after 347 days' cultivation. Porewater samples were collected in the evening prior to the harvest day, using Rhizon samplers (0.15  $\mu\text{m}$ , Rhizosphere Research Products, the Netherlands), which were set in the river sand compartment. The porewater samples were stored at – 80 °C for the analysis of organic ligand composition.

#### Plant sampling

At the end of the experiment, plants were separated into above-ground (shoots) and below-ground (roots) parts. Both parts were thoroughly washed with distilled water to remove surface contaminants, including adhered BR particles. Plant tissues were oven-dried at 70 °C for 48 h until a constant weight was achieved, and the dry weight was recorded. Fresh rhizosphere samples, consisting of root segments with attached BR particles, were collected for cross-sectioning and microscopic examination. The remaining BR samples were freeze-dried for various spectroscopic and physicochemical analyses.

#### Plant digestion and elemental analysis

The dried plant tissues were finely ground for chemical analysis. Aliquots of 100 mg of plant powder were digested in a mixture of 2 mL  $\text{H}_2\text{O}_2$  (30%, AR grade) and 8 mL  $\text{HNO}_3$  (70%, AR grade) in a polytetrafluoroethylene digestion tube equipped with a pressure relief valve, and left for 2 h for pre-digestion (Huang and Schulte 1985). Then the digestion was conducted in

the microwave digestion oven (MA174 -003, ETHOS EASY, Italy) with temperature ramped to 180 °C within 15 min and held for 30 min. After cooling to room temperature, the digestion solution was transferred to a centrifuge tube and diluted to 20 mL with ultrapure water (Millipore 18.2  $\text{M}\Omega\text{-cm}$  at 25 °C), which was further centrifuged at 3220  $\times g$  for 10 min. The supernatant was further diluted as required with 2%  $\text{HNO}_3$  for elemental analysis using inductively coupled plasma atomic emission spectrometry (ICP-AES 720ES, Varian Inc., Palo Alto, California).

#### Geochemical analysis

The organic acids in the rhizosphere porewater samples were quantified using high-performance liquid chromatography (LC- 20 AT, Shimadzu) coupled with refractive index detector (RID- 20 A) and conductivity detector (CDD- 10 A) and Agilent Hi-Plex H column (7.7  $\times$  300 mm, 8  $\mu\text{m}$ ). The pH and electrical conductivity (EC) of BR solid samples were measured in 1:5 (solid/liquid ratio) water extracts using a pH electrode (TPS 900) and an EC electrode (TPS 2100). Water-extractable (WE) and acid ammonium oxalate (AAO)-extractable Na, Al, Si, and Fe in BR were analyzed following a previously described procedure (Rayment and Lyons 2011). The methodological details are presented in the Supporting Information (SI, Text S1).

#### Mineralogical analysis

##### *High-resolution synchrotron based XRD and quantitative analysis*

The crystal structure of the BR samples under different plant species treatment were characterized by

using synchrotron XRD patterns with  $\lambda = 0.7749 \text{ \AA}$  (16 keV) at beam line BL01 C2 within the National Synchrotron Radiation Research Center (NSRRC) in Taiwan. The detailed test methods are provided in the SI (Text S2).

The XRD patterns of freeze-dried and finely ground BR samples were obtained using a Bruker D8 DISCOVERY diffractometer through the Bragg–Brentano  $\theta$ – $2\theta$  reflecting geometry equipped with a Johansson-type focusing Ge primary monochromator and a linear silicon strip detector LynxEye. The data were collected from 2 to  $80^\circ$  with a step of  $0.02^\circ$ , and  $2.896^\circ$  anti-scatter slit. The selected counting time was 1.2 s per step for an overall counting time of approximately 78 min. Phase identification was carried out with DIF-FRAC plus Evaluation Package V5.0 (Bruker AXS, Germany), which equipped the International Centre for Diffraction Data (ICDD) PDF 4+ 2022 database. Quantitative phase analysis was carried out via a Rietveld method using the TOPAS V6 software, and the amorphous substance content was identified by mixing the samples with 10% w/w fluorite ( $\text{CaF}_2$ ) as internal standard (Liao et al. 2015). The concentrations of all identified phase can be corrected proportionately via the following formula (Kolb et al. 2012):

$$\text{Corr}(W_a) = W_a \frac{\text{STD}_{\text{known}}}{\text{STD}_{\text{measured}}} \quad (1)$$

The amorphous phase  $W_{\text{amorphous}}$  value can then be calculated from:

$$W_{\text{amorphous}} = 1 - \sum_{j=1}^n \text{Corr}(W_j) \quad (2)$$

where,  $\text{Corr}(W_a)$  is the corrected  $\alpha$  phase weight percent;  $\text{STD}_{\text{known}}$  and  $\text{STD}_{\text{measured}}$  are the weighed concentration and analyzed concentration of standard material ( $\text{CaF}_2$ ), respectively.

#### Fe K-edge XAFS analysis

The freeze-dried and finely ground BR samples were analyzed for Fe K-edge (7112 eV) XAFS analysis at the beamline 01 C1, NSRRC, Taiwan. Details on the analysis and Fe mineral standards are provided in the SI (Text S3).

#### Al and Si K edge XANES analysis

The BR samples were measured by Al K and Si K NEX-AFS analysis at the soft X-ray (SXR) beamline in Australian Synchrotron, Australia. The sample was scanned four times under a partial electron yield (PEY) mode with an energy range from 1541 to 1621 eV for Al (0.1 eV resolution and  $1 \text{ mm}^2$  spot size) and from 1820 to 1900 eV for Si (0.2 eV resolution and  $1 \text{ mm}^2$  spot size). The resultant spectrum was processed using QANT software, including calibration, baseline correction and edge-step-normalization (Gann et al. 2016). The detailed processing methods are described in the SI (Text S4).

#### STEM-SAED Analysis

The rhizosphere BR samples were ultrasonically dispersed in DI water for 5 min. Then, aliquots of 20  $\mu\text{L}$  suspension were deposited on a copper grid (200 mesh, ProSciTech Pty. Ltd., Queensland, Australia) and place it in a vacuum drying oven at  $25^\circ\text{C}$  for 12 h. The samples were analyzed using the aberration-corrected Hitachi HF5000 S/TEM at 200 keV, in Centre for Microscopy and Microanalysis, The University of Queensland. The machine was equipped with energy-dispersive X-ray spectrometry (EDS, Oxford EDX  $2 \times 1 \text{ sr } 100 \text{ mm SDD EDX}$ ) detectors. TEM images were recorded by a CCD camera. Electron diffraction patterns were acquired in selected areas and recorded.

#### Micro-spectroscopic examination of root-BR interfaces

##### Thin-section preparation

Fresh BR samples with root interactions were cryo-embedded using OCT medium to preserve their structural integrity and maintain root-mineral interactions. Samples were sectioned at  $-26^\circ\text{C}$  into 20  $\mu\text{m}$  thick slices using a cryostat (Thermo Cryostar NX70). Thin sections were mounted on glass slides for  $\mu\text{-XRF}$  and on tape for SEM–EDS analysis.

##### Micro-XRF and SEM mapping analysis

Cryo-sectioned rhizosphere samples (20  $\mu\text{m}$  thick) mounted on silicone slides were subjected to elemental distribution analysis using micro-X-ray

fluorescence spectroscopy ( $\mu$ -XRF) at the Centre for Microscopy and Microanalysis, University of Queensland. The  $\mu$ -XRF system was a custom-built assembly by IXRF ATLAS X (TX, USA), equipped with dual 50 kV–1000  $\mu$ A sources and multicenter focusing optics. X-rays were generated using an XOS microfocus molybdenum target tube (17.4 keV, flux of  $2.2 \times 10^8$  photons/s) with a spot size of 25  $\mu$ m. Elemental signals were captured in plot mode via the Iridium instrument control package (IXRF System). Resulting elemental distribution maps, which elucidated interactions between roots and rhizosphere BR, were exported as grayscale 8-bit TIFF files using ImageJ software for subsequent analysis.

For SEM mapping, cryo-sectioned samples mounted on 3M tape were coated with a thin layer of carbon to ensure electrical conductivity. Samples were analyzed using a Hitachi SU3500 scanning electron microscope (Hitachi High-Technologies, Japan) operating at an accelerating voltage of 20 kV. SEM mapping provided detailed insights into the morphological and compositional variations at the root-mineral interface, complementing the  $\mu$ -XRF results.

### Statistical analysis

Differences in plant tissues element concentrations and physicochemical properties of BR among different treatments were assessed by one-way analysis of variance (ANOVA), followed by Tukey's test ( $P < 0.05$ ) using IBM SPSS Statistics software (Version 29).

## Results

### Root growth and formation of interfaces of roots-bauxite residue

Plant roots initially established in the sand compartment grew their roots towards the BR chamber (Figures S5–S7), extensively penetrating the BR matrix to have formed roots-BR interfaces (Fig. 1(a–d)). Among the tested species, Rhodes grass (halophyte) (*Chloris gayana*, Cg) exhibited the highest biomass production, followed by the halophyte *Atriplex nummularia* (An) and leguminous tree species *Acacia auriculiformis* (Aa). Cg plants initially established in the river sand (Figure S8(b)) showed an extensive

root growth into BR-chamber (Figure S9(b)), forming root-BR interfaces. This coincided with the enhanced mineral weathering and pH neutralization (see the latter sections). Similarly, salt bush An, a halophyte with dense lateral roots, produced significantly higher root biomass in BR (Figure S9(c)) than in the sand control (Figures S8(c) and Table S4(a)), highlighting its haloalkaliphilic attributes.

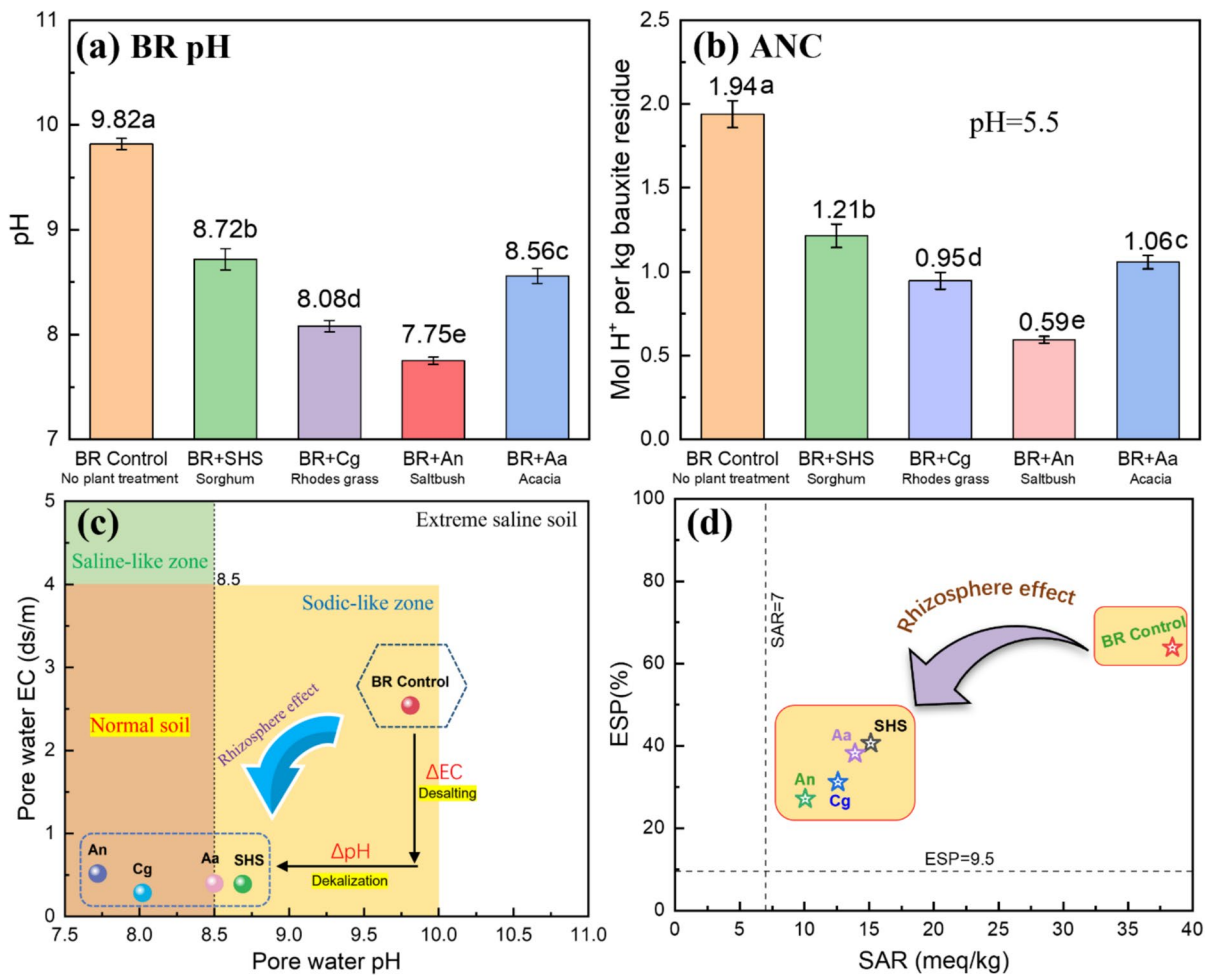
In contrast, *Sorghum Hybrid cv. Silk* (SHS) showed the lowest biomass in the BR treatment (Table S4(a), Figures S7–S9). The nonhalophyte SHS roots exhibited limited growth into BR (Figure S9(a)), with a lower root biomass, than those grown in river sand only (controls) (Table S4(a)). Leguminous tree species, Aa developed dense root mass with fresh nodules in both the river sand (Figure S8(d)) and BR chambers (Figure S9(d)). It is interesting to note that Aa plants had higher Al concentrations in shoots than other plant species (Table S4(d)).

The concentrations of Na and Al in plant tissues significantly increased in plants grown in the sand-BR chamber system (Table S4(d)), compared to those grown in river sand only. Sodium concentrations in Cg roots and shoots reached as high as 3.32 mg g<sup>-1</sup> dry weight (Table S4(b)) and 5.58 mg g<sup>-1</sup> dry weight (Table S4(c)), respectively. Sodium concentration in the shoot of Salt bush (An) plants was as high as 29.3 mg Na g<sup>-1</sup> dry weight. In contrast, the glycophytic species, SHS exhibited significantly lower salt and metal ion concentrations ( $P < 0.05$ ), coinciding with their reduced biomass and poor root growth in the BR chamber (Figure S9(a)).

### Geochemical responses in bauxite residue

Root activities significantly improved the physicochemical properties of BR interfaced by roots, lowering pH from highly alkaline (pH 9.82) to circum-neutral (pH 7.75–8.72) (Fig. 1(a)). Among the plant species tested, the magnitude of roots induced pH reduction followed the order of An (pH 7.75), Cg (pH 8.08), Aa (pH 8.56), and SHS (pH 8.72). The net pH neutralization of roots-interfaced BR among the plant species tested is dependent on the intensity of acidifying effects produced by roots of individual species and BR acid neutralizing capacity (ANC, SI Text S6).

The acid neutralizing capacity (ANC) of BR is determined by the residual free alkali in solution phase and structural alkali in solid phase (i.e., alkaline aluminosilicate minerals, such as sodalites). ANC



**Fig. 1** Changes in (a) pH, (b) acid neutralizing capacity (ANC), (c) pore water pH and EC, and (d) exchangeable sodium percentage (ESP) vs sodium adsorption ratio (SAR) in bauxite residue after 347 days under different plant root treatments. Note that (1) "BR Control" = untreated bauxite residue without plant colonization; "BR + SHS," "BR + Cg," "BR + An," and "BR + Aa" were BR colonized with *Sorghum* spp.

in the BR ( $1.94 \text{ mol H}^+ \text{ kg}^{-1}$  air dry wt) was significantly decreased by plant colonization (Fig. 1(b); SI Text S6), with the largest decrease in treatments with An and Cg (i.e.,  $0.59$  and  $0.95 \text{ mol H}^+ \text{ kg}^{-1}$ , respectively). Comparatively, BR colonized with nonhalophytes, Aa and SHS had a smaller ANC reduction, to  $1.06$  and  $1.21 \text{ mol H}^+ \text{ kg}^{-1}$  air dry wt, respectively. Plant colonization also significantly lowered the salinity (i.e., EC values) in porewater of roots-modified BR (Fig. 1(c)). Notably, the Na adsorption ratio (SAR) and exchangeable Na percentage (ESP)

Hybrid cv. Silk, Rhodes grass (*Chloris gayana*), saltbush (*Atriplex nummularia*), and legumes (*Acacia auriculiformis*), respectively. (2) Different letters above the columns indicate significant differences among treatments based on Tukey's test ( $P < 0.05$ ). (3) Critical values for ecosystem growth on tailings are  $\text{ESP} < 9.5\%$  and  $\text{SAR} < 7$ . The definitions of SAR and ESP are provided in SI Text S5

(Fig. 1(d)) significantly decreased in root-colonized BR compared to the control.

#### Alkaline minerals in roots-modified bauxite residue

Untreated BR (control) primarily consisted of hematite, anatase, sodium chloride, sodalite, and calcite (Fig. 2(a)). Synchrotron-based XRD analysis of BR modified by roots revealed that there were significant changes in the relative amounts of alkaline mineral in the BR, in response to root effects

of different plant species. Based on the changes of main diffraction peaks, sodalite (211, 110) and calcite (104) were substantially diminished, in response to roots. These weathering events were further confirmed by Quantitative XRD (q-XRD) refinement (Fig. 2b, Figures S13–14). Specifically, sodalite in BR modified by An and Cg roots accounted for 3.08% and 4.23%, respectively, compared to 11.32% in the control. Calcite in BR modified by these species accounted for 1.64% and 2.12%, respectively, compared to 11.38% in the control. Additionally, the primary peak (104) of NaCl was significantly lowered, coinciding with the reduced salinity (i.e., ECe).

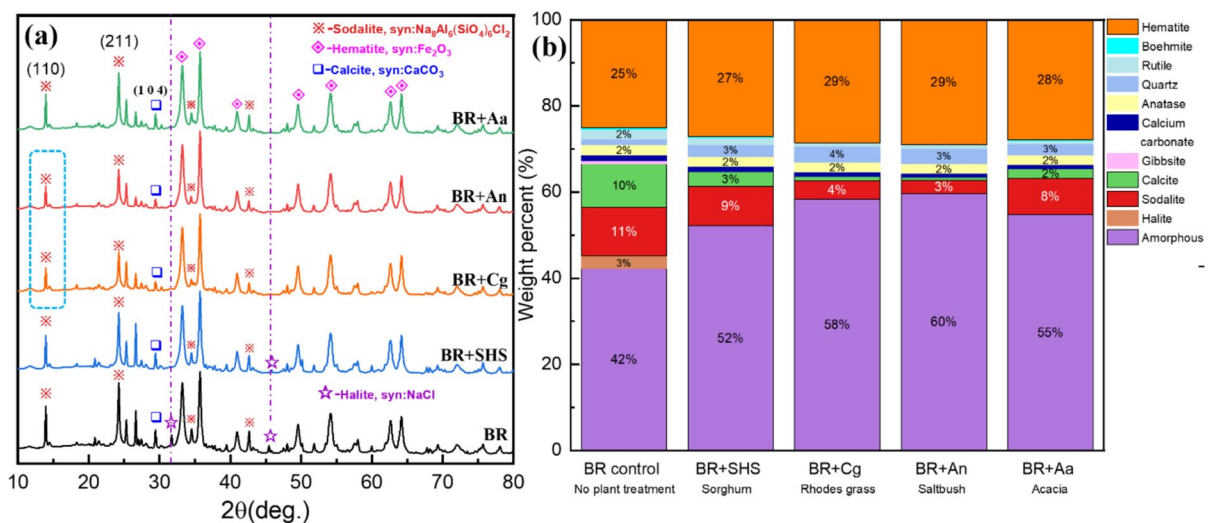
Meanwhile, compared to 42% in the control, the relative proportion of amorphous minerals increased in BR treated with An and Cg, accounting for 59.68% and 58.36%, respectively. Total organic carbon (TOC) concentrations increased in both rhizosphere porewater and BR (Figure S15(a–b)). Further analysis revealed that LMWOAs secreted by plant roots included succinic acid, formic acid, acetic acid, oxalic acid, citric acid and lactic acid (Figure S15(c–h)). Halophytes, An and Cg produced higher levels of acetic, oxalic, and citric acids compared to SHS and Aa (Figure S15(e–g)).

### Amorphous Al-Si-Fe minerals in roots-modified bauxite residue

An increased proportion of amorphous Al-Si-Fe minerals were detected in roots-modified BR. Plant colonization elevated concentrations of WE-Al/Si and AAO-Al/Si in BR (Fig. 3(b–c)). The Al K-edge XANES spectra of rhizosphere BR (Fig. 3(e)) revealed main peaks at 1568.2 eV and 1572.1 eV, indicating the predominant presence of Al in octahedral coordination with six surrounding oxygen atoms or hydroxide ions. Similarly, the Si K-edge XANES spectrum (Fig. 3(f)) exhibited a prominent peak at 1849.4 eV, corresponding to tetra-coordinated silicon-oxygen tetrahedra ( $\text{SiO}_4$ ).

The concentrations of WE-Fe and AAO-Fe in the BR (Fig. 3(d)) also increased in response to root activities. The Fe K edge EXAFS spectra (Fig. 3(g)) and linear combination fitting (LCF) result (Fig. 3(h)) further suggested a decrease in the relative proportion of hematite in roots-modified BR. In contrast, the proportion of Fe-Si and Fe-Al co-precipitates increased, particularly in BR colonized by Cg and Aa.

TEM-SAED and EDX results added further evidence that Al-Si-Fe rich secondary minerals were formed from roots-driven mineral weathering in the BR. Numerous



**Fig. 2** (a) Synchrotron based X-ray diffraction (SXR) spectra and (b) quantitative X-ray diffraction (q-XRD) showing the mineralogical changes in bauxite residues after treatments with

different pioneer plants. Note: 10% calcium fluoride was added as an internal standard for q-XRD quantification

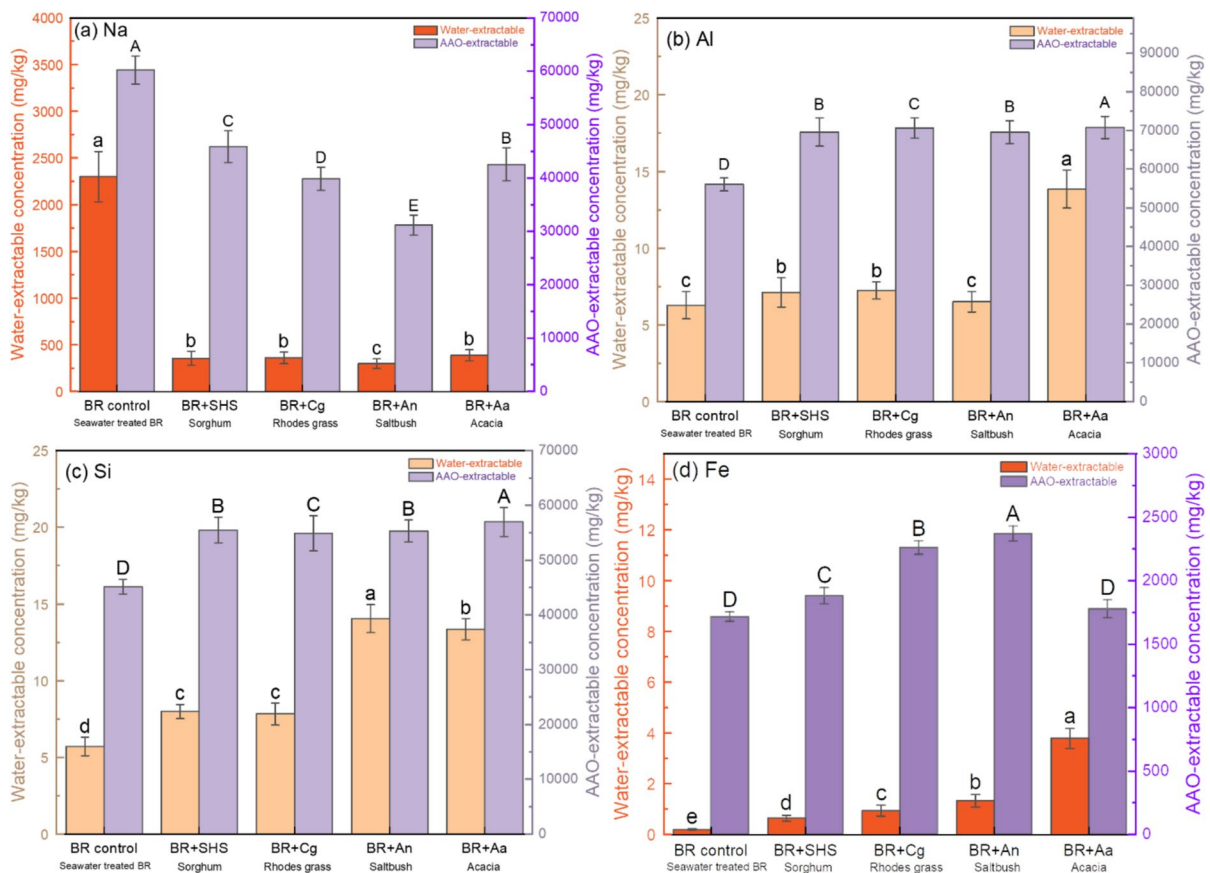
clusters of nanoscale particles (< 100 nm in diameter) with rounded edges and irregular distributions were observed to adhere onto roots (Fig. 4(a-d)). These nanominerals were primarily composed of Al (49.5%) and Si (40.8%) with minor Mg and Fe (Fig. 4(f)), in contrast with those of the control (untreated BR) (Table S2). These amorphous mineral phases were further corroborated by electron diffraction analysis (Fig. 4(e)) and coincided with findings of Fe K-edge XAFS and chemical extraction analyses (Fig. 3).

### Rhizosphere Na distribution

Roots-driven modification of BR-minerals was evidenced by fine and dense BR particles attached to fine

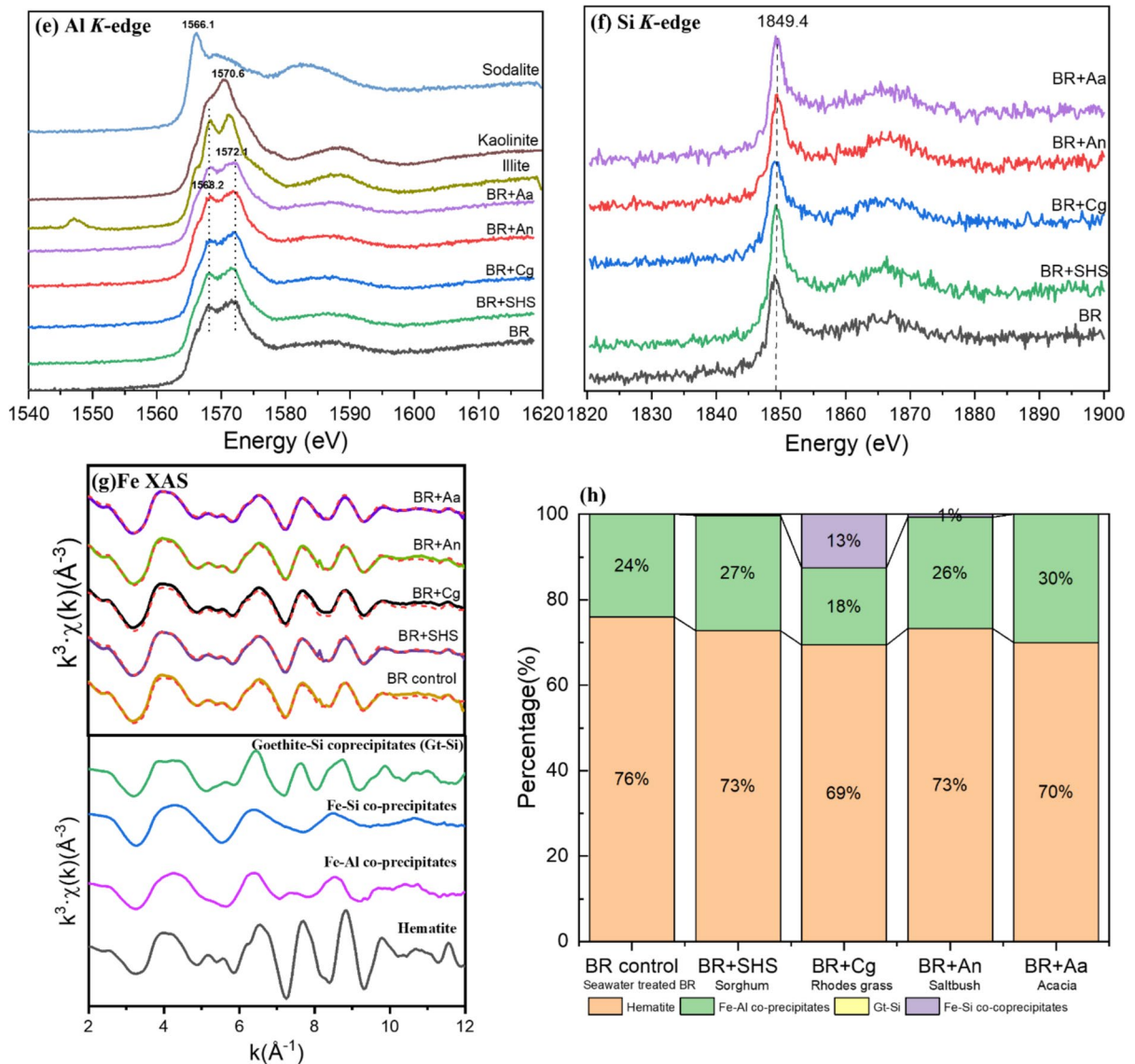
roots (Figures S16 -17). Total Na content in roots-modified BR was significantly reduced (Table S5). Among the plant species, An and Cg were the most effective in removing Na from the BR, with Na lowered to 3.85% and 4.15%, respectively, compared to 8.48% in the control BR. These mirrored the elevated Na concentrations in An and Cg plants with roots grown into BR (Table S4(d)). The Na<sup>+</sup> taken up by plants was at least, partially released from alkaline minerals (e.g., sodalite) through root-driven weathering, further promoting the formation of nanosized amorphous Al-Si minerals.

The  $\mu$ -XRF scans at macroscale (mm level) revealed that BR in the rhizosphere of An and Cg had little Na, forming a distinct zone of “Na



**Fig. 3** Water-extractable (WE) and acid ammonium oxalate (AAO)-extractable (amorphous pool) (a) Na, (b) Al, (c) Si, (d) Fe, (e) Al and (f) Si K edge NEXAFS spectra; (g) k space Fe K edge EXAFS spectra (lines) and (h) linear combination fitting (LCF, dashed lines) of bauxite residue after different pioneer plant treatments. Note that: (1) Different letters above

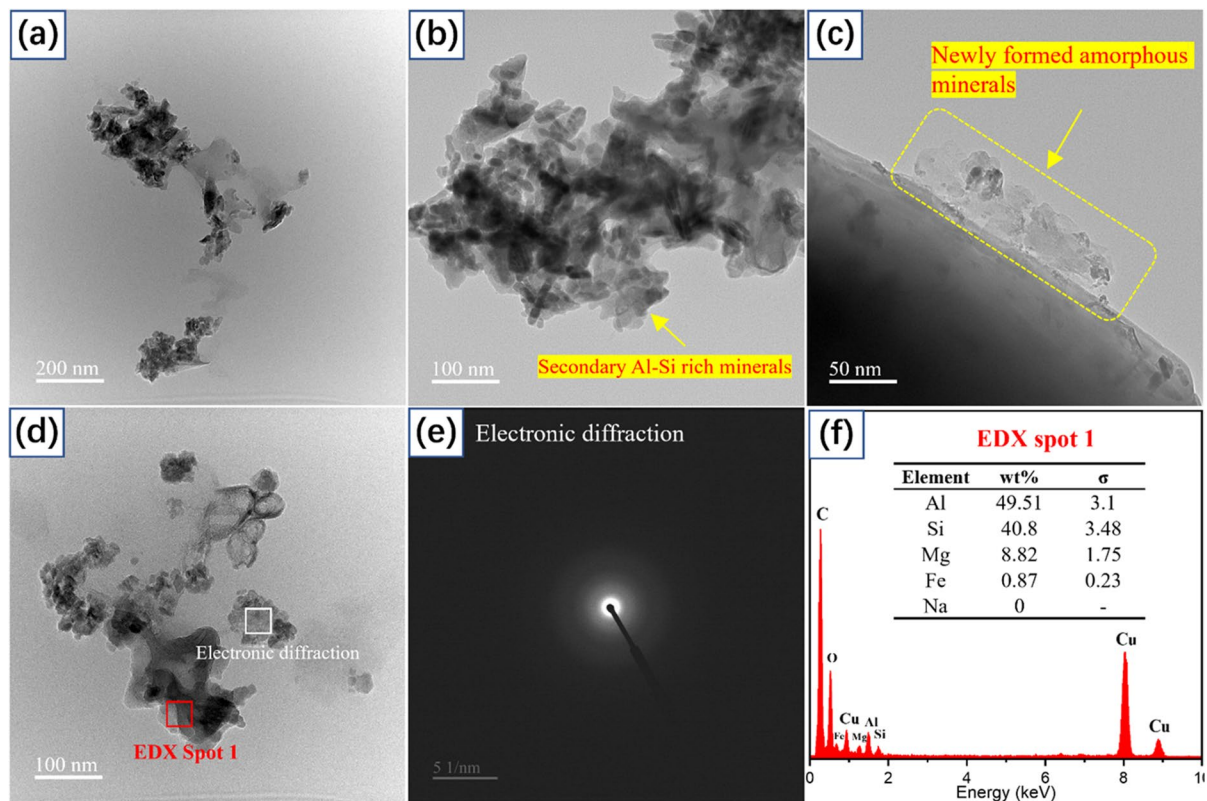
the columns show significant differences among different treatments based on Tukey's test ( $P < 0.05$ ). (2) Fe K edge EXAFS spectra of several key Fe standards are also shown, including hematite, Fe-Al co-precipitates, Fe-Si co-precipitates and goethite-Si coprecipitates (Gt-Si)



**Fig. 3** (continued)

depletion". In this zone, Na signal was diminished (Figure S18(b) and (f)), but Al and Fe were elevated (i.e., enriched), thus delineating the rhizosphere (Figure S18(c-d) and (g-h)). Besides, SEM-EDS examination revealed that after root interactions, many fine particles with honeycomb multi-cavity structures adhered to the roots (Figure S16 -17). SEM-EDS mapping confirmed substantial Na

depletion in mineral particles adhering onto roots (Fig. 5(a-b)). Importantly, aluminosilicate (Si-O-Al) skeleton of BR minerals remained intact after weathering (Fig. 5(c-f)). There were significant differences in elemental makeup between rhizosphere and non-rhizosphere BR particles, as revealed by SEM-EDS (Fig. 5(g)).



**Fig. 4** (a–d) Transmission electron microscopy coupled with (e) selected area electron diffraction (TEM-SAED) and (f) energy dispersive X-ray spectroscopy (EDX) of rhizosphere bauxite residue samples colonized by salt bush (*An*) roots

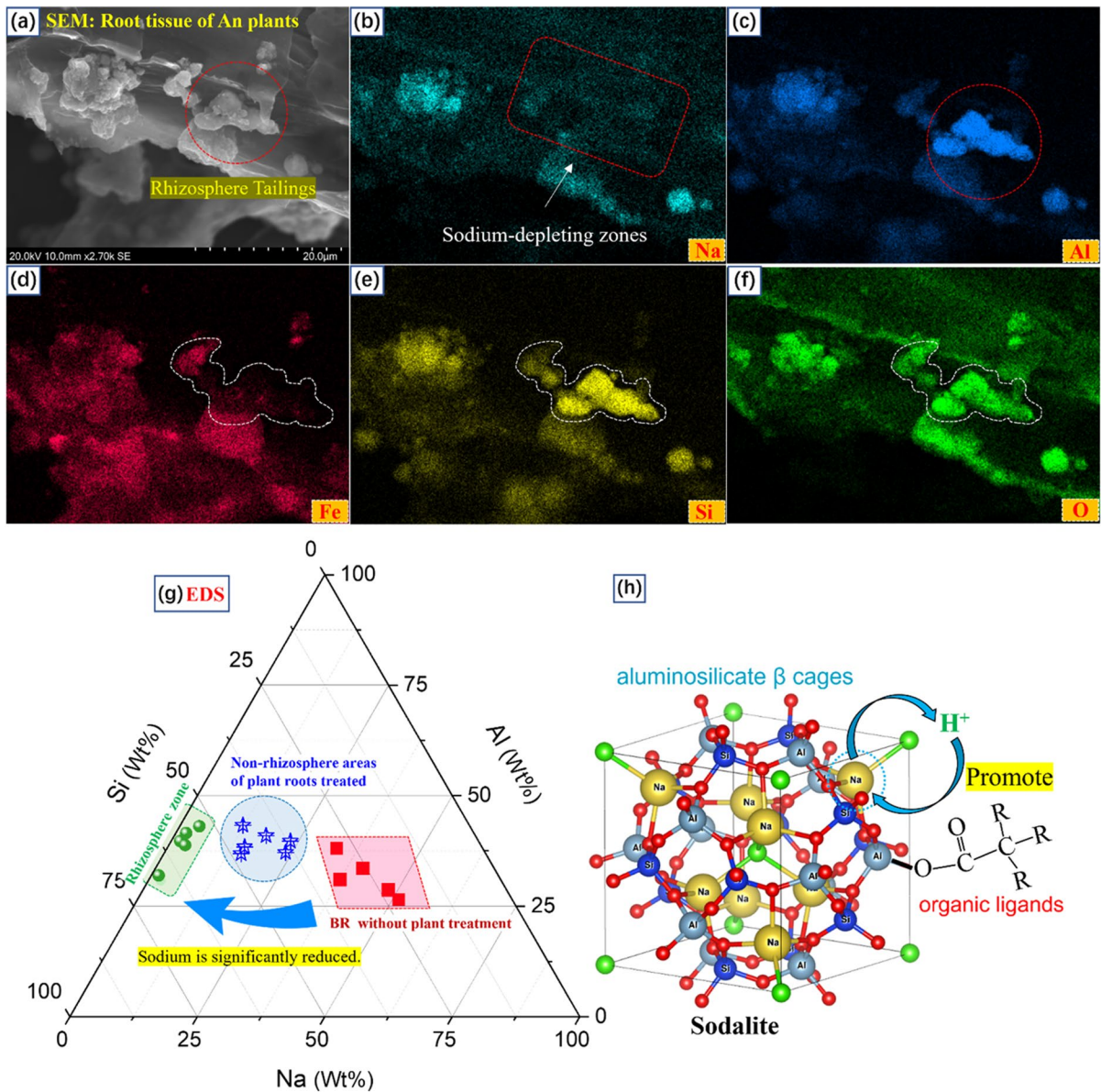
## Discussion

Haloalkalitolerant plant roots can grow into extreme alkaline niche of bauxite residue to form roots-mineral interfaces

Halophytes and native acacia are highly tolerant of salinity and alkalinity, and capable to extending roots towards BR niches to form extensive root matt surrounding and penetrating BR matrix (Fig. 1(a–d)). In the present study, *Acacia* plants in the sand-BR treatment grew the second highest amount of root mass, comparable to that of halophyte species (*Atriplex nummularia* (An)). The nonhalophyte, *Sorghum Hybrid cv. Silk* (SHS) appeared much less tolerant of extreme alkaline conditions, with the limited root growth in the BR treatment (Table S4(a), Figure S9(a)), compared to those in river sand control (Table S4(a)). The establishment of extensive roots-BR interfaces is a prerequisite for haloalkalitolerant

plants to improve niches of alkaline BR matrix. This is the basis for generating not only extensive physical penetration into BR matrix or profiles, but also biochemical responses in roots to modify BR-minerals, such as exuding acidic metabolites, including organic acids and biocarbonates.

One of the major biochemical responses in plant roots would be exudation of large amounts of organic acids into porewater (solution phase), as indicated by total organic carbon (TOC) concentration (Fig. 6(a–b)) and LMWOAs in both rhizosphere porewater (i.e., roots-BR interfaces) (Fig. 6(c–h)). Halophytes have an adaptive strategy to exudate organic acids in roots for buffering against extreme alkaline pH into the physiologically tolerant range (e.g., pH < 9.5), which would have enabled roots to penetrate BR matrix directly (Fig. 6(c–h)). Acidic exudates can lower the rhizosphere pH, creating a pH-buffered microenvironment for root growth and function (Yang and Guo 2018). The dissociation of organic acids would have

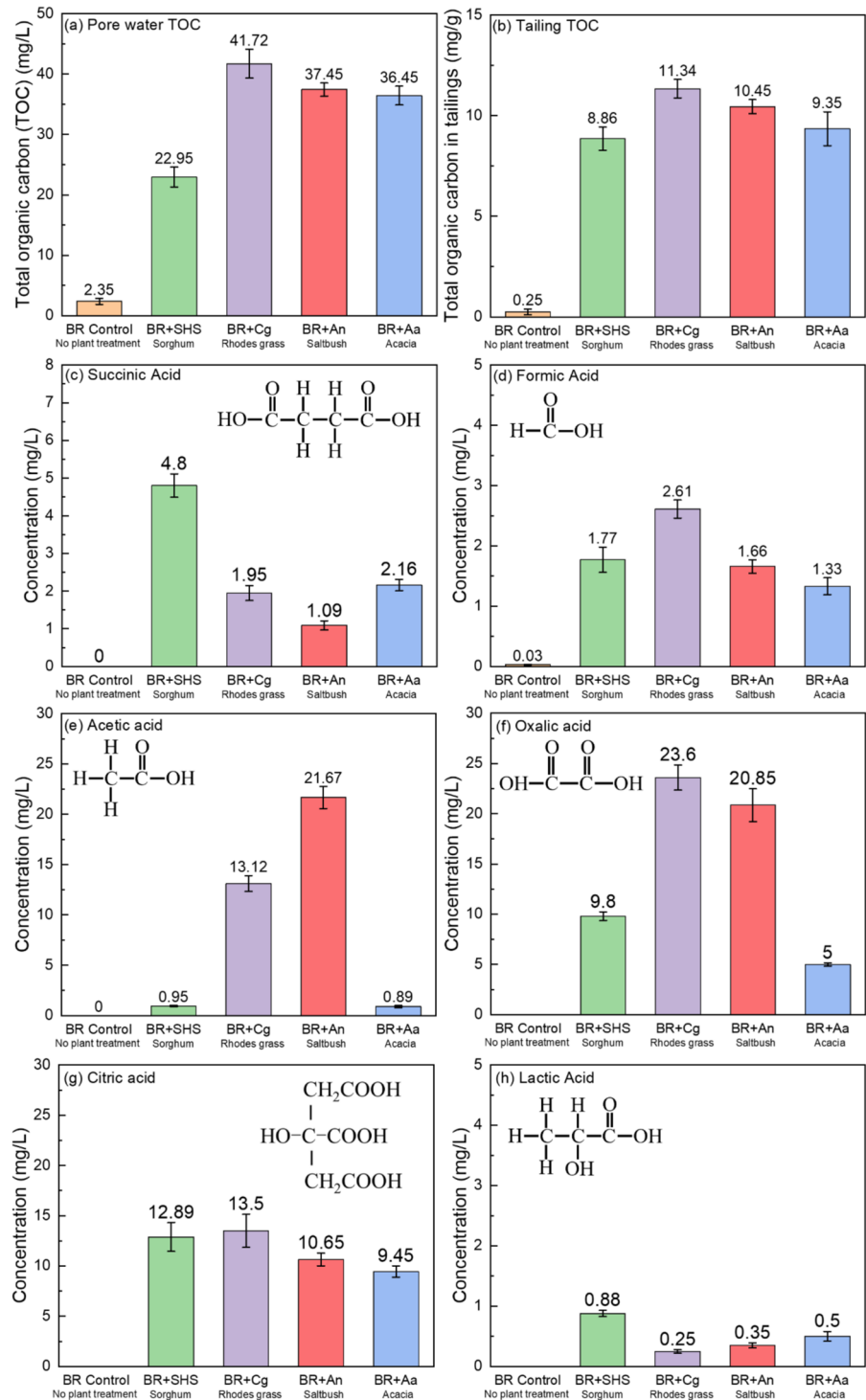


**Fig. 5** (a–f) SEM mapping of bauxite residue in rhizosphere of An plants, (g) pseudo-ternary compositional plot of Na–Al–Si (Each point represents the average element content in a separate area), (h) Model of the Na<sup>+</sup>–H<sup>+</sup> exchange process in sodalite

generated H<sup>+</sup>, to not only exchange with Na<sup>+</sup> (i.e., alkali) lodged inside aluminosilicates (e.g., sodalite) into porewater (i.e., solution), but also neutralize the dissolved alkali in porewater (Menezes-Blackburn et al. 2016; Wang et al. 2023). Meanwhile, organic acid anions, such as carboxyl groups can form chelation with exposed Si and Al atoms on the mineral surface to form stable complexes, accelerating sodalite weathering and alkali-exchange into solution (Hue

et al. 1986; Vachon et al. 1994; Wang et al. 2020). Other minor biochemical processes in roots interfacing alkaline BR may include H<sup>+</sup> release coupled with cation uptake (e.g., Ca<sup>2+</sup>, K<sup>+</sup>, Na<sup>+</sup>, and Mg<sup>2+</sup>) (Reid and Hayes 2003) and production of CO<sub>2</sub> from root respiration and formation of H<sub>2</sub>CO<sub>3</sub> in the rhizosphere (Chen et al. 2015). These major and minor biochemical responses in roots of haloalkalitolerant plants would have lowered and buffered the strongly

**Fig. 6** Concentration of total organic carbon (TOC) in (a) pore water, (b) BR and (c–h) low molecular weight organic acids (LMWOAs) in root exudates of pioneer plants



alkaline pH of BR in the immediate root surfaces, enabling the growth of roots into BR matrix even at pH > 10.

Halophytes are known to have a coupled alkalinity and salinity tolerance, which can grow healthily in soil with saturated EC > 40 mS/m and pH up to 10 (Loch et al. 2004; Saslis-Lagoudakis et al. 2014). Native acacia, such as *Acacia auriculiformis* (Aa) has evolved with coupled physiological tolerance of salinity (EC > 40 mS/m) and alkaline pH (Bui et al. 2014). These species have highly adaptive rooting strategies to cope with extreme salinity without inhibitory effects on plant growth, if partial roots are established in slightly/moderately saline (EC < 20 mS/m) niche (Barrett-Lennard et al. 2009). The partial establishment of roots in the improved niche (i.e., sand supplied with nutrient solution) rendered the tolerance of plant roots when growing into the harsh matrix, BR (Figures S5–S7).

#### Geochemical improvements in roots-modified bauxite residue

Through rhizosphere interactions in roots-BR interfaces, one of the key geochemical changes is the irreversible pH neutralization. Porewater pH in the interfaces was found to have lowered from highly alkaline (pH 9.82) to circumneutral (pH 7.75–8.72) (Fig. 1(a)). This may have resulted from the exudation of acidic metabolites (Fig. 6(c–h)), leading to continual neutralization of dissolved alkali in solution or porewater. Among the plants tested, *Atriplex nummularia* (An) plants had the strongest effects on the pH neutralization in BR (pH down to 7.75), followed by *Chloris gayana* (Cg) (pH 8.08), *Acacia auriculiformis* (Aa) (pH 8.56) and *Sorghum spp.* hybrid cv. Silk (SHS) (pH 8.72) plants. The specific rhizosphere mechanism of acacia (Aa) roots was not investigated, but which may have additional acidifying mechanism of proton production in biological nitrogen fixation, in addition to direct root-exudation of organic acids. Fresh nodules were observed in roots of Aa plants in the present study, though BNF function in nodules was not verified. The overall results of roots-mediated pH neutralization were much stronger in halophytes (An, Cg) and native acacia (Aa), than nonhalophyte (SHS).

The residual alkalinity in roots-interfaced BR is dependent on the residual amount of alkaline

minerals (e.g., sodalite, structural alkali in BR) in the BR, which accounts for the large part of BR acid neutralizing capacity (ANC, SI Text S6). The ANC in BR was significantly decreased by plant colonization (Fig. 1(b)), with the largest reduction in BR modified by roots of halophytes (An and Cg) (from 1.94 to 0.59 and 0.95 mol H<sup>+</sup> kg<sup>−1</sup>, respectively). BR colonized with the nonhalophytes, Aa and SHS, demonstrated small reductions in the ANC, to 1.06 and 1.21 mol H<sup>+</sup> kg<sup>−1</sup>, respectively, which would have been caused by different amounts of root surfaces interacting with BR and roots/capacity to generate acidic metabolites. The halophytes (An and Cg) used here would have generated much more extensive root surface area to interface BR, together with their intrinsic capacity to produce organic acids in roots. The BR-roots interactions are combined effects of physical (i.e., roots' total surface area) and biochemical (i.e., the capacity and intensity to generate acidic metabolites at the interfaces) mechanisms in roots. As a result, the sustainability of plant-mediated neutralization effects in different plant species would ultimately be determined by the magnitude of root-mediated weathering of BR minerals, which will be discussed later.

Apart from the pH changes, the significantly lowered salinity (indicated by EC values) in porewater of roots-modified BR (Fig. 1(c)) further reveal the effective weathering and dealkalization driven by root activities. Notably, the Na adsorption ratio (SAR) and exchangeable Na percentage (ESP) (Fig. 1(d)) significantly decreased in root-colonized BR compared to the control. This reduction in Na levels in BR-porewater is likely attributed to root uptake of Na<sup>+</sup> released from alkaline mineral weathering in the root-modified BR matrix. Furthermore, plants (particularly halophytes) can take up Na<sup>+</sup> in porewater, which would have contributed to the reduction of SAR and ESP (Fig. 1(d)). These processes not only neutralized BR's alkalinity but also improved its geochemical stability, laying the groundwork for sustainable technosol development. The magnitude and persistence of roots-induced geochemical improvements (e.g., pH neutralization) are determined by the magnitude of accelerated weathering of alkaline minerals (e.g., sodalites) in BR, coupled with the physical and biochemical responses of colonizing plants.

The decrease of salinity (EC) and sodicity (SAR, ESP) in roots-modified BR would have been caused by plant uptake of dissolved Na from roots-mediated

weathering of alkaline minerals. Halophytes (An and Cg) were most effective in taking up Na released from the BR, with elevated Na concentrations in shoots (Table S4(d)), corresponding to lowered Na concentrations in BR. For example, saltbush An has developed a physiological strategy to take up Na for sustaining metabolic activities (Hussin et al. 2013; Zhang et al. 2023). Salt bush (An) plants removed large amounts of Na ( $1120 \text{ mg pot}^{-1}$ ), with shoot Na concentration as high as  $29.3 \text{ mg g}^{-1}$  dry matter. This species can maintain intracellular ionic homeostasis under high-salt environments (Belkheiri and Mulas 2013). The  $\mu$ -XRF scans at macroscale (mm level) and SEM-EDS mapping, further confirmed that BR adhering onto roots of An and Cg was depleted of Na, forming a distinct “Na depletion zone” (Figure S17(b) and (f)), but with Al and Fe enrichment (Figure S17(c-d) and (g-h); Figures S15 - 16, Table S5; Fig. 5(a-b)). Importantly, while Na was depleted, the aluminosilicate (Si–O–Al) skeleton of minerals remained intact after weathering (Fig. 5(c-f)), thus maintaining cation exchange capacity for nutrient retention and sequestration of organic matter (Huang and Violante 1986; Milenković et al. 2016). Additionally, the disappearance of sodium chloride’s primary peak (104) corresponded to reduced salinity, suggesting root uptake of soluble Na.

Halophytes and salt-tolerant plants can accumulate osmoprotectants (e.g., proline, betaine, and sugar alcohols), to maintain cellular osmotic balance, enhancing salinity and alkalinity tolerance (Zhao et al. 2020). In contrast, as an exotic pasture species, SHS has a limited tolerance and root growth in the highly alkaline-saline BR environment, suggesting its unsuitability to be used as a biological driver in the early phase of soil formation in BR. The legume Aa accumulated higher Al concentrations in shoots than other plant species (Table S4(d)), exhibiting the high Al toxicity tolerance in native tree species (Dell et al. 2003).

Overall, clear species-specific differences were observed in rhizosphere-driven geochemical improvements of BR. Halophytic species, especially *Atriplex nummularia* and *Chloris gayana*, consistently outperformed the glycophyte SHS and the leguminous tree Aa, in neutralizing alkaline pH conditions, reducing ANC, and enhancing Na uptake. These differences can be attributed to their physical and biochemical attributes in roots, such as root architecture

(e.g., fibrous vs tap-roots) organic acid exudation capacity, and salt tolerance strategies. Halophytes not only formed more extensive root-mineral interfaces but also secreted higher levels of carboxyl-rich LMWOAs, accelerating sodalite dissolution and  $\text{Na}^+$ - $\text{H}^+$  exchange. In contrast, SHS exhibited limited root colonization and poor dealkalization performance, while Aa showed moderate effectiveness, likely due to its ability to tolerate Al toxicity and contribute to acidification via biological nitrogen fixation. These findings underscore the importance of selecting halophytes plant species for effective rhizosphere-mediated weathering and long-term BR rehabilitation.

#### Roots-driven mineral weathering and dealkalization of bauxite residue

Plant roots drove the weathering of alkaline minerals in BR through a combination of mechanical penetration and rhizosphere chemical interactions, promoting mineral dissolution and amorphous mineral formation. Sodalite features  $\text{Na}^+$  ions encapsulated within aluminosilicate  $\beta$ -cages formed by alternately arranged  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra (Wang et al. 2020). Approximately 25% of  $\text{Na}^+$  resides in channels between  $\beta$ -cages and is readily exchangeable via  $\text{Na}^+$ - $\text{H}^+$  cation exchange (Eq. 1) (Wang et al. 2020, 2023). The remaining 75% of  $\text{Na}^+$  is tightly bound within the aluminosilicate framework, requiring higher energy for hydrolysis and release (Eq. 2) (Khaitan et al. 2009; Wang et al. 2023). As roots penetrate the BR matrix (Figures S9 and S15), they exert localized mechanical pressure, disrupt interparticle bonds, and create microcracks on mineral surfaces (Dunne 1990).

The effectiveness of rhizosphere-driven alkaline mineral weathering varied with plant species tested here. Overall speaking, halophytes have shown much stronger effects on BR weathering in roots-BR interfaces, than the less tolerant species (i.e., SHS), as confirmed by synchrotron-based XRD analysis (Fig. 2b, Figures S13 - 14). Halophytes An and Cg were found to be most effective in driving the weathering of alkaline minerals in BR, since they produced higher levels of acetic, oxalic, and citric acids than non-halophytes SHS and Aa (Fig. 6(e–g)). These organic acids, being rich in carboxyl functional groups, exhibit stronger chelating properties and are more effective in breaking down sodalite’s structure. The carboxyl groups in these acids can bind to Al

and Si atoms of aluminosilicate sheets, reducing the activation energy for mineral dissolution and facilitating the hydrolysis and release of structural alkali ions (e.g.,  $\text{Na}^+$ ) (Drever 1994; Ma 2005). Interestingly, the acacia species here also caused a similar magnitude of weathering of alkaline minerals. It is known that native *Acacia* has developed coupled salinity and alkalinity tolerance (Bui et al. 2014), of which roots can exude protons while fixing atmospheric nitrogen in root nodules (Yan et al. 1996). The complete removal of alkali lodged inside the  $\beta$ -cage of sodalites requires highly acidic conditions, to break down Si–O–Al linkages and release  $\text{Na}^+$  into the solution phase (Peng et al., 2020; Wang et al. 2016). However, a partial removal of alkali with organic acids is sufficient to lower alkaline pH into moderately alkaline pH range suitable for the growth of haloalkalitolerant plant species to advance soil formation.

As a result of roots-driven mineral weathering, neoformation of amorphous Al–Si–Fe minerals was observed (Fig. 3(a)). Plant colonization elevated the concentrations of WE–Al/Si and AAO–Al/Si in BR (Fig. 3(b–c)). The Al K-edge XANES spectra of rhizosphere BR (Fig. 3(e)) revealed main peaks at 1568.2 eV and 1572.1 eV, indicating that Al predominantly exists in octahedral coordination with six surrounding oxygen atoms or hydroxide ions (Li et al. 1995a). In contrast, Al atoms in sodalite usually form oxy-aluminum tetrahedra with oxygen atoms in a tetra-coordinated structure (Hasha et al. 1988; Pauling 1930). Similarly, the Si K-edge XANES spectrum (Fig. 3(f)) exhibited a prominent peak at 1849.4 eV, suggesting the presence of tetra-coordinated silicon-oxygen tetrahedra ( $\text{SiO}_4$ ) (Li et al. 1995b). The concentrations of WE–Fe and AAO–Fe in the BR (Fig. 3(d)) also increased in response to root activities. The Fe K edge EXAFS spectra (Fig. 3(g)) and linear combination fitting (LCF) result (Fig. 3(h)) further demonstrated that the relative proportion of hematite in BR decreased, whereas the proportion of Fe–Si and Fe–Al co-precipitates increased, particularly in BR colonized by Cg and Aa. TEM-SAED and EDX results added further evidence that Al–Si–Fe rich secondary minerals were formed from roots driven mineral weathering in the BR. As shown in Fig. 4(a–d), numerous clusters of nanoscale particles (< 100 nm in diameter) with rounded edges and irregular distributions were observed around plant roots. The elemental composition of these nano-minerals, primarily comprising Al (49.5%) and Si (40.8%)

with minor Mg and Fe (Fig. 4(f)). These secondary minerals may be neoformed during weathering of sodalite and via the co-precipitation of dissolved Al, Si, and other ions in the rhizosphere.

The formation of Al–Si–Fe coprecipitates from locally supersaturated weathering solutions is recognized as a multifaceted process, primarily driven by the synergistic hydrolysis and polymerization of dissolved cations (Bi et al. 2004). Dissolution of aluminosilicate minerals such as sodalite, would have released hydroxyl forms of  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions (e.g.,  $[\text{Al}(\text{OH})_4^-]$  and  $[\text{H}_3\text{SiO}_4^-]$ ). These charged species may interact through electrostatic forces and hydrogen bonding, enabling the formation of initial nucleation centers (Jun et al. 2016). The high Lewis acidity of  $\text{Al}^{3+}$  facilitates the formation of Al–O–Si bonds through bridging with silicic acid molecules or silicate ions (Hensen et al. 2010). Further deprotonation and the establishment of oxygen bridges drive polymerization would have resulted in the formation of larger Al–O–Si networks in corner-sharing configurations. The presence of inorganic ions (such as  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ ) and organic matter (root exudates) can introduce structural irregularities or bonding defects, thereby impeding Al(III) polymerization (Nail et al. 1976), facilitating the formation of amorphous phases (Huang and Violante 1986). These amorphous mineral phases were further corroborated by electron diffraction analysis (Fig. 4(e)) and align with findings from Fe K-edge XAFS and chemical extraction analyses (Fig. 3). These amorphous Al–Si–Fe minerals act as key cementing agents for stabilizing organic matter and supporting soil aggregate formation (Wu et al. 2023), which underpins soil-like structure development in BR-technosol.

## Conclusion

The present findings have confirmed that haloalkalitolerant plants with roots partially established in improved niches can tolerate extremely alkaline and saline conditions of unimproved BR matrix or profiles, forming extensive roots–BR interfaces. At the interfaces, halophytic plant species exhibited strong physical penetration into alkaline BR, and released large amounts of LMWOAs with carboxyl groups (e.g., acetic acid, oxalic acid, and citric acid) in porewater. These roots–mineral interactions enhanced the weathering of alkaline minerals (e.g., sodalites) and neoformation of

secondary amorphous nano Al-Si-Fe minerals with high specific surface area and affinity for organics. These processes not only contributed to BR dealcalization and irreversible pH neutralization, but also high potential of organo-mineral association for aggregate formation. Therefore, haloalkalitolerant plant species, particularly native halophytes, should be incorporated as key biological drivers in combination with microbial dealcalization initiated by organic matter inputs, in order to achieve irreversible neutralization in a spatially consistent manner. This will accelerate BR-technosol development for large-scale bauxite residue rehabilitation.

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## Declarations

**Competing interests** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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