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

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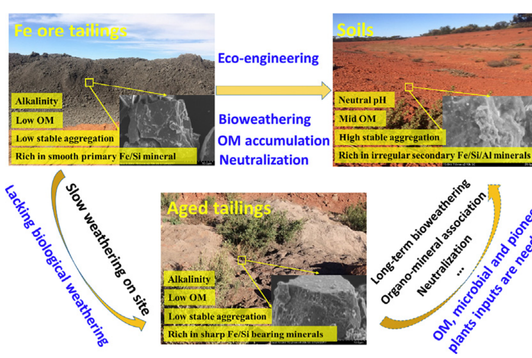
HIGHLIGHTS

- 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.

GRAPHICAL ABSTRACT



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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_2-BET around 1.2 m^2 g^{-1}). 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*

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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.

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 (100 s – 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 tailings into soil 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 characterize 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 (Fig. 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 (Fig. S1). Fresh tailings (newly deposited, <1 month) were sampled from the surface layer of tailings newly deposited in a tailings storage facility. Aged tailings (approximately four years