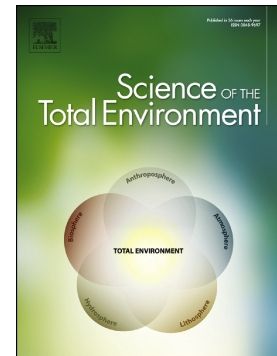


## Accepted Manuscript

Geochemical and mineralogical constraints in iron ore tailings limit soil formation for direct phytostabilization

Songlin Wu, Yunjia Liu, Gordon Southam, Lachlan Robertson, Tsz Ho Chiu, Adam T. Cross, Kingsley W. Dixon, Jason C. Stevens, Hongtao Zhong, Ting-Shan Chan, Ying-Jui Lu, Longbin Huang



PII: S0048-9697(18)33615-5  
DOI: doi:[10.1016/j.scitotenv.2018.09.171](https://doi.org/10.1016/j.scitotenv.2018.09.171)  
Reference: STOTEN 28675  
To appear in: *Science of the Total Environment*  
Received date: 27 July 2018  
Revised date: 12 September 2018  
Accepted date: 13 September 2018

Please cite this article as: Songlin Wu, Yunjia Liu, Gordon Southam, Lachlan Robertson, Tsz Ho Chiu, Adam T. Cross, Kingsley W. Dixon, Jason C. Stevens, Hongtao Zhong, Ting-Shan Chan, Ying-Jui Lu, Longbin Huang, Geochemical and mineralogical constraints in iron ore tailings limit soil formation for direct phytostabilization. *Stoten* (2018), doi:[10.1016/j.scitotenv.2018.09.171](https://doi.org/10.1016/j.scitotenv.2018.09.171)

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

# Geochemical and mineralogical constraints in iron ore tailings limit soil formation for direct phytostabilization

Songlin Wu<sup>a</sup>, Yunjia Liu<sup>a</sup>, Gordon Southam<sup>b</sup>, Lachlan Robertson<sup>a</sup>, Tsz Ho Chiu<sup>a</sup>, Adam T. Cross<sup>c</sup>, Kingsley W. Dixon<sup>c</sup>, Jason C. Stevens<sup>d,e</sup>, Hongtao Zhong<sup>e</sup>, Ting-Shan Chan<sup>f</sup>, Ying-Jui Lu<sup>f</sup>, Longbin Huang<sup>a\*</sup>

<sup>a</sup> Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Brisbane, Queensland 4072, Australia

<sup>b</sup> School of Earth & Environmental Sciences, The University of Queensland, Brisbane, Queensland 4072, Australia

<sup>c</sup> ARC Centre for Mine Site Restoration, School of Molecular and Life Science, Curtin University, GPO Box U1987, Bentley, WA 6102, Perth, Australia

<sup>d</sup> Kings Park Science, Department of Biodiversity, Conservation and Attractions, Kattidj Close, Kings Park, WA 6005, Australia

<sup>e</sup> School of Biological Sciences, The University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Perth, Australia

<sup>f</sup> National Synchrotron Radiation Research Center, Hsinchu Science Park, Hsinchu 30076, Taiwan

\* Corresponding Author: Longbin Huang

Tel: +61 7 3346 3130, fax: +61 7 3346 4056, e-mail: [l.huang@uq.edu.au](mailto:l.huang@uq.edu.au)

**Abstract:**

The present study aimed to characterize key physico-chemical and mineralogical attributes of magnetite iron (Fe) ore tailings to identify potential constraints limiting *in situ* soil formation and direct phytostabilization. Tailings of different age, together with undisturbed local native soils, were sampled from a magnetite mine in Western Australia. Tailings were extremely alkaline (pH > 9.0), with a lack of water stable aggregate and organic matter, and contained abundant primary minerals including mica (e.g., biotite), with low specific surface area (N<sub>2</sub>-BET around 1.2 m<sup>2</sup> g<sup>-1</sup>). These conditions remained relatively unchanged after four years' aging under field conditions. Chemical extraction and spectroscopic analysis [e.g., X-ray diffraction (XRD) and synchrotron-based Fe K edge X-ray absorption fine structure spectroscopy (XAFS) analysis] revealed that the aging process decreased biotite-like minerals, but increased hematite and magnetite in the tailings. However, the aged tailings lacked goethite, a compound abundant in natural soils. Examination using backscattered-scanning electron microscope - energy dispersive X-ray spectrometry (BSE-SEM-EDS) revealed that aged tailings contained discrete sharp edged Fe-bearing minerals that did not physically integrate with other minerals (e.g., Si/Al bearing minerals). In contrast, Fe minerals in native soils appeared randomly distributed and closely amassed with Si/Al rich phyllosilicates, with highly eroded edges. The lack of labile organic matter and the persistence of alkaline-saline conditions may have significantly hindered the bioweathering of Fe-minerals and the biogenic formation of secondary Fe-minerals in tailings. However, there is signature that a native pioneer plant, *Maireana brevifolia* can facilitate the bioweathering of Fe-bearing minerals in tailings. We propose that eco-engineering inputs like organic carbon accumulation, together with the introduction of functional microbes and pioneer plants, should be adopted to accelerate bioweathering of Fe-bearing minerals as a priority for initiating *in situ* soil formation in the Fe ore tailings.

**Keywords:** Fe-ore tailings, soil structure, mineral bioweathering, Fe (oxy)hydroxides, mine-site rehabilitation

## 1. Introduction

The extraction and processing of Fe ores have been generating millions of tons of tailings occupying thousands of hectares of natural landscapes worldwide. Australia is one of the major Fe-ore mining countries in the world, with an estimated 51,545 Mt of Fe ore reserve, accounting for 28% of the world's iron ore resources (from Australia's Identified Mineral Resources 2016). These tailings are poly-mineral wastes possessing unfavourable chemical properties and fine physical texture without water-stable aggregates to facilitate water infiltration, thus inhibiting microbial and plant colonization. These conditions may result in the long-term deterioration of environmental health and quality without adequate rehabilitation or ecological restoration (Cross and Lambers, 2017; Huang et al., 2012; Jamieson, 2011). The progress of tailings rehabilitation globally has been limited primarily by a lack of natural soils to reconstruct functional root zones for revegetation (Huang et al., 2012). Unlike sulfidic tailings (e.g. Cu-, Pb-Zn, etc.), magnetite Fe-ore tailings are not acutely toxic, but lack the properties and functions of soil which support sustainable plant growth (Cross and Lambers, 2017). The key constraints include: (1) a lack of primary physical structure (e.g., aggregates and macropores) and chemical properties (e.g., low cation-exchange capacity and stable soil carbon); (2) lack of available nutrients like N and P that restrict plant growth; and (3) extreme physico-chemical characteristics (e.g., acidic or alkaline pH, high salinity, resulted from the mineralogy and geochemistry of the magnetite ore mined, as well as the alkaline chemicals added in the reverse flotation process). Conventional cover methods require large volumes of soil resources to cover vast areas of tailings at mine sites (100s – 1000s of hectares), and are

constrained both by cost and the scarcity of natural topsoil resources. Furthermore, standard tailing cover designs have been shown to detrimentally impact on plant establishment potential (Robson et al., 2018). Eco-engineering soils from tailings has been advocated as a paradigm-shifting technology for rehabilitating tailings landscapes at metal mines, in order to offset the large volumes of soil resources and substantially decrease associated financial costs (Huang et al., 2014).

The composition of primary and secondary minerals derived from metal mine ore and/or mineral processing provide a mineralogical basis for purpose-engineered soil formation and development (Li and Huang, 2015). The development of water-stable aggregate is critical to the progression of soil formation, as stable soil aggregation resulted from integrated physico-chemical and biological activities is one of the most important parameter determining soil structure and quality (Bronick and Lal, 2007), and is a key aspect of eco-engineered soil formation. Stable soil aggregate formation results from the interactions of secondary minerals with organic matter (e.g., assimilates or products of microbial activities and rhizosphere processes) in most soils (Duiker et al., 2003; Gargiulo et al., 2014; Li and Huang, 2015; Tisdall and Oades, 1982; Yuan et al., 2016). As a result, before designing eco-engineering methods, it is useful to characterise the properties of aged and fresh tailings to assess key factors limiting organo-mineral interactions and the aggregation of tailings particles.

Iron minerals may undergo dissolution, complexation, precipitation and/or aggregation in cascaded and/or coupled fashion, through various biotic (e.g., roots, microbes) and/or abiotic (e.g., pH, redox potential, and complexation of organic ligands) weathering processes in soils (Schwertmann, 1993). Secondary Fe-minerals particularly contribute to soil aggregation and soil structure development (Duiker et al., 2003; Gargiulo et al., 2014), as they usually have a greater capacity for binding organic matter and facilitates organo-mineral association for stable aggregate formation (Chen et al., 2014a; Kleber et al., 2015; Regelink et al., 2015; Steffens et

al., 2017). Secondary Fe-minerals (e.g., short-range-order (SRO) minerals such as ferrihydrite) have higher capacity than crystalline Fe minerals in organic matter adsorption/binding, due to a higher specific surface area (SSA) and large numbers of hydroxyl groups present on mineral surfaces (Cao et al., 2011; Chen et al., 2014b; Torn et al., 1997; Xiao et al., 2016). Subsequently, the weathering of crystalline Fe-minerals into secondary Fe-minerals is one of the prerequisites for organo-mineral interactions and aggregation.

The Fe-ore mineral weathering and organo-mineral are fundamental to eco-engineering magnetite-Fe tailings into functional soils (or technosols). However, the composition and morphology of Fe-bearing minerals in tailings remain poorly understood under mediterranean and semi-arid climatic conditions at mine sites. As a result, before designing eco-engineering methods, it is essential to characterize the properties of tailings substrate resources (fresh vs aged) to assess key factors limiting organo-mineral interactions and the aggregation of tailings particles. Additionally, some native plant species have been observed to survive in tailings under field conditions (Cross and Lambers, 2017), and it is important to determine whether the colonization of these pioneer plants has resulted in accelerated weathering of Fe-ore minerals.

This study sampled fresh, aged magnetite Fe-ore tailings and topsoil covering the tailings at a typical Fe-ore mine site in Western Australia (Figure S1), and characterized their physico-chemical and mineralogical attributes (especially Fe-mineral phases and speciation) compared with undisturbed native soil. In addition, the potential role of a native pioneer plant (*Maireana brevifolia*) to accelerate Fe-ore weathering was evaluated by examining the physico-chemical properties and weathering effects of Fe-minerals in tailings under the canopies of these plants. Fe-mineral phases and speciation, as well as Fe-rich mineral morphology, were characterized by using an integrated suite of methods including chemical extraction and various micro-spectroscopy. It was expected that: (1) magnetite tailings would have different physico-chemical traits, physical structure, mineralogical phases and morphology (especially Fe

minerals composition and morphology) compared with native soils; (2) Fe-bearing minerals would have undergone weathering in aged tailings exposed to field conditions, forming Fe (oxy)hydroxides (e.g., hematite, magnetite, goethite); and (3) native pioneer plant root activities would have accelerated Fe-mineral weathering in the magnetite Fe-ore tailings. The expected findings will provide the basis for setting goals and criteria in the ecological engineering of soil formation of the tailings, for direct phytostabilization of the Fe-ore tailings with native plant communities.

## 2. Materials and methods

### 2.1. Sampling design

The tailings were sourced from a major magnetite mining operation located approximately 400 km northeast of Perth in the Midwest region of Western Australia (Figure S1). Fresh tailings (newly deposited, less than 1 month) were sampled from the surface layer of tailings newly deposited in a tailings storage facility. Aged tailings (approximately four years old) as well as aged topsoil (representing a capping layer approximately 10–40 cm deep overlaying the tailings of the same age) were sampled from a field trial set up in 2013. This field trial was comprised of tailings both with and without a topsoil capping layer, and the area was planted with native plant species including one of the dominant pioneer species *Maireana brevifolia* in July 2013. Aged tailings samples were collected both from bare areas without plant cover and the area underneath *M. brevifolia* individuals growing in uncapped tailings. In comparison, topsoil samples were collected from bare areas without plants and area underneath canopies of *M. brevifolia* individuals growing in topsoil-capped tailings. Additionally, native soils were collected from undisturbed sites adjacent to the sampled field plots for reference. Thus sampling included six types of tailings/soil samples: fresh tailing (FT), aged tailing-bare (AT-B), aged tailing-under canopy of plant (root affected area) (AT-R), topsoil-bare (TS-B), topsoil-

under canopy of plants (root affected area) (TS-R) and native soil (NS), among which four randomly selected replicates (or locations) were sampled for each sample type. Aliquots (ca. 30 g) of subsamples of these samples were immediately stored in a dryshipper prefilled with liquid nitrogen for X-ray diffraction (XRD), backscattered electron-scanning electron microscope-energy dispersive X-ray spectrometry (BSE-SEM-EDS) and synchrotron-based Fe K-edge X-ray absorption fine structure spectroscopy (XAFS) after freeze drying. The bulk samples (ca. 300 g) were air-dried and stored at room temperature for physico-chemical analysis (pH, EC, total carbon and nitrogen, water-stable aggregates, and N<sub>2</sub>-BET specific surface area) (Eusterhues et al., 2005).

## ***2.2. Analysis of pH, EC, total organic carbon and nitrogen concentration***

The pH and electrical conductivity (EC) of tailings and topsoil samples were determined in water extracts (solid:water=1:5 (w/w)) by using a pH electrode (TPS 900-P) and an EC electrode (TPS 2100), respectively. Total organic carbon (TOC) were determined by dry-combustion with a LECO CNS-2000 Analyzer (LECO Corporation, San Jose, MI, USA) after acid-removal of inorganic carbon. Total nitrogen concentrations were determined using a LECO CNS-2000 Analyzer (Kowalenko, 2001).

## ***2.3. Water stable aggregate distribution***

Water stable aggregates (WSA) were measured by separating the three soil/tailing aggregate fractions following the wet-sieving method (Kemper and Rosenau, 1986). Two sieves were used to collect three aggregate size fractions: (1) 2000 – 250  $\mu\text{m}$  (fraction containing macroaggregates); (2) 250 – 53  $\mu\text{m}$  (fraction containing microaggregates); (3) < 53  $\mu\text{m}$  (silt and clay fraction). For each tailing/soil replicate, 50 g of air-dried sample were placed on the



series of sieves and submerged into deionised water for 1 hour to equilibrate. Then the aggregates of different sizes were separated by manually moving the sieves up and down (within 3 cm) for 2 min (100 up-down cycles) [modified from Kemper and Rosenau (1986)]. The residues on each sieve were collected into PVC tubes and dried at 40 °C for 96 hours until constant weight. The proportion of water stable aggregates (WSA) of different sizes was expressed as the ratio of the dry weight of WSA to total sample dry weight. Mean weight diameter (MWD) of water stable aggregates was calculated as follows:

$$MWD = \sum_{k=1}^{n+1} \frac{r_k + r_{k-1}}{2} \times m_k$$

Where  $k=1, 2, 3$ , representing different fractions,  $r_0=2000 \mu\text{m}$ ,  $r_1=250 \mu\text{m}$ ,  $r_2=53 \mu\text{m}$ ,  $r_3=0 \mu\text{m}$ ,  $m_k$  is the proportion of aggregate fractions on the  $k^{\text{th}}$  sieve, and  $n$  is the number of the sieves.

#### **2.4. Specific surface area analysis**

For specific surface area (SSA) analysis, the air-dried samples were gently crushed, and sieved through 200  $\mu\text{m}$  sieves to remove stones, and then degassed for 12 h to pressures of 2 Pa at 200 °C. Brunauer-Emmett-Teller (BET) specific surface area (SSA) were measured by nitrogen sorption at 77K using a Micromeritics Tristar 3020 (Micromeritics Instrument Corporation, Norcross, GA, USA).

#### **2.5. Chemical fractionation**

All tailings and topsoil samples were sequentially fractionated to quantify the distribution of Fe, Al, Mn and Si using an acetic acid extraction (i.e., weak acid-soluble pool), an acid ammonium oxalate (AAO) extraction (amorphous pool) and a citrate/bicarbonate/dithionite

(CBD; crystalline pools) extraction (Rayment and Lyons, 2011). AAO-extractable Fe/Al should include amorphous Fe (such as ferrihydrite) and Al, organically-complexed Fe and Al and Fe minerals containing Fe<sup>2+</sup> such as magnetite (McKeague and Day, 1966; Parfitt and Childs, 1988). CBD-extractable Fe/Al should include oxides and hydroxides of Fe (e.g., hematite, goethite, lepidocrocite and maghemite) and Al (Parfitt and Childs, 1988). Acetic acid extraction was conducted by shaking 1 g of air-dried sample in 40 mL 0.11 M acetic acid solution for 24 h at room temperature. AAO extraction was conducted by shaking 0.5 g of air-dried sample in 40 mL AAO solution (0.175 M (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub> + 0.10 M H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>) for 4 h in darkness. CBD extraction was conducted by shaking 0.5 g of air-dried samples in 40 mL CBD solution (0.3 M sodium citrate + 5 ml 1 M sodium bicarbonate + 1.00 g sodium dithionite) for 16 h in darkness. All samples were centrifuged (2400 ref), and filtered through 0.22 µm filter member and the elements were analyzed by inductively coupled plasma-optical emission spectrometry (ICP-OES, 720ES, Varian Inc., Palo Alto, California, USA).

## 2.6. XRD analysis

Subsamples were freeze-dried and ground to a fine powder at an anaerobic chamber for XRD analysis using a Bruker D8 DISCOVER diffractometer. The diffractometer was of 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 detector was open to 2.896° during the data acquisition. Long-line fine-focus copper tube was operated at 40 kV and 40 mA. X-ray diffraction data were collected between 10° and 80° with a step of 0.05°, and XRD traces were processed using the Diffrac<sup>plus</sup> Evaluation Package V3.1 (Bruker AXS, Germany) and the PDF-2 mineral database (2013 release).

### 2.7. Fe K-edge XAFS Analysis

Freeze-dried and finely-ground powder samples were also used for Fe K-edge (7,112 eV) XAFS analysis, which was conducted on beamline 17C at the national synchrotron radiation research centre (NSRRC) in Taiwan. The following Fe standards were selected: (1) magnetite, (2) hematite, (3) goethite, (4) ferrihydrite, (5) siderite, (6) Fe(III) phosphate, (7) biotite, (8) olivine, (9) illite (10) vermiculite (11) pyrite, (12) Fe(II) gluconate hydrate, (13) Fe(II) glutathione, (14) Fe(III) oxalate, (15) Fe(II) humic acid, (16) Fe(II) histidine, (17) Fe(III) histidine. Magnetite, hematite, goethite, pyrite, siderite, Fe(III) phosphate, and Fe(II) gluconate hydrate were supplied by Sigma Aldrich (Sydney, Australia). Olivine, illite, vermiculite and biotite were purchased from Ward's science (<https://www.wardsci.com>). Ferrihydrite (2-line) was synthesized according to (Schwertmann and Cornell, 2000). Briefly, 40 g  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was dissolved in 500 ml MilliQ water and 1.0 M KOH was added to adjust the pH to 7–8. The products were centrifuged, dialysed and freeze-dried before use. Iron-organic matter complexes were prepared through mixing 0.1 M Fe(II)/Fe(III) solutions with organic matter (i.e. oxalate acid, humic acid, histidine, glutathione) at a ratio of 1:5 mole at pH 5.5 (adjusted using 0.5 M NaOH).

An energy range of -200 to 800 eV relative to the Fe K edge absorption was used to acquire spectra of Fe-minerals/compounds in the tailings and topsoil samples and solid Fe reference compounds in transmission mode under ambient conditions. Fe K edge XAFS spectra of Fe-organic matter complexes were collected at fluorescence mode. Data was collected using the following energy ranges: -200 – -20 eV (10 eV steps with 2s per interval), -20 – 30 eV (0.35 eV steps with 2s per interval), and 30 – 800 eV (4 eV steps with 4s per interval).

The energy scale was calibrated using Fe foil as an internal standard (calibration energy was 7112.0 eV). The foil was placed between the I1 and I2 ion chambers and collected

simultaneously with each sample spectrum. XAFS data was normalized (baseline and background corrections) using the ATHENA from DEMETER (or IFEFFIT) software package (CARS, University of Chicago) (Ravel and Newville, 2005). The X-ray absorption near edge spectroscopy (XANES, -20 to 30 eV) and extended X-ray absorption spectroscopy (EXAFS,  $k$  space, from 2.5 to 12.5) were analyzed by principal component analysis (PCA), and magnetite, goethite, ferrihydrite, siderite, biotite and pyrite were selected for linear combination fitting (LCF) analysis by using the ATHENA from IFEFFIT (DEMETER) software package (Ravel and Newville, 2005). The minimal R-factor, Chi-square and Reduced Chi-square were used for quality control of the fitting.

### **2.8. BSE/SEM-EDS analysis**

The freeze-dried samples were coated with carbon for scanning electron microscopy (SEM) analysis. SEM analysis was conducted using a Hitachi SU3500 SEM with an accelerating voltage of 5-15 kV. Back-scattered electron (BSE) was conducted using the same instrument with an accelerating voltage of 20 kV which was equipped for electron dispersive X-ray spectroscopy (EDS) to detect the elemental concentrations in the areas of interest.

### **2.9. Statistical analysis**

The significant differences of pH, TOC, TN, N<sub>2</sub>-BET SSA, WSA percentage, as well as acetate acid, AAO and CBD extractable element concentrations among different treatments were assessed by one-way ANOVA at  $P < 0.05$  with Duncan test.

### 3. Results

#### 3.1. pH, EC, total organic carbon and nitrogen concentration

The fresh and aged tailings and topsoil covering the aged tailings had a pH range of 8.1 to 9.9, while the native soil pH was around 6.2. After four years of aging in the field, the pH of surface tailings remained above 8.0. The pH in the bare aged tailings and topsoil covering the tailings were lower than that under the canopy of *M. brevifolia* plants (Figure 1,  $P < 0.05$ ).

Generally, the salinity (EC values) in the fresh and aged tailings was higher ( $> 1 \text{ mS cm}^{-1}$ ) than that in the topsoil and native soils ( $P < 0.05$ ). However, aged tailings under canopy of *M. brevifolia* had lower EC values than bare aged tailings. Total organic carbon (TOC) and total nitrogen (TN) concentrations in tailings were much lower than those in the topsoil and native soils (Figure 1,  $P < 0.05$ ). Moreover, the TOC and TN concentrations of topsoil under the canopy of *M. brevifolia* plants were much higher than those of bare topsoil from the bare area without any plants.

#### 3.2. Water stable aggregate distribution

The abundance of microaggregates (53–250  $\mu\text{m}$ ) and macroaggregates (250–2000  $\mu\text{m}$ ) in native soils and topsoil covering tailings was significantly greater than that in the fresh and aged tailings, regardless of the presence of *M. brevifolia* plants (Figure 2). In contrast, the abundance of clay-size fraction ( $< 53 \mu\text{m}$ ) in topsoils and native soils were much lower than that in fresh and aged tailings ( $P < 0.05$ ). The native soil contained much higher proportions of macroaggregates, compared to the topsoil covering the tailings. In addition, the MWD values of topsoil and native soils were much higher than those of the tailings, with the highest value of 0.71 mm in native soil.

### 3.3. Specific surface area

The specific surface areas (SSA, N<sub>2</sub>-BET) of native soil particles were more than 20 m<sup>2</sup> g<sup>-1</sup>, which was about 20 times higher than that of the fresh tailings (Figure 2C). The aging processes under field conditions increased SSA value of the tailings to around 4.5 m<sup>2</sup> g<sup>-1</sup>, which remained much lower than that of soils. In addition, the topsoils covering the tailings had a lower SSA value than native soils did ( $P < 0.05$ ). The topsoil under the canopies of *M. brevifolia* had a lower SSA than the bare topsoils.

### 3.4. Chemical extraction of Fe, Si, Al, and Mn

Fresh tailings contains large amounts of acetic acid-extractable Fe (5,160 mg kg<sup>-1</sup>), K (6,820 mg kg<sup>-1</sup>), Ca (8,920 mg kg<sup>-1</sup>) and Mg (601 mg kg<sup>-1</sup>) (Table 1). Acetate-extractable Fe, Ca and K in aged tailings, topsoil and native soil were lower than those in fresh tailings ( $P < 0.05$ ).

AAO- and CBD-extractable Fe, Si, Al and Mn were characterized in the tailings and topsoils covering the tailings (Figure 3). The aged tailings had higher concentrations of AAO- and CBD- extractable Fe than the fresh tailings and soils did. In contrast to Fe, AAO- extractable Si concentrations in the aged tailings and soils were lower than those in the fresh tailings. However, CBD- extractable Si concentrations were higher in the aged tailings, compared with the fresh ones. Soil samples contained more AAO- and CBD-extractable Al than the tailings samples did regardless of aging. The aging effect under field conditions without organic amendments did not change the distribution of AAO- and CBD- extractable Al in the tailings. The levels of AAO- and CBD- extractable Mn in the aged tailings and soils were much higher than those in the fresh tailings. In the aged tailings, the CBD-extractable Fe concentrations in the tailings collected from the area under the canopy of *M. brevifolia* plants were lower than those from the bare area without plants. The ratio of AAO-extractable Fe to CBD-extractable

Fe ( $Fe_o/Fe_d$ ) in fresh tailings was much higher than that in the aged tailings and topsoils, and the native soils in reference sites had the lowest  $Fe_o/Fe_d$  value among the samples.

### 3.5. Mineralogy--XRD analysis

Generally, the tailing and soil samples contained a large proportion of quartz, with minor amounts of magnetite, hematite, goethite, as well as mica (such as biotite ( $K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$ ), muscovite ( $Al_{2.908}H_{0.12}KO_{10}Si_{3.092}$ ), and pyroxene-ideal ( $MgO_3Si$ )) (Figure 4). The peaks of magnetite and hematite in aged tailings were higher than those of fresh tailings, topsoil and native soils. Kaolinite and vermiculite were detected in the topsoil and native soil samples, but not in any tailings sample. No difference in the XRD pattern of aged tailings or topsoils was observed between the bare areas and canopy areas of *M. brevifolia* plants.

### 3.6. Fe speciation- Synchrotron based Fe K-edge XAFS

In the pre-edge of Fe K edge XANES, Fe(III) was usually characterized by adsorption centred around 7113.5 eV, while Fe(II) was characterized around 7111.5eV (Figure 5). In the present samples, most of the Fe K-edge XANES spectra of the samples had pre-peaks at 7113.5eV in the first derivative of the normalized adsorption, indicating a major occurrence of Fe(III) in all samples. The shoulder of the pre-peak of XANES spectra of fresh tailings at 7111.5 eV was slightly higher than that of other samples, indicating more Fe(II) in fresh tailings than in other samples.

In Fe K-edge XANES spectra of fresh tailings, typical peaks at about 7125, 7130 and 7144 eV were found which were the white lines of XANES spectra of biotite, indicating the presence of

biotite in fresh tailings (Figure 5). Peaks at around 7133 eV (the white line of ferrihydrite and hematite) were also found in all samples especially aged tailings and soils, indicating that Fe (oxy)hydroxides may exist in both aged tailings and topsoils.

Iron-K-edge EXAFS was conducted to further quantify the percentage of different Fe species in the tailing/soil samples. In the  $k$  space, a range of 2.5-12.5 was selected for PCA and LCF analysis. Based on PCA, six Fe standard compounds were chosen for LCF analysis, including biotite, hematite, magnetite, goethite, ferrihydrite and Fe(III)-oxalate (Figure 6 and Table S1). In fresh tailings, ferrihydrite and biotite-like mica were the main components, while in aged tailings the percentage of biotite decreased, but those of hematite and magnetite increased. The topsoils contained similar amounts of biotite, ferrihydrite and hematite to aged tailings, but had around 15% percent goethite instead of magnetite. Native soils contained more hematite, goethite, and even some Fe(III)-oxalate (Fe(III)-carboxyl) compared with tailings and topsoil samples, but no biotite.

No major differences were observed in Fe-mineral composition between tailings (or topsoil) samples from unvegetated bare areas compared with samples underneath the canopies of *M. brevifolia* plants.

### **3.7. Morphology and Fe distribution in Fe-bearing minerals—SEM analysis**

Iron-bearing minerals in tailings and topsoils were characterized for understanding surface morphology, which is one of the critical factors influencing organo-mineral interactions (Figure 7 and S2). From the BSE image, the white area was enriched with Fe (confirmed by EDS analysis, Figure S2), and considered as Fe-rich minerals. Generally, Fe-minerals in fresh tailings appeared angular, with flat surfaces and sharp/irregular edges. In addition, Fe-bearing minerals and Si-bearing minerals (dark area in BSE image) were not embedded or integrated (Figure 7). Iron- and Si-minerals in aged tailings appeared finer in particle size, with sharp



edges compared with the fresh tailings. Newly-formed Fe-oxides were observed in aged tailings (Figure 7). Despite this, the Fe (oxy)hydroxides formed and other minerals (e.g., Si/Al minerals) ) remained physically unbound or not integrated based on SEM observations. In contrast, Fe-mineral particles in soils were morphologically rounded and physically interspersed and amassed with Si/Al-rich minerals, leading to the formation of possible cemented aggregates (Figure 7 and S2). Compared with the aged tailings from bare areas, the Fe-rich minerals in aged tailings below the canopy of *M. brevifolia* showed signs of bioweathering as the surface of the tailing minerals became eroded (Figure 7F).

#### 4. Discussion

This study suggests that the natural processes of altering and improving physico-chemical properties of tailings were very slow under semi-arid mediterranean climatic conditions. Natural aging processes under field conditions (ca. four years) did not increase organic carbon and total nitrogen content in tailings. Most importantly, physical structure remained poor with little water stable macro-aggregates evident in tailings after four years of field exposure without additional eco-engineering inputs (Figure 2). The poor physical structure of tailings was associated with unsuitable mineralogy, low specific surface area, and unstable Fe-bearing mineral phases and morphology. These key findings highlight the need for significant changes of mineralogical and (geo)chemical conditions in the tailings to facilitate and accelerate *in situ* soil formation. Additionally, the observed weathering phenomenon in aged tailings collected below the canopy of a native plant species (Figure 7F) suggests that tolerant pioneer plants may enhance bioweathering processes in the rhizosphere. This is likely to occur through rhizosphere biological activities and *in situ* organic carbon inputs (e.g., litters, root exudates and debris).

#### *4.1. Slow changes of physico-chemical characteristics in the tailings under field conditions*

The magnetite Fe-ore tailings were extremely alkaline (up to pH 9.5) and moderately saline (up to 1.5 mS cm<sup>-1</sup>). The extreme alkalinity of tailings may have resulted from the intrinsic mineralogy and geochemistry of the magnetite ore mined (pH 9.8, solid: water is 1:5), in addition to the resultant effects of alkaline chemicals such as molecular amine or NaOH added in the reverse flotation process (Filippov et al., 2010). The fine grinding and flotation processes associated with ore processing may also have facilitated the dissolution of Fe, Si, Al and K borne in associated minerals (e.g., biotite), resulting in elevated concentrations of acid extractable Fe, Si, Al and K in the tailings and potentially contributes to the elevated salinity. Similarly, Courtney et al. (2013) found that the bauxite tailings remained strongly alkaline and saline over a long-term storage period without amendments. However, Kong et al. (2017) found that the alkalinity and salinity decreased during the long-term natural aging (5-20 years). These differences may be because of mineralogical and geochemical differences and local climatic conditions (such as temperature and water supply). The mineralogy of Fe ore tailings is characteristic of abundant primary minerals (with low surface area) such as biotite with little amorphous secondary minerals, but bauxite residues are rich in alkaline minerals (e.g., sodalities). Besides, the local climatic conditions (such as seasonal rainfalls, temperature) may have significantly influenced the aging processes via regulating redox reactions, dissolution/precipitation, and mineral transformation. The lack of organic matter and nitrogen in the tailings is typical of metal mine tailings such as Pb-Zn tailings, and is a constraint to productive biological activities (e.g., soil microbes and root colonization) (Li and Huang, 2015; You et al., 2018a). The high pH (alkaline) and elevated salinity in the topsoil covering the aged tailings most likely reflected several years of capillary transport of tailings porewater by evapotranspiration.

It was particularly interesting to have observed the colonization of the pioneer native plant species *M. brevifolia* on the aged tailings without any topsoil inputs. The pH of tailings under the canopy of *M. brevifolia* plants was higher than that of adjacent bare areas, contrary to the expectation that soil pH may have been lowered by the excretion of organic acids by roots (Hinsinger et al., 2003). It is speculated that the increased pH may be due to the excretion of  $\text{HCO}_3^-$  or  $\text{OH}^-$  by plant roots because of excessive uptake of anions over cations, especially nitrate (Marschner, 1995). However, little has been known about the plant physiology and rhizosphere biology of this native species in the literature.

The abundance of microaggregates (53 – 250  $\mu\text{m}$ ) and macroaggregates (250 – 2000  $\mu\text{m}$ ) in fresh tailings were much lower than that in soils. Besides, the aging processes did not improve water stable aggregation (Figure 2A). This may due to the lack of secondary minerals with high surface area that acting as cements for aggregate formation in the tailings. This is partially confirmed by the fact that the tailings had a much lower SSA value ( $\text{N}_2$ -BET) than that soils did (Figure 3 C). Certainly, the lack of labile organic carbon is another critical factor limiting organo-mineral interactions and aggregation (Yuan et al., 2016).

#### ***4.2. Bulk spectroscopic analysis revealed Fe-bearing mineral transformation during field aging***

Amorphous Fe-minerals (e.g., Fe-(oxy)hydroxides) are important for soil aggregation and water-stability (Duiker et al., 2003). Secondary Fe-minerals are important not only to direct “gluing” effects to bind silicate particles together, but also for interactions with organic molecules (Duiker et al., 2003). As a result, the weathering of primary Fe-minerals and formation of amorphous secondary Fe-minerals is likely to be critical processes in the *in situ* soil formation of tailings.

Consistent with our assumption, the fresh tailings exhibited a markedly different Fe-bearing mineralogy from that of aged topsoil and native soil. The fresh tailings mainly consisted of biotite-like mica, ferrihydrite and a small amount of magnetite (Figure 6), while topsoil samples contained mainly Fe (oxy)hydroxides (hematite, goethite, ferrihydrite), with little or no biotite-like minerals. The ferrihydrite in the fresh tailings may have resulted from the crushing and flotation processes (Bruckard et al., 2015), during which Fe ions may have been dissolved from Fe-bearing mica and converted into ferrihydrites in the alkaline environment (Schwertmann and Cornell, 2000). The biotite-like minerals in the tailings were originated from magnetite ore, which is rich in primary minerals including various mica (Ramanaidou and Wells, 2014). The Fe (oxy)hydroxides in native soils are products of long-term weathering of the primary minerals on a geological time scale, resulting from various physico-chemical and biological (plants and microbes) weathering events (Cornell and Schwertmann, 1996). These Fe (oxy)hydroxides usually had higher specific surface area than primary minerals like biotite (Eusterhues et al., 2005; Hodson, 2006). This may be why the specific surface area (SSA) of soils were much higher than that of the tailings.

The tailings had undergone *in situ* weathering (albeit slow) and transformation of Fe-minerals through dissolution, oxidation and crystallization under field conditions, even without substantial amendments. The results of Fe K edge EXAFS, chemical fractionation and XRD analysis revealed that the percentage of biotite-like mica in the aged tailings proportionally declined, coinciding with the presence of various Fe (oxy)hydroxides (hematite and magnetite) compared with the fresh tailings. The weathering of biotite may be due to protonation, deprotonation, and the subsequent detachment of Fe/Si/Al species under dynamic changes of environmental conditions such as temperature, oxygen and water relations (Bray et al., 2015; Murakami et al., 2003). Following the decrease of biotite-like primary minerals and the increase of Fe oxides, the SSA value of tailings increased from about  $1.17 \text{ m}^2 \text{ g}^{-1}$  in the fresh

tailings to  $4.5 \text{ m}^2 \text{ g}^{-1}$  in the aged tailings. Some phyllosilicates such as vermiculite and smectite in topsoils may have resulted from the long-term weathering of primary mineral (such as biotite) (Murakami et al., 2003; Wilson, 1966). The concentrations of amorphous  $\text{Fe}_o$  in the aged tailings were higher than that in the fresh tailings (Figure 3), which may have resulted from the dissolution of biotite-Fe and precipitation of Fe under alkaline conditions in field-aged tailings. Besides, as revealed by XRD and Fe K edge XAFS, some more magnetite was formed, in which the  $\text{Fe}^{2+}$  can also be extracted by AAO (McKeague and Day, 1966; Parfitt and Childs, 1988). The levels of crystalline Fe ( $\text{Fe}_d$ ) (mainly Fe-oxides) extracted by citrate/bicarbonate/dithionite (CBD) (Chao and Zhou, 1983) in the aged tailings and soil were also much higher than that in the fresh tailings, suggesting the occurrence of conversion of biotite or ferrihydrites into Fe (oxy)hydroxides in the aged tailings. This was confirmed by the Fe K-edge EXAFS analysis. Coincidentally, the peaks of hematite in XRD patterns of aged tailings and topsoils were higher than those of fresh tailings. During the weathering processes in the field, Fe (oxy)hydroxides (ferrihydrite, hematite, magnetite) may form as a result of precipitation or crystallization of dissolved Fe(III)/Fe(II) ions (Murakami et al., 2003), which may explain the higher CBD-extractable Fe concentrations in the aged tailings compared with that in the fresh tailings. In contrast, the tailings contained less AAO- and CBD-extractable Al than the soils did, which may result from the lower primary mica mineral weathering or the lower total Al concentration in the tailings than the soils (tailings Al concentration was  $7 \text{ g kg}^{-1}$ , whereas soil Al concentration was  $65 \text{ g kg}^{-1}$ ). Despite these weathering events, kaolinite as the end product of Si bearing mineral weathering was not detected in the aged tailings, implying that the weathering process remained at its early phase (Braga et al., 2002; Grant, 1963; Jolicoeur et al., 2000; Rebertus et al., 1986). The higher  $\text{Fe}_o/\text{Fe}_d$  value in the tailings than that in soils may result from the lack of Fe-Al-Si bearing cements structures that reduce the mobility of Fe in both the fresh and aged tailings.

#### ***4.3 BSE/SEM-EDS analysis revealed the poor morphology and distribution pattern of Fe minerals in the tailings for stable aggregate hierarchy formation***

Organo-mineral interactions and the formation of assemblages depend on the mineralogical and geochemical characteristics of Fe-mineral particles, as well as the density and composition of functional groups of organic substances. Iron-bearing minerals vary greatly in their capacity to bind organic matter depending on their phases (specific surface area, crystallinity, charge balance) (Chen et al., 2014a; Kleber et al., 2015; Steffens et al., 2017). Compared with crystalline Fe-minerals, amorphous Fe-minerals (e.g., ferrihydrite) have a higher capacity for organic matter binding due to their high specific surface area (SSA) and abundant hydroxyl groups (Cao et al., 2011; Torn et al., 1997; Xiao et al., 2016). The surface morphology and distribution of tailings minerals are critical factors influencing organo-mineral interactions, mineral-mineral interactions and aggregation of tailing particles for soil structure development. About four years' field exposure of Fe-ore tailings facilitated the weathering of Fe bearing mica minerals and Fe-(oxy)hydroxide formation as identified by bulk chemical extraction, XRD and Fe K-edge EXAFS analysis. However, a lack of association was observed between those Fe (oxy)hydroxides with other Si/Al bearing minerals as revealed by BSE-SEM-EDS (Figure 7 and S2).

SEM examination revealed that most Fe-rich mineral particles in tailings appeared as unbound individuals exhibiting smooth surfaces and angular/sharp edges. In contrast, Fe-rich minerals in the topsoil and native soils were aggregated in clusters with rough surfaces, which was consistent with its high SSA value compared with the tailings. Iron-mineral particles in tailings exhibited a smooth surface, without eroded micro-pits, micropores and cracks for interactions with other minerals and organic groups (Lehmann et al., 2008; Vogel et al., 2014). Additionally, the affinity of Fe-minerals for organic ligands would also be lowered by alkaline conditions, as high pH favours the dominance of negative charges at the surface of the minerals for

interacting and limit the adsorption of organic acid to Fe (oxy)hydroxides through electrostatic attraction (Yuan et al., 2017). Accelerated weathering of Fe-minerals in the tailings is likely to require neutralization of pH conditions as a pre-requisite to (mineral-) organo-mineral interactions and formation of water-stable aggregates.

In addition to amorphous Fe-minerals from Fe-mineral bioweathering, organic matter is of great importance for the development of organo-mineral association and microaggregates (precursors of water-stable aggregates and soil-like physical structures) in tailings (Kleber et al., 2015; Tisdall and Oades, 1982; Yuan et al., 2016). Additionally, without organic matter various heterotrophic microbes would not colonize and evolve (You et al., 2018a). Significant building up of organic matter in tailings from the natural colonization of microbes and tolerant native plants is unlikely without substantial organic matter amendments and within a reasonable timeframe, which was demonstrated by the poor organic carbon status in the aged tailings even after four years exposure to field conditions. The extreme pH conditions and elevated salinity in the tailings would greatly constrain plant and microbial development (Rietz and Haynes, 2003), reducing the production and accumulation of organic matter. Organic inputs can activate heterotrophic microbial activity (such as microbial decomposers), which can then produce low molecular weight organic acids like acetic acid and citric acid and favor the pH decrease and primary mineral weathering. In addition, soil microbes can also produce more heterogeneous recalcitrant organic matters with high capacity for interacting with minerals (Kallenbach et al., 2016). As a result, the inputs of exogenous organic matter in the tailings would be necessary to initiate organo-mineral association and water-stable aggregation (You et al., 2018a, 2018b; Yuan et al., 2016).

#### **4.4. Potential roles of pioneer plants in accelerating mineral weathering and physico-chemical property development**

The observed weathering phenomenon (i.e., eroded surface of Fe-rich minerals; Fig. 7F) in the aged tailings collected below *M. brevifolia* plants indicated the potential of tolerant pioneer plants in accelerating bioweathering processes of Fe-rich primary minerals. It is worth noting that *M. brevifolia* has been the dominant plant species surviving in the magnetite Fe-ore tailings under field conditions. The root activities or rhizosphere microbes may have driven the bioweathering of Fe bearing minerals through their root exudates like acetate acid and citric acid (Calvaruso et al., 2006). Our previous studies (You et al., 2018a; Yuan et al., 2016) indicated that pioneer plant cultivation significantly improved physico-chemical characteristics of tailings, including stable aggregate formation. Rhizosphere interactions in tailings may not only facilitate the development of soil aggregate hierarchy and soil physico-chemical properties, but also favor microbial community development for soil ecological function construction (Zahar et al., 2008; Huang et al., 2012). Thus tolerant pioneer plants should be introduced into tailings as soon as the primary physico-chemical conditions become permissible through the initial organic and inorganic amendments, in order to enhance bioweathering and mineralogical transformation in tailings leading towards aggregation and soil structure development.

#### **5. Conclusions**

The present study has revealed key geochemical and mineralogical factors of alkaline Fe-ore tailings which would limit *in situ* soil formation for supporting native vegetation rehabilitation. These factors included highly alkaline, low organic matter content and poor physical structure, due to dominance of primary Fe-bearing mica (mainly biotite-like minerals) with low specific surface area for water stable aggregate formation. Specifically, Fe K edge XAFS, in couple with XRD and chemical extraction analyses, revealed that Fe rich minerals were undergoing



transformation during the natural aging under field conditions. The percentage of Fe rich primary mineral (biotite-like) decreased, while more hematite formed in the tailings after 4 years' aging. However, there was still less secondary Fe minerals (e.g. goethite) in the aged tailings than in natural soils, indicating that the weathering process remained at its early phase. Accelerated weathering of Fe-rich mica coupled with amorphous Fe/Si phyllosilicate formation, and the inputs of organic matter would be necessary to initiate and accelerate aggregation and soil structure formation, as natural weathering is too slow under the semi-arid climatic conditions of the trial site. The rhizosphere effects of native pioneer plants such as *M. brevifolia* may be harnessed to accelerate the weathering of Fe-rich minerals and tailings particle aggregation, which may represent an important process contributing to *in situ* soil formation in the tailings and improve rehabilitation and restoration outcomes.

### **Acknowledgement**

The authors acknowledge the Australian Microscopy & Microanalysis Research Facility at the Centre for Microscopy and Microanalysis, The University of Queensland for assistance in XRD and BSE-SEM-EDS analysis. Dr. Jyh-Fu Lee in NSRRC 17C is acknowledged for the beamtime support, and thanks to Dr Julius Motuzas in UQ for help on N<sub>2</sub>-BET analysis. The authors would also like to thank Hans Lambers for comments and suggestions on the writing. The work is financially supported by Australia Research Council (ARC) Linkage project (ARC-LP 019806) (Australian Research Council, Kara Mining Ltd, Botanic Gardens & Parks Authority), as well as ARC Industrial Transformation Training Centre for Mine Site Restoration (Project Number ICI150100041). The UQECR funding (613767) is also acknowledged.

**References:**

- Braga MAS, Paquet H, Begonha A. Weathering of granites in a temperate climate (NW Portugal): granitic saprolites and arenization. *Catena* 2002; 49: 41-56.
- Bray AW, Oelkers EH, Bonneville S, Wolff-Boenisch D, Potts NJ, Fones G, et al. The effect of pH, grain size, and organic ligands on biotite weathering rates. *Geochimica et Cosmochimica Acta* 2015; 164: 127-145.
- Bronick CJ, Lal R. Soil structure and management: a review. *Geoderma* 2007; 124: 3-22.
- Bruckard W, Smith L, Heyes G. Developments in the physiochemical separation of iron ore. *Iron Ore*. Elsevier, 2015, pp. 339-356.
- Calvaruso C, Turpault MP, Frey-Klett P. Root-associated bacteria contribute to mineral weathering and to mineral nutrition in trees: a budgeting analysis. *Applied and Environmental Microbiology* 2006; 72: 1258-66.
- Cao Y, Wei X, Cai P, Huang Q, Rong X, Liang W. Preferential adsorption of extracellular polymeric substances from bacteria on clay minerals and iron oxide. *Colloids and Surfaces B: Biointerfaces* 2011; 83: 122-127.
- Chao T, Zhou L. Extraction techniques for selective dissolution of amorphous iron oxides from soils and sediments. *Soil Science Society of America Journal* 1983; 47: 225-232.
- Chen C, Dynes JJ, Wang J, Karunakaran C, Sparks DL. Soft X-ray spectromicroscopy study of mineral-organic matter associations in pasture soil clay fractions. *Environmental Science & Technology* 2014a; 48: 6678-6686.
- Chen C, Dynes JJ, Wang J, Sparks DL. Properties of Fe-organic matter associations via coprecipitation versus adsorption. *Environmental Science & Technology* 2014b; 48: 13751-13759.
- Cornell RM, Schwertmann U. *The iron oxides*. VCH, Weinheim, Germany 1996.
- Courtney R, Harrington T. and Byrne KA. Indicators of soil formation in restored bauxite residues. *Ecological Engineering* 2013; 58: 63-68.
- Cross AT, Lambers H. Young calcareous soil chronosequences as a model for ecological restoration on alkaline mine tailings. *Sci Total Environ* 2017; 607-608: 168-175.

- Duiker SW, Rhoton FE, Torrent J, Smeck NE, Lal R. Iron (hydr) oxide crystallinity effects on soil aggregation. *Soil Science Society of America Journal* 2003; 67: 606-611.
- el Zahar Haichar F, Marol C, Berge O, Rangel-Castro JI, Prosser JI, Balesdent Jm, et al. Plant host habitat and root exudates shape soil bacterial community structure. *The ISME journal* 2008; 2: 1221.
- Eusterhues K, Rumpel C, Kögel- Knabner I. Organo- mineral associations in sandy acid forest soils: importance of specific surface area, iron oxides and micropores. *European Journal of Soil Science* 2005; 56: 753-763.
- Filippov LO, Filippova IV, Severov VV. The use of collectors mixture in the reverse cationic flotation of magnetite ore: The role of Fe-bearing silicates. *Minerals Engineering* 2010; 23: 91-98.
- Gargiulo L, Mele G, Terribile F. Effects of iron-based amendments on soil structure: a lab experiment using soil micromorphology and image analysis of pores. *Journal of Soils and Sediments* 2014; 14: 1370-1377.
- Grant WH. Chemical Weathering of Biotite-Plagioclase Gneiss. *Clays & Clay Minerals* 1963; 12: 455-463.
- Hinsinger P, Plassard C, Tang C, Jaillard B. Origins of root-mediated pH changes in the rhizosphere and their responses to environmental constraints: a review. *Plant and soil* 2003; 248: 43-59.
- Hodson ME. Does reactive surface area depend on grain size? Results from pH 3, 25 C far-from-equilibrium flow-through dissolution experiments on anorthite and biotite. *Geochimica et Cosmochimica Acta* 2006; 70: 1655-1667.
- Huang L, Baumgartl T, Mulligan D. Is rhizosphere remediation sufficient for sustainable revegetation of mine tailings? *Ann Bot* 2012; 110: 223-38.
- Huang L, Baumgartl T, Zhou L, Mulligan D. The new paradigm for phytostabilising mine wastes—ecologically engineered pedogenesis and functional root zones. *Life-of-Mine* 2014. AUSIMM, 2014, pp. 663-674.
- Jamieson HE. Geochemistry and mineralogy of solid mine waste: essential knowledge for predicting environmental impact. *Elements* 2011; 7: 381-386.

- Jolicoeur S, Ildefonse P, Bouchard M. Kaolinite and gibbsite weathering of biotite within saprolites and soils of central Virginia. *Soil Science Society of America Journal* 2000; 64: 1118-1129.
- Kallenbach CM, Frey SD, Grandy AS. Direct evidence for microbial-derived soil organic matter formation and its ecophysiological controls. *Nat Commun* 2016; 7: 13630.
- Kemper W, Rosenau R. Aggregate stability and size distribution. In Klute Ed. 'Methods of soil analysis, Part 1: Physical and mineralogical methods'. Soil Science Society of America: Madison, Wisconsin, USA 1986b, pp. 425–442.
- Kleber M, Eusterhues K, Keiluweit M, Mikutta C, Mikutta R, Nico PS. Mineral–Organic Associations: Formation, Properties, and Relevance in Soil Environments. *Adv Agron* 2015; 130: 1-140.
- Kong X, Guo Y, Xue S, Hartley W, Wu C, Ye Y and Cheng Q. Natural evolution of alkaline characteristics in bauxite residue. *Journal of Cleaner Production* 2017;143: 224-230.
- Kowalenko CG. Assessment of Leco CNS-2000 analyzer for simultaneously measuring total carbon, nitrogen, and sulphur in soil. *Communications in Soil Science and Plant Analysis* 2001; 32: 2065-2078.
- Lehmann J, Solomon D, Kinyangi J, Dathe L, Wirick S, Jacobsen C. Spatial complexity of soil organic matter forms at nanometre scales. *Nature Geoscience* 2008; 1: 238.
- Li X, Huang L. Toward a new paradigm for tailings phytostabilization—nature of the substrates, amendment options, and anthropogenic pedogenesis. *Critical Reviews in Environmental Science and Technology* 2015; 45: 813-839.
- Marschner H. Mineral nutrition of higher plants. *Folia Geobotanica & Phytotaxonomica* 1989; 24 (2): 215-217.
- McKeague J, Day J. Dithionite-and oxalate-extractable Fe and Al as aids in differentiating various classes of soils. *Canadian journal of soil science* 1966; 46: 13-22.
- Murakami T, Utsunomiya S, Yokoyama T, Kasama T. Biotite dissolution processes and mechanisms in the laboratory and in nature: Early stage weathering environment and vermiculitization. *American Mineralogist* 2003; 88: 377-386.
- Parfitt R, Childs C. Estimation of forms of Fe and Al—a review, and analysis of contrasting soils by dissolution and Mossbauer methods. *Soil Research* 1988; 26: 121-144.

- Ramanaidou E, Wells M. Sedimentary hosted iron ores. Publisher: Elsevier 2014.
- Ravel B, Newville M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *Journal of Synchrotron Radiation* 2005; 12: 537.
- Rayment GE, Lyons DJ. Soil chemical methods: Australasia. Vol 3: CSIRO publishing, 2011.
- Rebertus R, Weed S, Buol S. Transformations of biotite to kaolinite during saprolite-soil weathering. *Soil Science Society of America Journal* 1986; 50: 810-819.
- Regelink IC, Stoof CR, Rousseva S, Weng L, Lair GJ, Kram P, et al. Linkages between aggregate formation, porosity and soil chemical properties. *Geoderma* 2015; 247-248: 24-37.
- Rietz D, Haynes R. Effects of irrigation-induced salinity and sodicity on soil microbial activity. *Soil Biology and Biochemistry* 2003; 35: 845-854.
- Robson T, Golos PJ, Stevens J, Reid N. Enhancing tailings revegetation using shallow cover systems in arid environments: Hydrogeochemical, nutritional, and ecophysiological constraints. *Land Degradation & Development* 2018; 1-12.
- Schwertmann HCU, Cornell RM. Iron Oxides in the Laboratory: Preparation and Characterization. *Clay Minerals* 2000; 27: 393-393.
- Schwertmann U. Relations between iron oxides, soil color, and soil formation. *Soil Science Society of America* 1993; *Soil Color. SSSA Special Publication* (eds J.M. Bigham & E.J. Cziolkosz): 51–69.
- Steffens M, Rogge DM, Mueller CW, Höschen C, Lugmeier J, Kölbl A, et al. Identification of distinct functional microstructural domains controlling C storage in soil. *Environmental science & technology* 2017; 51: 12182-12189.
- Tisdall JM, Oades JM. Organic matter and water- stable aggregates in soils. *European Journal of Soil Science* 1982; 33: 141-163.
- Torn MS, Trumbore SE, Chadwick OA, Vitousek PM, Hendricks DM. Mineral control of soil organic carbon storage and turnover. *Nature* 1997; 389: 170-173.
- Vogel C, Mueller CW, Hoschen C, Buegger F, Heister K, Schulz S, et al. Submicron structures provide preferential spots for carbon and nitrogen sequestration in soils. *Nat Commun* 2014; 5: 2947.

- Wilson M. The weathering of biotite in some Aberdeenshire soils. *Mineralogical Magazine* 1966; 35: 1080-1093.
- Xiao J, He X, Hao J, Zhou Y, Zheng L, Ran W, et al. New strategies for submicron characterization the carbon binding of reactive minerals in long-term contrasting fertilized soils: implications for soil carbon storage. *Biogeosciences* 2016; 13: 3607-3618.
- You F, Dalal R, Huang L. Biochar and biomass organic amendments shaped different dominance of lithoautotrophs and organoheterotrophs in microbial communities colonizing neutral copper(Cu)-molybdenum(Mo)-gold(Au) tailings. *Geoderma* 2018a; 309: 100-110.
- You F, Dalal R, Huang L. Initiation of soil formation in weathered sulfidic Cu-Pb-Zn tailings under subtropical and semi-arid climatic conditions. *Chemosphere* 2018b; 204: 318-326.
- Yuan M, Xu ZP, Baumgartl T, Huang L. Organic Amendment and Plant Growth Improved Aggregation in Cu/Pb-Zn Tailings. *Soil Science Society of America Journal* 2016; 80: 27-37.
- Yuan M, Xu ZP, Nguyen T, Baumgartl T, Huang L. Interaction of Humic Acid with Cu/Pb-Zn Tailings of Different Degrees of Weathering. *Soil Science Society of America Journal* 2017; 81: 712.

**Figure captions:**

**Figure 1.** Basic chemical properties, including pH and electrical conductivity (EC), total organic carbon (TOC) and total nitrogen (TN) concentrations in fresh tailings, aged tailings, topsoils covering tailings and native soils collected from a major magnetite mining operation located approximately 400 km northeast of Perth in the Midwest region of Western Australia. Note: “FT” represents fresh tailings, “AT” represents aged tailings, “TS” represents topsoils covering the tailings, “NS” represents native soils, “B” represents bare area, “R” represents soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root affected area). Each value is the mean  $\pm$  standard deviation (SD) ( $n = 4$ ). Different letters indicate statistically significant differences ( $P < 0.05$ ).

**Figure 2.** The percentage of water-stable aggregates (WSA) (A) and mean weight diameter (MWD) (B), as well as specific surface area (N<sub>2</sub>-BET) of fresh tailings, aged tailings, topsoils covering tailings and native soils collected from a major magnetite mining operation in Western Australia. Note: “FT” represents fresh tailings, “AT” represents aged tailings, “TS” represents topsoils that covering tailings, “NS” represents native soils, “B” represents bare area, “R” represents soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root affected area). Each value is the mean  $\pm$  standard deviation (SD) ( $n = 4$ ). Different letters indicate statistically significant differences ( $P < 0.05$ ).

**Figure 3.** Acid ammonium oxalate (AAO) extractable (amorphous pool)- and citrate/bicarbonate/dithionite (CBD) (crystalline pools)- extractable Fe (A), Si (B), Al (C), Mn (D), as well as the ratio of AAO- extractable Fe to CBD- extractable Fe (E) in fresh tailings, aged tailings, topsoils covering tailings and native soils in a major magnetite mining operation in Western Australia. Note: “FT” represents fresh tailings, “AT” represents aged tailings, “TS” represents topsoils that covering tailings, “NS” represents native soils, “B” represents bare area,

“R” represents soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root affected area). Each value is the mean  $\pm$  standard deviation (SD) ( $n = 4$ ). Different letters indicate statistically significant differences ( $P < 0.05$ ).

**Figure 4.** X-ray diffraction (XRD) spectra of fresh tailings, aged tailings, topsoils covering tailings and native soil collected from a major magnetite mining operation in Western Australia.

Note: Q: Quartz; M: magnetite; H: hematite; Mi: mica, such as biotite ( $K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$ ), muscovite ( $Al_{2.908}H_{0.12}KO_{10}Si_{3.092}$ ) and Pyroxene-ideal ( $MgO_3Si$ ); K: Kaolinite-1A; Ve: Vermiculite ( $Mg_{0.7}(Mg,Fe,Al)_6(Si,Al)_8O_{20}(OH)_4 \cdot 8H_2O$ ).

Note: “FT” represent fresh tailings, “AT” represent aged tailings, “TS” represent topsoils that covering tailings, “NS” represents native soils, “B” represent bare area, “R” represent soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root affected area).

**Figure 5.** Fe K edge XANES spectra of fresh tailings, aged tailings, topsoils covering tailings and native soils in a major magnetite mining in Western Australia. A. first derivative of absorption. B, Fe K-edge XANES spectra of different samples and Fe standard compounds. In B, dotted spectra are Fe standard compounds, black one represents hematite, red one represents magnetite, blue one represents biotite, purple one represents ferrihydrite, green one represents goethite. Note: “FT” represent fresh tailings, “AT” represent aged tailings, “TS” represent topsoils that covering tailings, “NS” represents native soils, “B” represent bare area, “R” represent soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root affected area).

**Figure 6.** A.  $k$  space Fe K-edge EXAFS spectra (line) and LCF (dashed) highlight the distinct Fe-bearing phases within the fresh tailings, aged tailings, topsoils covering tailings and native soils. B. Results of the fitting Fe K-edge EXAFS spectra of the three samples from a major magnetite mining operation in Western Australia. Note: “FT” represents fresh tailings, “AT”



represents aged tailings, “TS” represents topsoils that covering tailings, “NS” represents native soils, “B” represents bare area, “R” represents soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root affected area).

**Figure 7.** Backscattered electron- scanning electron microscope (BSE-SEM) showing morphology of Fe-bearing minerals in fresh tailings (A, D), bare aged tailings (B and E), aged tailings under the canopy of *Maireana brevifolia* (C and F), bare topsoils (G and J), topsoils under the canopy of *Maireana brevifolia* (H and K), and native soils (I and L). All samples were collected from a major magnetite mining operation located approximately 400 km northeast of Perth in the Midwest region of Western Australia.

**Table 1.** Acetate extractable element concentrations in fresh tailings, aged tailings, topsoils covering tailings and native soils in a major magnetite mining operation located approximately 400 km northeast of Perth in the Midwest region of Western Australia. Note: “FT” represents fresh tailings, “AT” represents aged tailings, “TS” represents top soils that covering tailings, “NS” represents native soils, “B” represents bare area, “R” represents soil/tailing under the canopy of the pioneer plant *Maireana brevifolia* (root effected area). Each value is the mean  $\pm$  SD (n = 4). Different letters indicate statistically significant differences (one-way ANOVA followed by Duncan test,  $P < 0.05$ ).

Acetate acid extractable elements concentrations (mg kg <sup>-1</sup> )						
Name	Fe	Ca	K	Mg	Si	Al
FT	5160 $\pm$ 388a	8920 $\pm$ 1014a	6820 $\pm$ 1660a	601 $\pm$ 73.2a	1451 $\pm$ 46.7a	44.4 $\pm$ 3.26bc
AT-B	848 $\pm$ 131b	2700 $\pm$ 938b	1320 $\pm$ 1050b	354 $\pm$ 174b	346 $\pm$ 29.4cd	47.1 $\pm$ 11.3bc
AT-R	929 $\pm$ 143b	2230 $\pm$ 591bc	790 $\pm$ 132b	285 $\pm$ 71.8bc	376 $\pm$ 25.1c	56.7 $\pm$ 13.5ab
TS-B	372 $\pm$ 110c	986 $\pm$ 198d	410 $\pm$ 87.7b	166 $\pm$ 26.4c	303 $\pm$ 43.2d	46.8 $\pm$ 1.89bc
TS-R	808 $\pm$ 165b	1737 $\pm$ 363bcd	940 $\pm$ 151b	420 $\pm$ 80.3b	493 $\pm$ 51.0b	62.5 $\pm$ 11.5a
NS	21.4 $\pm$ 1.84d	1550 $\pm$ 56cd	303 $\pm$ 21.9b	397 $\pm$ 29.1b	113 $\pm$ 16.5e	37.7 $\pm$ 6.34c

**Highlights:**

- Magnetite Fe ore tailings were strongly alkaline and lack of organic carbon;
- Biotite weathering in the tailings without amendments were very slow;
- Fe oxides in the tailings lacked association with Al-/Si- minerals for aggregation;
- Natural weathering of the tailings resulted in little physicochemical improvements;
- Pioneer plants and microbes would be required to accelerate tailings weathering.

ACCEPTED MANUSCRIPT

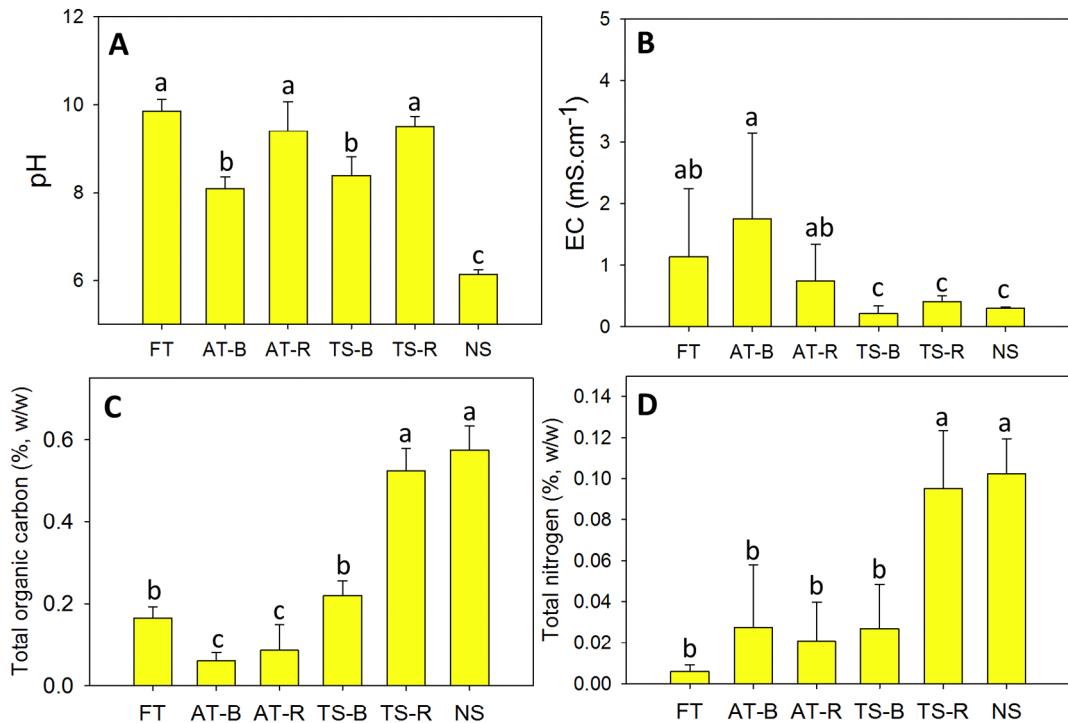


Figure 1

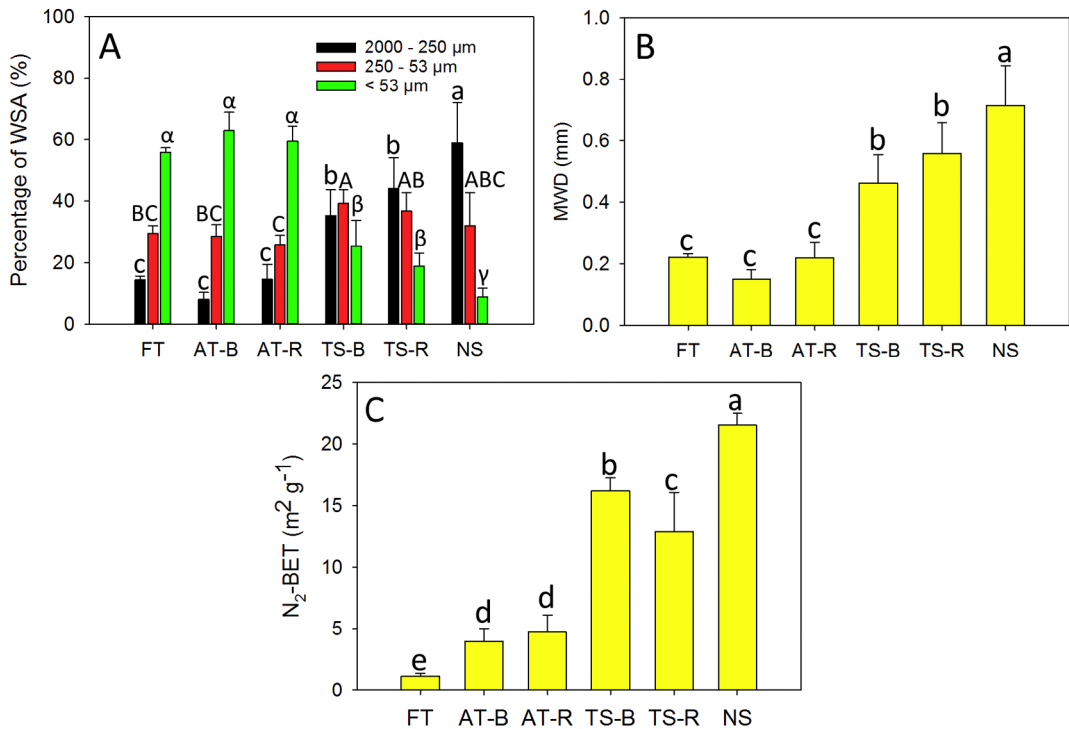


Figure 2

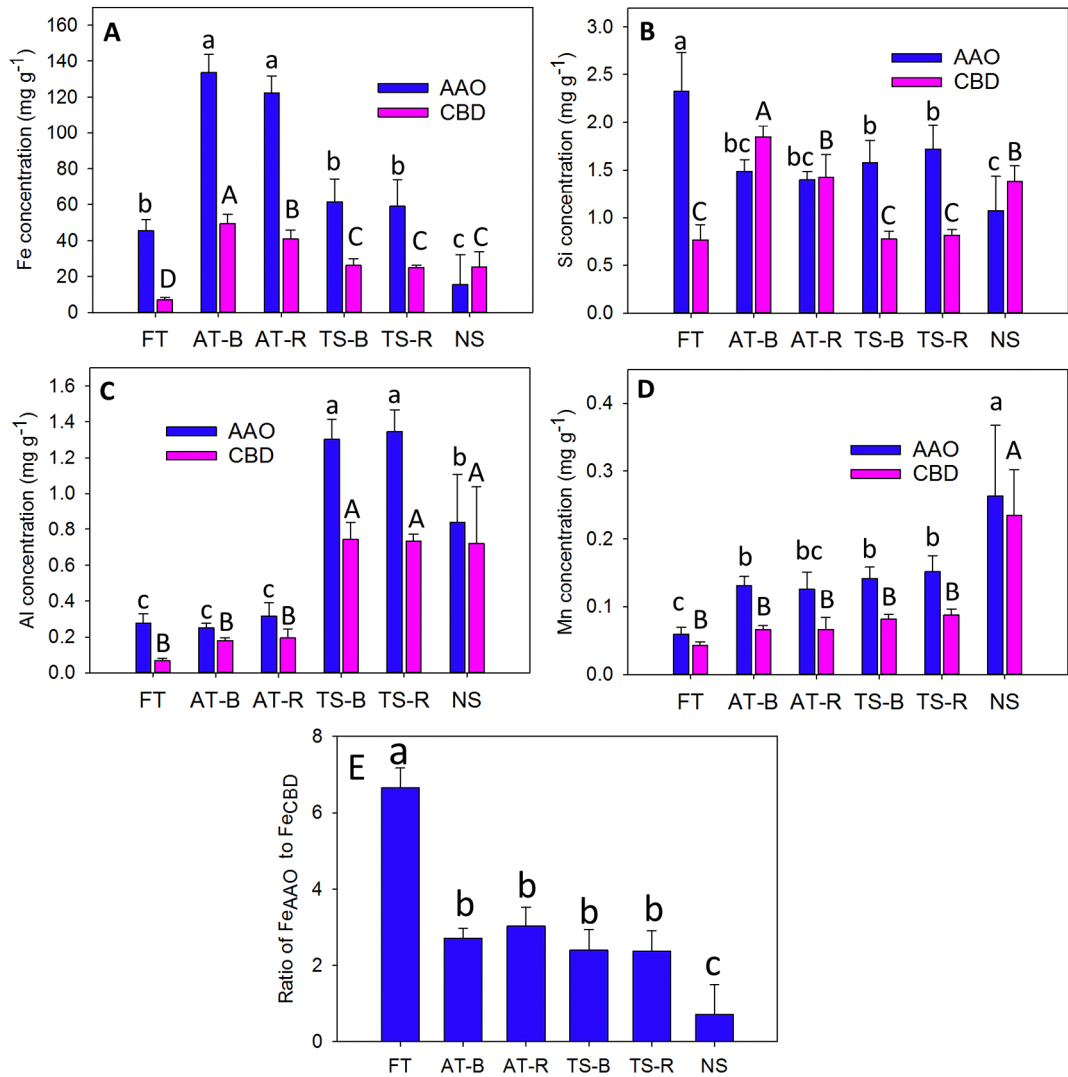


Figure 3

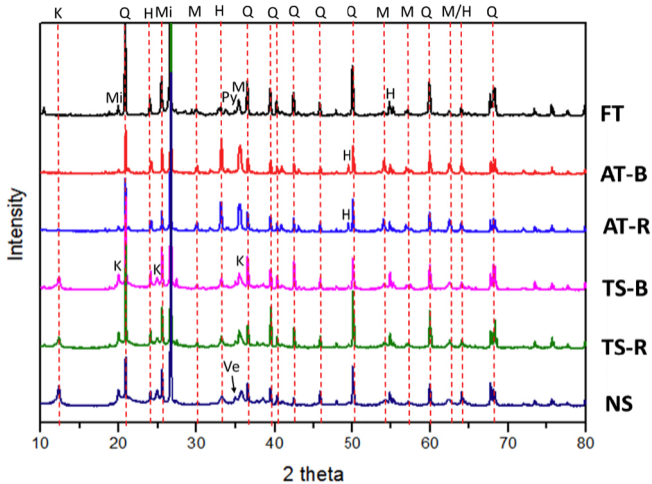
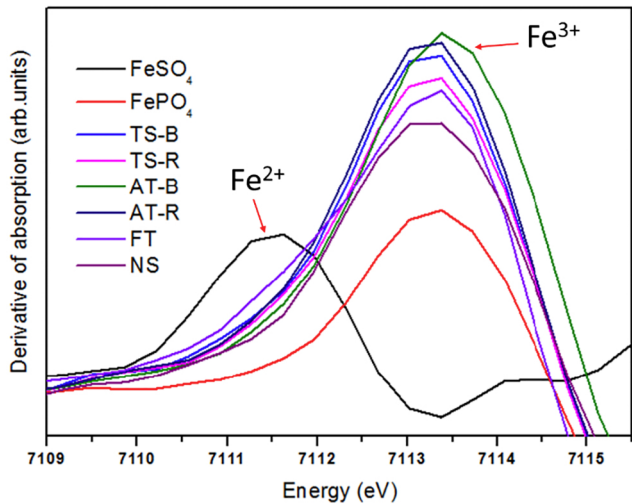


Figure 4

A



B

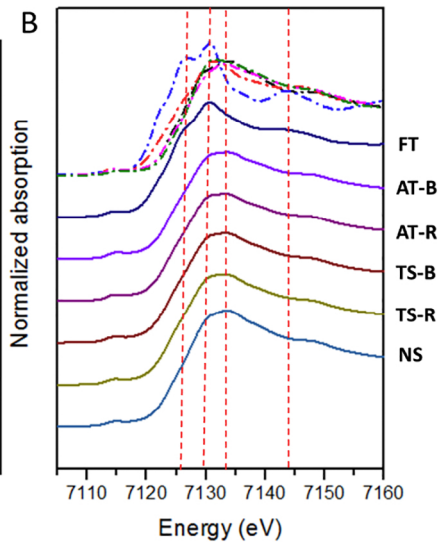


Figure 5



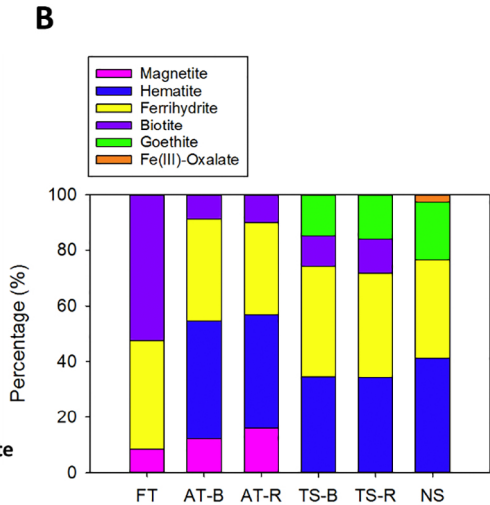
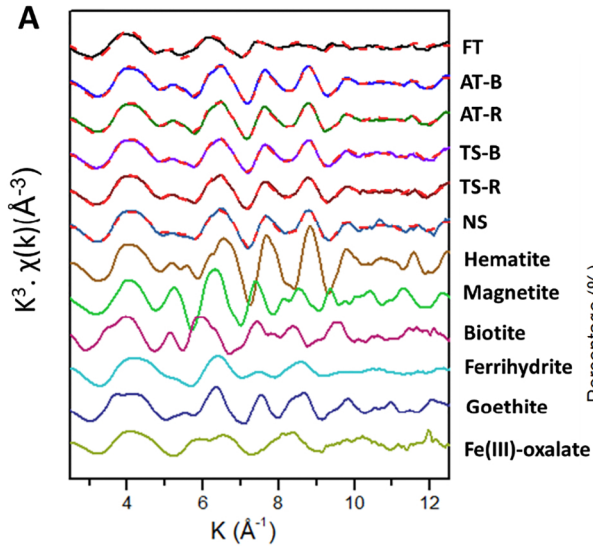


Figure 6

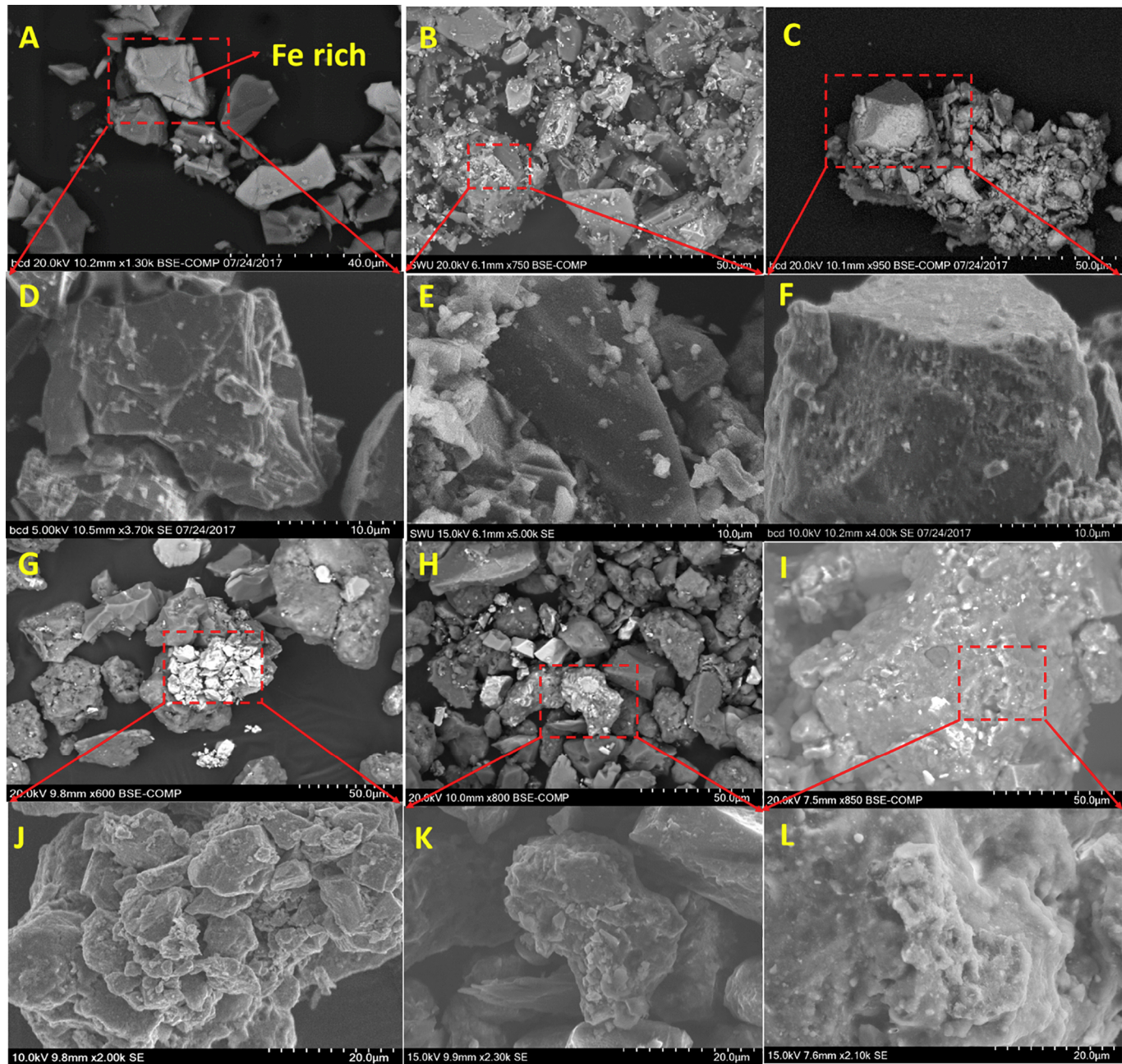


Figure 7