Rapid arsenic(V)-reduction by fire in schwertmannite-rich soil enhances arsenic mobilisation

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ABSTRACT

Arsenic in acid sulfate soil (ASS) landscapes commonly associates with schwertmannite, a poorly crystalline Fe(III) mineral. Fires in ASS landscapes can thermally transform Fe(III) minerals to more crystalline phases, such as maghemite ($\gamma\text{Fe}_2\text{O}_3$). Although thermal genesis of maghemite requires electron transfer via organic matter pyrolysis, the possibility of fire causing concurrent transfer of electrons to schwertmannite-bound As(V) remains unexplored. Here, we subject an organic-rich soil with variable carbon content (~9-44% organic C) mixed (4:1) with As(V)-bearing schwertmannite (total As of 4.7-5.4 $\mu\text{mol g}^{-1}$), to various temperatures (200-800°C) and heating durations (5-120 min). We explore the consequences for As and Fe via X-ray absorption spectroscopy, X-ray diffraction, ^{57}Fe Mössbauer spectroscopy and selective extracts. Heating transforms schwertmannite to mainly maghemite and hematite at temperatures above 300-400°C, with some transitory formation of magnetite, and electrons are readily transferred to both Fe(III) and As(V). As(V) reduction to As(III) is influenced by a combination of temperature, heating duration and carbon content and is significantly ($P < 0.05$) positively correlated with Fe(II) formation. During 2 h heating, higher carbon content favours greater As(III) and Fe(II) formation, while peak As(III) formation (~44-70%) occurs at relatively modest temperatures (300°C) and diminishes at higher temperatures. Kinetic heating experiments reveal fast maximum As(III) formation (~90%) within 5-10 min at 400-600°C, followed by partial re-oxidation to As(V) thereafter. In contrast, heating As(V)-schwertmannite in the absence of soil-organic matter did not cause reduction of As(V) or Fe(III), nor form maghemite; thus highlighting the critical role of organic matter as an electron donor. Importantly, combusted organic soil-schwertmannite mixtures display greatly enhanced mobilisation of As(III)_{aq} species within 1 h of re-wetting with water. The magnitude of As(III)_{aq} mobilisation is positively correlated with solid-phase As(III) formation. Overall, the results suggest that moderate fires in ASS landscapes, even of short duration, may generate considerable labile As(III) species and cause a pulse of As(III)_{aq} mobilisation following initial re-wetting. Further research is warranted to examine if analogous As(III) formation occurs during combustion of organic-rich soil containing common As-bearing Fe(III) minerals such as ferrihydrite and goethite.

KEYWORDS: Arsenic; XANES; Iron; Maghemite; Schwertmannite; Acid sulfate soil

1. INTRODUCTION

Heat from fires profoundly influences the evolution of iron minerals in soils (Cornell and Schwertmann, 2003; Ketterings et al., 2000; Taylor and Schwertmann, 1974). Fire-induced thermal alteration of common Fe(III)-oxyhydroxide minerals, such as goethite (αFeOOH), drives dehydroxylation and topotactic transformations that tend to increase iron oxide crystallinity (Cudennec and Lecerf, 2005; Landers et al., 2009). Depending on fire intensity (Fitzpatrick, 1988; Roman et al., 2013) and soil organic matter content (Clement et al., 2011), these transformations often lead to the formation of both hematite ($\alpha\text{Fe}_2\text{O}_3$) (Yusiharni and Gilkes, 2012) and maghemite ($\gamma\text{Fe}_2\text{O}_3$) (Löhr et al., 2017) - an Fe(III) oxide with a cubic spinel structure similar to magnetite (Cornell and Schwertmann, 2003).

A variety of Fe minerals play important roles regulating the environmental fate and behaviour of arsenic, particularly in redox-active sedimentary environments (e.g. Fendorf et al., 2010a; Johnston et al., 2015). Schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) is a poorly-crystalline, meta-stable Fe(III)-oxyhydroxysulfate mineral (Bigham et al., 1996), commonly observed in both acid mine drainage environments and the organic-rich surface sediments of acid sulfate soil (ASS) landscapes (Burton et al., 2006; Johnston et al., 2011a; Sullivan and Bush, 2004). In ASS landscapes, schwertmannite is an important host-phase for arsenic and exerts a major control on its mobility (Burton et al., 2008a; Johnston et al., 2011b).

While schwertmannite is metastable under oxic-acidic conditions, aging may slowly transform it to more thermodynamically stable goethite (Bigham et al., 1996). However, under reducing conditions, dissimilatory Fe(III) reduction may initiate rapid dissolution of schwertmannite and trigger the release of co-associated As (Burton et al., 2008a; Burton et al., 2014; Johnston et al., 2016). In addition, at circum-neutral pH, the presence of aqueous Fe(II) can trigger a rapid (hrs) Fe(II)-catalysed dissolution-precipitation reaction whereby schwertmannite transforms to goethite (Burton et al., 2008b). The propensity of schwertmannite to accumulate in surface sediments of ASS landscapes usually reflects local surface-water conditions (low pH, iron and sulfate-rich) or

upward evaporative flux of shallow groundwater that is rich in iron and sulfate (e.g. Sullivan and Bush, 2004; Burton et al., 2006; Johnston et al., 2011a; Fitzpatrick et al., 2017).

Australian ASS landscapes are prone to extreme climate fluctuations that drive large oscillations in water levels and local redox conditions (Johnston et al., 2014; Walker, 1972). Periods of low rainfall and prolonged drought conditions can lead to drying of organic-rich surface sediments in ASS landscapes, thereby promoting large wild-fires (Grogan et al., 2003; Henderson and Sullivan, 2010; White et al., 1997). Wild-fires have been documented in the field to thermally transform Fe(III) minerals within ASS surface sediments, resulting in the formation of maghemite and hematite (Grogan et al., 2003). The presence of organic matter during burning plays a crucial role in Fe mineral genesis by facilitating electron transfer to Fe(III), thereby generating Fe(II) and encouraging formation of maghemite (Cornell and Schwertmann, 2003; Grogan et al., 2003; Taylor and Schwertmann, 1974).

A recent study by Johnston et al. (2016) demonstrated that heating synthetic As(V)-bearing schwertmannite to temperatures $>400^{\circ}\text{C}$ leads to formation of nano-hematite ($\alpha\text{Fe}_2\text{O}_3$). Heating also caused As(V) that was initially structurally incorporated within the schwertmannite to become increasingly surface complexed with the neo-formed hematite. However, the study by Johnston et al. (2016) focused on a synthetic mineral system that lacked natural soil or any soil-derived organic materials. This is an important omission, as combustion of schwertmannite-rich surface soils in ASS landscapes requires the presence of sufficient organic matter.

Pyrolysis of natural organic matter can generate reducing gases, which can cause electron transfer to As(V) and lead to formation of As(III). For example, incineration of the As-hyperaccumulating plant, *Pteris vittata*, has been shown to cause some reduction of As(V) to As(III) (Yan et al., 2008). In addition, several studies have reported the formation and subsequent partial volatilization of As(III) species during combustion of chromated copper arsenate (CCA) treated wood (Helsen et al., 2003; Helsen et al., 2004). However, the likelihood of As(III) formation as a

result of fire in organic-rich soils causing transfer of electrons to schwertmannite-bound As(V) is essentially unknown and, to our knowledge, unstudied. Any formation of As(III) by fire in ASS landscapes is likely to have important implications for surface waters following eventual re-wetting of soil, as As(III) species are generally more mobile and more toxic than As(V) species in aquatic systems (Fendorf et al., 2010b; Smedley and Kinniburgh, 2002).

This study aims to explore how combustion-induced heating and pyrolysis of organic-rich soil containing As(V)-bearing schwertmannite may influence As speciation and the subsequent mobility of As in ASS landscapes subject to wild-fires. Here, we mix As(V)-coprecipitated schwertmannite with a natural surface soil from an ASS landscape and varying amounts of organic matter (*Melaleuca quinquenervia* leaf litter) and subject these mixtures to heating (in air) at a range of temperatures (200-800°C) and time periods (5-120 minutes). We quantify changes in mineralogy and Fe and As speciation via X-ray absorption spectroscopy (XAS), X-ray diffraction (XRD), ^{57}Fe Mössbauer spectroscopy and selective extracts.

2. METHODS

2.1 *Synthesis of As(V)-coprecipitated schwertmannite mixtures*

As(V)-coprecipitated schwertmannite was synthesized by dissolving 1.5 kg of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ in 50 L of water and then adding 800 mL of 30% H_2O_2 (Regenspurg et al., 2004). $\text{Na}_2\text{HAsO}_4 \cdot 7\text{H}_2\text{O}$ (~9000 mg) was dissolved in the initial solution (prior to the addition of H_2O_2) to generate an As(V) concentration in the synthetic schwertmannite of ~2000 mg kg^{-1} - well within the range reported for naturally occurring schwertmannite (Carlson et al., 2002). The resulting suspension was rinsed 5 times with deionized water and subsequently dried at 50°C. Dried material was finely ground and mineralogy verified by X-ray diffractometry (Bruker D4 Endeavor).

An organic-rich surface soil (0-10 cm depth; ~9.1% total organic carbon) was collected from a local ASS seasonal wetland [Tuckean Nature Reserve, New South Wales, Australia - described by Burton et al. (2006)]. Soil was air-dried at 40°C and sieved (500 μm) to remove coarse

particulates. Fresh leaf material was collected from *Melaleuca quinquenervia* trees in a local ASS seasonal wetland and oven-dried at 40°C for 2 weeks prior to being ground and sieved (500 µm). *Melaleuca quinquenervia* was selected as a source of organic carbon, as it is a dominant vegetation type in many coastal ASS landscapes (e.g. Johnston et al., 2003) and thus a common source of soil organic matter in these environments.

Three different soil:schwertmannite mixtures were prepared, with varying carbon contents, at ratios of 4:1:0, 3:1:1 and 1:1:3 soil:schwertmannite:leaf-material; these are hereafter referred to as low carbon, medium carbon and high carbon treatments respectively. This range of carbon contents (~9-44%) was chosen to span the likely range of organic carbon observed in combustible surface soils in coastal ASS landscapes (Johnston et al., 2005). A key purpose of using a natural organic-rich soil plus additional organic amendments, is to provide a realistic and environmentally relevant matrix. By mass, the proportion of As(V)-schwertmannite added to each of the three treatments was the same. The quantity of schwertmannite-Fe in treatments used here (~2100 µmol g⁻¹ reactive Fe) falls within ranges previously observed in near-surface (0-5 cm) soils of Fe-rich ASS landscapes (Johnston et al., 2011b; Keene et al., 2014). The near-total Fe, As and organic C contents of the initial soil:schwertmannite mixtures ranged from 2100-2300 µmol g⁻¹ Fe, 4.7-5.3 µmol g⁻¹ As and 9.1-44.2 % organic carbon.

2.2 *Heating and thermal transformation experiments*

The dried soil:schwertmannite mixtures were subject to either a) no heating (initial material) or b) thermal transformation by heating in ceramic crucibles for 2 h at 200, 300, 400, 500, 600, 700 and 800°C in a high-temperature controlled muffle furnace (MTI Corporation, KSL-1700X) in air. An additional As(V)-schwertmannite-only sample (i.e. no soil or organic carbon) was subject to thermal transformation by heating in ceramic crucibles for 2 h at 200, 400, 600, and 800°C. These temperatures were selected to bracket the likely range of temperatures associated with ground-based wildfires (Certini, 2005; Eggleton and Taylor, 2008).

In addition, the medium carbon mixture was also subject to a kinetic thermal transformation experiment, whereby ceramic crucibles were placed in a pre-heated high-temperature muffle furnace (MTI Corporation, KSL-1700X) in air at 200, 400 and 600°C for varying times (5, 10, 30, 60 and 120 min). This experiment was performed to simulate a range of exposures times to a ground-based wildfire front.

2.3 *Solid-phase extracts*

Dried solid-phase material was stored at room temperature in sealed plastic vials prior to being subject to a series of separate selective extracts. A 1:5 water extract (1 g soil: 5 mL deionized water; 1 h orbital shaker at 125 rpm, in the dark) was performed on each sample to examine aqueous As speciation. pH was measured immediately on the unfiltered water extract using a pH meter (HACH HQd) and calibrated electrode. Filtered (0.45 µm; enclosed syringe filter) aliquots of water extracts were analysed within 4-8 hrs of water extraction for aqueous As speciation by ion pairing chromatography (Wu and Sun, 2016). In brief, arsenic speciation was determined via high performance liquid chromatography (HPLC; Perkin-Elmer Flexar) coupled with inductively coupled plasma mass spectrometry (ICP-MS; Perkin Elmer Nexion 350D), using a C₁₈ (5µm) column and mobile phase of 1mM tetra-butyl ammonium hydroxide, 0.5 mM EDTA and 5% ethanol in de-ionized water (flow rate 1 mL min⁻¹; 20µL injection). Triplicate analysis on 10% of samples confirmed an analytical precision for As(III) within ±2% and for As(V) within ±6%.

An estimate of exchangeable As (As_{ex}) was determined by extraction with 1 M NaH₂PO₄, which targets weakly to strongly sorbed As (Keon et al., 2001). Near-total As (As_{tot}) and near-total Fe (Fe_{tot}) were extracted by microwave-assisted aqua regia digestion in PTFE containers (APHA, 2005). Filtered (0.45 µm; enclosed syringe filter) aliquots of these extracts were quantified by ICP-MS (Perkin-Elmer ELAN-DRCe) with repeat extraction and analysis on 10% of samples revealing an analytical precision within ±8%. Reactive Fe(II) [Fe(II)_{HCl}] was determined colourimetrically by the 1,10 phenanthroline method after extraction by 1 M HCl (Claff et al.,

2010), with total reactive Fe (Fe_{HCl}) also determined after addition of hydroxyl-amine hydrochloride. Repeat extractions and analysis of 5% of samples had analytical precision within $\pm 10\%$. Total organic carbon was quantified by a LECO Trumac CNS analyser.

2.4 *X-ray diffraction*

Samples were examined using powder X-ray diffraction (XRD; 5° – 80° 2θ with a 0.025° 2θ step-size and a 3 s count-time) with a Bruker D4 Endeavor fitted with a Co X-ray source and Lynx-Eye detector. Diffraction patterns, including determination of integral peak intensity and full width at half maximum, were analysed using the DIFFRAC-plus evaluation software package (Bruker AXS, Karlsruhe, Germany).

2.5 *X-ray absorption spectroscopy*

The oxidation state of As in solid-phase samples was quantified by X-ray absorption spectroscopy (XAS). Arsenic K-edge X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS - selected samples only) spectra were collected at the 1.9T Wiggler XAS beamline at the Australian Synchrotron, Melbourne. The X-ray energy was controlled by a Si(111) monochromator and calibrated against the first inflection point of the absorption edge of an As metal foil. Dry powder samples were sealed with Kapton tape under ambient conditions in 1 mm thick Al sample holders before being placed in a He-purged cryostat cooled to ~ 4 K where 1-4 replicate spectra were collected by a 100 element array Ge solid-state detector (CANBERRA, France) in fluorescence mode. X-ray exposure time was limited using a fast-shutter system, and multiple scans of the same sample revealed no apparent change in As oxidation state due to beam damage.

The AUTOBK algorithm in Athena was used for standard background subtraction and edge-height normalization (Ravel and Newville, 2005). Normalized XANES spectra were merged and the speciation of As in selected samples was quantitatively determined by least squares linear combination fitting (LCF) of As XANES spectra against diluted reference standards. Reference

standards used in LCF include As(V)-bearing schwertmannite, sodium arsenite, arsenite sorbed to hematite and arsenite sorbed to cellulose powder. No energy shift was included in the LCF and the sum of the fitted fractions was not constrained (LCF results are presented normalised to 100%). The proportions of As(III) fitted by the three different As(III) standards was summed to determine the total proportion of As(III). Normalized EXAFS spectra (from selected samples only) were extracted using the AUTOBK algorithm ($R_{\text{bkg}} = 0.9$; k -weight = 3; spline k -range 3–11 $\text{\AA}^{-1}$) and Fourier-transformed over the k -range 3–11 $\text{\AA}^{-1}$ using a Kaiser-Bessel window (width = 2.5).

Additionally, we assessed the stability of solid-phase As speciation in dry, thermally transformed samples by collecting additional As K-edge XANES spectra on 5 select samples at the NSRRC, Taiwan on bending magnet beamline 17C1, 11 months apart from XAS data collection at the Australian Synchrotron in Melbourne. Samples were sealed with Kapton tape in sample holders before being placed in a He-purged sample chamber at room temperature where 4-6 replicate spectra were collected in fluorescence mode. The X-ray energy was calibrated against the first inflection point of the absorption edge of $\text{Na}_2\text{HAs}^{\text{V}}\text{O}_4$ (11874 eV). Spectra were processed as described above and the speciation of As in selected samples was quantitatively determined by LCF of first derivative XANES spectra against diluted reference standards of As(V)-bearing schwertmannite and sodium arsenite.

Fe K-edge XANES spectra were collected on As(V)-schwertmannite-only samples at the NSRRC, Taiwan on bending magnet beamline 17C1. X-ray energy was calibrated against an inline Fe(0) foil. Dry powder samples were sealed with kapton tape before being placed in a sample chamber where two replicate spectra were collected at ambient temperature in fluorescence mode using an Lytle detector. The Athena program was used for standard background subtraction and edge-height normalization (Ravel and Newville, 2005). Iron speciation was assessed qualitatively by comparison of the K-edge position with known Fe(III)-bearing (schwertmannite and hematite) and Fe(II)-bearing (siderite) standards.

2.6 Mössbauer spectroscopy

^{57}Fe Mössbauer spectroscopy was used to determine the valency of Fe, as well as assist in identifying changes in mineralogy and the structural environment of Fe in solid-phase samples. Dried and powdered samples were ground to uniform size using an agate mortar and pestle, then weighed into self-supporting HDPE sample holders with a sample area of 1.76 cm^2 . Samples were prepared as to contain approximately 10 mg cm^{-2} of Fe. All spectra were collected at ambient temperature (290K to 292K) using an MR351A Mössbauer system with an MA-250 velocity transducer and the resultant data collected on a 1024 channel MCD (Fast ComTec GmbH). The velocity transducer was operated in constant-acceleration mode (set to $\pm 10\text{ mm s}^{-1}$), with a $1.85\text{ GBq }^{57}\text{Co}$ source mounted onto the transducer (Wissell Inc.). The velocity of the transducer was calibrated using an αFe foil at ambient temperature and fit to a sextet with a B_{hf} of 33.1 T . All Mössbauer parameters are reported relative to the centre of the αFe spectrum. Spectra were folded, evaluated and fitted using the MossA software program (Prescher et al., 2012). Where observed, Fe(II)/Fe(III) sub-spectra are assigned a nominal valency of 2.5 (Dyer et al., 2006; Vandenberghe and De Grave, 2013).

3. RESULTS

3.1 Solid-phase extracts

Total organic C in the initial low, medium and high carbon soil:schwertmannite mixtures was 9.1, 22.0 and 44.2% respectively (Table 1). Organic C decreased substantially as both combustion duration and temperatures increased (Table 1). Near-total As and Fe in the soil:schwertmannite mixtures was between $4.48\text{--}8.58\text{ }\mu\text{mol g}^{-1}$ and $2053\text{--}3219\text{ }\mu\text{mol g}^{-1}$ respectively in all treatments and in general, tended to increase at higher temperatures / longer combustion periods (Table 1). Increases in both As and Fe on a dry-weight basis are expected, due to a combination of dehydroxylation of schwertmannite, loss of SO_4 at temperatures above 600°C (Johnston et al., 2016) and substantial mass loss of organic carbon that occurs during the combustion process. The relative behaviour of As and Fe, as indicated by the ratio of As_{Tot} to Fe_{Tot} , indicates minimal loss of

As relative to Fe in response to increasing combustion temperature (Table 1).

Total reactive Fe (Fe_{HCl}) in soil:schwertmannite mixtures diminished as combustion temperatures and combustion duration increased (data not shown), reflecting changes in mineralogy and increasing crystallinity. However, the $\text{Fe(II)}_{\text{HCl}}$ fraction increased markedly initially, rising to attain maxima of $\sim 600 \mu\text{mol g}^{-1}$ around $300\text{--}400^\circ\text{C}$ in the 2 hr combustion series before decreasing at higher temperatures (Fig. 1). In the kinetic experiments at 400 and 600°C , the $\text{Fe(II)}_{\text{HCl}}$ fraction attained maxima of $\sim 1300\text{--}1500 \mu\text{mol g}^{-1}$ ($\sim 50\text{--}57\%$ of total Fe) within the first $\sim 5\text{--}30$ minutes, prior to decreasing markedly at longer combustion times (Fig. 1).

Initial soil:schwertmannite mixtures had very low As_{ex} ($\sim 0.03 \mu\text{mol g}^{-1}$), which indicates that As was not readily desorbed, despite exposure to a relatively concentrated phosphate-based extractant ($1 \text{ M NaH}_2\text{PO}_4$). Hence, most As was likely initially incorporated within the schwertmannite, possibly exchanging for SO_4 in the tunnel structure (e.g. Burton et al., 2009; Fukushi et al., 2004), and thus largely unable to participate in surface exchange reactions. The As_{ex} fraction increased substantially upon heating above 400°C , achieving a maxima of $5.51 \mu\text{mol g}^{-1}$ at 800°C , consistent with observations described by Johnston et al. (2016). The pH of most water-extracts was between 3 and 5 (Table 1), although some high-carbon treatments and several medium-carbon, short-combustion duration treatments (600°C) had pH values above 6. Water-extract pH values were not significantly ($r^2 = 0.14$; $P > 0.1$) correlated with loss of carbon on combustion (Fig. SI1).

3.2 As speciation

The LCF results from solid-phase As K-edge XANES are presented in Fig. 1a,b while spectra are depicted in Fig. 2 (for fit results see Table SI1). Initially, all As was present as As(V), with no detectable contribution from As(III). Heating a schwertmannite-only sample that lacked any soil or organic matter did not lead to any reduction of As(V) (Fig. SI2). In the 2 hr combustion series experiments, As(III) attained maxima of $\sim 40\%$ (low carbon treatments) and $\sim 70\%$ (medium and high carbon treatments) of total As at 300°C , before declining at higher temperatures (Fig. 1a and

2a, b, c).

In the 400 and 600°C treatments from the kinetic experiments, As(III) rapidly attained maxima of ~90% of total As within 10 minutes, before declining substantially at longer combustion durations (Fig. 1b and 2d, e, f). In contrast, in the 200°C treatment, As(III) slowly increased in response to increasing combustion duration, but attained a maxima of only 24% by 2 h, in conjunction with a relatively minor overall loss of organic C (~2%; Table 1).

Closer inspection of the As K-edge XANES spectra for the sample from 10 min in the 600°C kinetic experiment, reveals a shoulder on the As K-edge at a slightly lower energy position than any of the As(III) standards (Fig. 2f). The Fourier transformed As-EXAFS spectra for samples from the 600°C kinetic experiment reveals that in addition to a backscattering peak consistent with first-shell As-O coordination, the 10 min sample indicates (transitory) formation of a backscattering peak that is consistent with a first-shell sulfur-coordinated As species (Fig. SI3).

The proportion of As(III) formed in soil:schwertmannite treatments during heating remained relatively stable when preserved as dry powders. This is demonstrated by repeat analysis of 5 select samples at different synchrotrons 11 months apart ($r^2 = 0.98$, $y = 1.07$; Fig. SI4).

3.3 Fe speciation and mineralogy

The parameters from fitting of Mössbauer spectra (292 K) are summarised in the Supplementary Information section, Tables SI2-5, while selected Mössbauer spectra with associated fit components are shown in Fig. 3 and 4 (see Fig. SI5-7 for remaining fitted spectra). The initial (unheated) samples are characterized by two distinct asymmetric Fe(III) doublets, with isomer shift (δ_{Fe} ~0.33-0.38) and quadrupole splitting (Δ ~0.53-0.79) values that are broadly consistent with schwertmannite (e.g. Bigham et al., 1990; Murad and Cashion, 2004).

As heating temperature increased above 300°C, Mössbauer spectra display progressive evolution of Fe(III) sextets, indicating increasing magnetic ordering that is consistent with the spectral

behaviour of maghemite and hematite at 292 K. Sextets are initially broad and composed of overlapping sub-spectra. Samples with the most complex sub-spectra fits are typically those subject to intermediate combustion temperatures (i.e. between 300-600°C; Fig. 3 and 4, Table SI2-5; Fig. SI5-7). Above 600°C, sextet broadening diminishes markedly and doublets account for a decreasing proportion of the total spectral area. The sum of the magnetically ordered phases present in fitted Mössbauer spectra can be used to approximate the sum of maghemite and hematite in the samples. This indicates that maghemite and hematite abundance generally increases with increasing temperature and combustion time, accounting for between 55-87% in samples heated to 700-800°C (Table SI2-4).

Fe(II) doublet sub-spectra ($\delta_{\text{Fe}} = \sim 0.8\text{-}1.2$; $\Delta = \sim 2.0\text{-}3.2$) are clearly evident in samples subject to combustion temperatures $\geq 300^\circ\text{C}$ (Fig. 3, 4; Tables SI2-5; Fig. SI5-7). In addition, several samples (i.e. 600°C - 5, 10 and 30 min combustion time) display distinctive Mössbauer sextet sub-spectra that are consistent with magnetite (Fig. 4). For example, magnetic hyperfine field (B_{hf}) and isomer shift (δ_{Fe}) parameters ($\sim 44.6\text{-}45.2$ T and $\sim 0.60\text{-}0.64$ mm s⁻¹ respectively; Table SI5) for sub-spectra [Fe(II)/(III)-s2] for 600°C at 5, 10 and 30 min, accord with those expected for octahedrally coordinated Fe(II)/Fe(III) in magnetite at 292K (e.g. Vandenberghe and De Grave, 2013). These values are also consistent with parameters derived (from our instrumentation) for octahedrally coordinated Fe(II)/Fe(III) in a magnetite standard ($B_{\text{hf}} = 45.6$ T; $\delta_{\text{Fe}} = 0.61$ mm s⁻¹; Fig. SI8).

The proportion of Fe(II) determined via ⁵⁷Mössbauer spectroscopy (Fig. 5) displays similar overall trends to those based on the Fe(II)_{HCl} extraction (Fig. 1). While absolute values are highly correlated and agree well, Fe(II)_{HCl} is slightly higher than ⁵⁷Mössbauer Fe(II) ($y = 1.08 x$; $r^2 = 0.80$; where $y = \text{Fe(II)}_{\text{HCl}}$; Fig. SI9). The proportion of solid-phase As(III) formed during combustion is significantly ($P < 0.05$) positively correlated with both Fe(II)_{HCl} ($r^2 = 0.67$) and Mössbauer derived ⁵⁷Fe(II) ($r^2 = 0.73$) (Fig. 6). However, the relationship is non-linear and suggests that As(V) was reduced (in proportional terms) somewhat preferentially to Fe(III).

For heated schwertmannite-only treatments, Fe K-edge XANES spectra display stable K-edge energy positions consistent with Fe(III) and there is no indication of any Fe(II) formation (Fig. SI10).

The overall results from XRD are consistent with fits to the Mössbauer spectra. They clearly indicate that both maghemite and hematite became increasingly dominant Fe mineral phases as heating temperatures increased above 400°C (see Supplementary Information, Fig. SI11 and SI12). Despite the similar unit cell structure of maghemite and magnetite leading to closely overlapping X-ray diffraction peaks, some minor separation of peaks appears at higher diffraction angles (e.g. da Costa et al., 1995). Close inspection of X-ray diffraction data (for 61-78° 2 θ) from the 600°C, 10 min combustion time sample, indicates (similar to Mössbauer spectra) that magnetite formed temporarily and was subsequently replaced by maghemite and hematite by 2 hr combustion (Fig. 7).

Qualitative analysis of normalized XRD peak intensity ratios indicate that maximum maghemite-Fe was observed around 600°C (Fig. 8a), whereas hematite-Fe became more prevalent at the highest temperatures (Fig. 8b). Maghemite and hematite diffraction peaks progressively sharpened (as measured by full width at half maximum) as temperatures increased, suggesting development of increasing crystallinity and long-range order (Fig. SI13). In the schwertmannite-only sample, schwertmannite transformed to hematite-only as temperatures increased, with no evidence of any maghemite formation (Fig. SI14).

3.4 *As mobility and speciation in water extracts*

The mobilisation of As(III) and As(V) species in 1:5 water extracts of soil:schwertmannite treatments are displayed in Fig. 9. Mobilisation of As in unheated treatments was very low (<0.3 $\mu\text{mol kg}^{-1}$). However, As mobilisation in water increased by ~3 orders of magnitude as combustion temperatures increased, reaching ~20-25 $\mu\text{mol kg}^{-1}$ in some treatments (Fig. 9a, b, e, f). In all combusted treatments >80% of the As mobilised was inorganic As(III)_{aq} species, with a notable

exception of samples heated to 800°C, in which As(V)_{aq} became more abundant (Fig. 9). In the 2 hr combustion series experiments, As(III)_{aq} attained maxima in the 300-400°C treatments. In the kinetic experiments, As(III)_{aq} mobilisation generally increased with combustion time, although more complex behaviour was evident in the 400°C treatment.

The concentration of water soluble As(III)_{aq} in the 2 hr combustion series experiments were significantly positively correlated ($r^2 = 0.61$; $P < 0.05$) with solid-phase As(III) determined by As K-edge XANES (Fig. 10a). However, the positive correlation was not significant ($r^2 = 0.27$) in the kinetic experiments (Fig. 10b). As(III)_{aq} mobilisation was not correlated with the pH of water extracts (Fig. SI15).

4. DISCUSSION

4.1 *Temperature, carbon and time-dependent generation of As(III) and Fe(II)*

To our knowledge, this is the first study to demonstrate that schwertmannite-bound As(V) can be reduced to As(III) during heating and combustion in the presence of soil and natural organic matter. Importantly, As(III) formation can occur quickly and at relatively moderate temperatures (i.e. ~90% As(III) in 10 min at 400°C). A considerable proportion Fe(III) was also reduced to Fe(II), albeit more temporarily, during the combustion process. The thermal and temporal patterns of Fe(III) and As(V) reduction were broadly similar and electron transfer to As(V) and Fe(III) was significantly ($P < 0.05$; Fig. 6) positively correlated.

The quantity of organic matter in the soil:schwertmannite mixtures was clearly a crucial factor in transferring electrons to both As(V) and Fe(III), as evident by a) the greater proportion of As(III) and Fe(II) formation in the medium and high carbon treatments (compared to low organic carbon) and b) the absence of As(III) and Fe(II) in the schwertmannite-only treatments.

Formation of As(III) and Fe(II) can be readily explained by interaction of As(V) / Fe(III) with reducing compounds originating from organic matter degradation during pyrolysis. Heating induced pyrolysis of organic matter breaks covalent bonds in cellulose, hemicellulose and lignin,

thereby generating various low molecular weight products (Evans and Milne, 1987) and radicals with unpaired valence electrons, as well as a range of reduced gaseous compounds including H_2 , CH_4 , CO and H_2S (Liu et al., 2017). At temperatures above $\sim 300^\circ C$, CO and H_2 rich atmospheres are well known to readily transfer electrons to Fe(III)-oxides (e.g. Jozwiak et al., 2007). In addition, reduced species generated by heating labile organic matter have previously been shown to promote electron transfer to inorganic As(V), as demonstrated by Helsen et al. (2004), who found thermal decomposition of glucose enhanced reduction of As(V) (as As_2O_5) to As(III).

The findings presented here also have parallels with combustion of both *Pteris vittata* (Yan et al., 2008) and CCA treated wood (Wasson et al., 2005), wherein pyrolysis has been demonstrated to drive partial reduction of As(V) to As(III) and cause some volatilization of As(III), particularly at temperatures $>400^\circ C$ (Cuyper and Helsen, 2011; Helsen et al., 2003). Our findings also have a precedence with transition metals other than Fe. For example, it has been demonstrated that both Cu (Liu et al., 2012) and Ni (Richardson et al., 2010) can be reduced to zerovalent species as a result of electron transfer during pyrolysis of organic matter at temperatures $\leq 500^\circ C$.

An important finding of this study is that moderate combustion temperatures (~ 300 - $400^\circ C$) formed the most As(III). The $200^\circ C$ treatment was clearly insufficient for either fast or substantial reduction of As(V) (i.e. As(III) maxima of only 36% was achieved after 2 h in the high carbon treatment at $200^\circ C$). In contrast, temperatures of ~ 300 - $400^\circ C$ appear to represent an important threshold at which electron transfer to As(V) [and Fe(III)] was much more pronounced and rapid. This observation is broadly consistent with the fact that thermal decomposition of cellulose, and thus substantive generation of reducing gases, typically requires temperatures greater than ~ 280 - $300^\circ C$ (Evans and Milne, 1987).

In contrast, at higher temperatures (~ 700 - $800^\circ C$) and 2h combustion, As(III) formation remained low ($<20\%$), in conjunction with comparatively lower $Fe(II)_{HCl}$ and lower ^{57}Fe Mössbauer-derived $Fe(II)$ ($<15\%$). This suggests that neo-formed As(III) and $Fe(II)$ species were partially oxidised by

the combination of higher temperatures and longer duration of heating. The suggestion that a longer duration of heating may lead to partial re-oxidation of neo-formed As(III) and Fe(II) is confirmed by the kinetic experiments themselves. For example, the fast (<10 min) initial formation of As(III) (~90%) and Fe(II) (>40%) at 400 and 600°C was followed by substantial decreases in both species at progressively longer combustion intervals (Fig. 1). Such behaviour is consistent with the fact that heating in this study was conducted in air - thus any initial pulse of reducing gases generated during degradation of organic compounds is likely to have been followed by their eventual exhaustion and the re-establishment of an oxidizing atmosphere at longer heating durations.

Alternatively, the decreases in As(III) at longer heating duration could be partly explained by some volatilization of As(III) at temperatures >400°C, thus leading to an increase in the relative proportion of residual As(V) species. Some mass loss of total As due to volatilization of As(III) has been previously observed during thermal treatment of As₂O₃ adsorbed on activated carbon (Cuypers et al., 2009), and has also been demonstrated during combustion of CCA treated wood (Helsen et al., 2003). A maximum estimate of As(III) volatilization that may have occurred during heating in the experiments reported here can be derived by a) assuming there is no mass loss of Fe during the heating process and b) comparing changes in the ratios of near-total As to near-total Fe in the treatments, relative to corresponding ratios in the initial un-heated samples. This analysis suggests the maximum possible loss of near-total As via volatilization (compared to initial unheated material) is ~12%. This is insufficient to explain the 30-40% decrease in As(III) observed at later time intervals in the 400-600°C kinetic experiments, thus confirming that partial re-oxidation of neo-formed As(III) at longer heating intervals was an important process in these experiments.

Heating organic-rich samples in air can create a highly dynamic, localised and transient chemical environment (e.g. Liu et al., 2017). This is effectively illustrated by the fact that one sample from the 600°C kinetic experiment (10 min) displayed XAS spectra consistent with formation of a

transitory sulfur-coordinated As species. The Fourier transform of As K-edge EXAFS spectra for selected samples from the 600°C heating duration series (Fig. SI3) are dominated by a primary backscattering contribution consistent with first-shell As(V)-O or As(III)-O (e.g. Maillot et al., 2013), in addition to a lower amplitude backscattering contribution that is consistent with second-shell As-Fe (e.g. Morin et al., 2008; Ona-Nguema et al., 2005). However, the 600°C - 10 min sample also displays an additional backscattering contribution that is consistent with what would be expected for first-shell As-S coordination (e.g. Johnston et al., 2012; Langner et al., 2012; Root et al., 2009). H₂S can be generated during pyrolysis of biomass at temperatures >600 °C due to decomposition of organic sulfur compounds and this can lead to accumulation of inorganic sulfides in char residue (Knudsen et al., 2004; Liu et al., 2017). Hence, the occurrence of a transitory first-shell As-S coordination (as suggested by this data) may reflect the formation (and subsequent degradation) of a transitory As-sulfide species formed via reaction between As and H₂S. However, further investigation is required to resolve this.

4.2 *Iron mineral transformation*

The progressive transformation of schwertmannite to maghemite, followed by hematite at higher temperatures, broadly accords with prior studies (e.g. Cornell and Schwertmann, 2003; Mazzetti and Thistlethwaite, 2002). It is also consistent with several investigations demonstrating the formation of maghemite via burning of organic-rich, goethite-bearing soils (Grogan et al., 2003; Ketterings et al., 2000). Qualitative analysis of XRD data suggests that maximum abundance of maghemite occurred at ~600°C, prior to diminishing substantially by 800°C, at which point hematite became the dominant Fe mineral. This is broadly consistent with the observations of Siddhu (1988), which show that maghemite steadily transforms to hematite at temperatures above 320°C, but the transformation kinetics are relatively slow until temperatures exceed 500°C. The absence of maghemite in the schwertmannite-only treatments concurs with prior studies that conclude organic matter is an essential component for thermal genesis of maghemite in soils (Cornell and Schwertmann, 2003; Taylor and Schwertmann, 1974).

X-ray diffractograms indicate that maghemite and hematite were the dominant (crystalline) Fe-mineral phases that formed during heating at temperatures $\geq 300^{\circ}\text{C}$. The evolution of Mössbauer spectra are broadly consistent with results from XRD. Maghemite and hematite are the dominant Fe minerals in this system that display sextets at room temperature as a result of magnetic hyperfine splitting (Cornell and Schwertmann, 2003; Murad and Cashion, 2004). Sextet parameters (i.e. hyperfine fields mostly ~ 50 T and low to negative quadrupole splitting) are consistent with a mixture of maghemite and hematite, while the diversity of fitting parameters and sub-spectra observed may reflect a range of particle size characteristics (Dyar et al., 2006; Murad and Cashion, 2004; Vandenberghe et al., 2000).

Mössbauer data also indicate that up to $\sim 40\%$ of Fe was transformed (temporarily) to Fe(II) species, yet the precise mineralogical form of this Fe(II) is less clear. Although Mössbauer and X-ray diffraction data both provide evidence consistent with the transitory formation of magnetite, this observation only applies to a few samples (Fig. 4 and 7; Table SI5). While somewhat unexpected, the formation of magnetite accords with a field-based study of Longworth et al. (1979), who provided evidence supporting a fire-based pathway of magnetite genesis in organic-rich natural soil. Magnetite also readily oxidizes and transforms to maghemite during heating in air (da Costa et al., 1995), which is consistent with the transitory occurrence of magnetite reported here and its subsequent disappearance at longer heating intervals. Accurately quantifying the amount of magnetite in this system via Mössbauer is not possible because Mössbauer cannot distinguish between the tetrahedrally coordinated Fe(III) of magnetite and maghemite, thus rendering it unable to distinguish between non-stoichiometric magnetite and magnetite-maghemite mixtures (da Costa et al., 1998; Vandenberghe et al., 2000). Aside from some transitory magnetite, available data are insufficient to support a definitive conclusion regarding the possible formation of other discrete Fe(II) mineral phase(s). It is possible that Fe(II) species were very poorly crystalline nano-particles, complexed with organic compounds, or sorbed to ash / char and Fe(III) mineral surfaces. The precise form(s) of Fe(II) requires further investigation.

There was generally good agreement between the estimates of Fe(II) concentrations based on 1M HCl extracts and ^{57}Fe Mössbauer spectra and the combined use of these two approaches strengthens the overall conclusions regarding heating-induced changes in Fe valency. However, discrepancies between the two approaches, particularly at lower concentrations of Fe(II) (<5% of total Fe), may reflect the combined, yet contrasting limitations of both techniques. For example, while concentrations of Fe(II) appear slightly higher in 1 M HCl extracts (based on the overall slope of the regression; Fig. SI9), at low pH Fe(III) can be chemically reduced during extraction by interactions with phenolic functional groups (Deiana et al., 1995). *Melaleuca quinquenervia* leaf material contains abundant phenolic compounds (Moharram et al., 2003). Hence, 1 M HCl extracts in these phenolic-rich samples may result in chemical reduction of Fe(III) and thus cause an over-estimate of Fe(II). In addition, although Mössbauer is free from reductive or oxidative interferences associated with chemical extraction techniques (Dyar et al., 2006), quantitative interpretation of complex spectra containing multiple, overlapping, broad-peaks (such as occurred here at intermediate temperatures), may be hampered by statistically equivalent, non-unique fits (Vandenbergh et al., 2000).

4.4 *Enhanced mobilisation of As(III) on re-wetting*

The changes in solid-phase As speciation greatly enhanced (i.e. ~three orders of magnitude) the solubility of inorganic As(III) species in water. Enhanced mobility of As in water likely reflects the increasing surface complexation of As (as estimated by As_{ex} ; Table 1) that occurred during thermally-induced mineral transformation, in conjunction with increasing abundance of As(III) itself. As(III) species are often more mobile in groundwater / surface water systems (Burton et al., 2008a; Diwakar et al., 2015; Fendorf et al., 2010a; Takahashi et al., 2004). Although both As(V) and As(III) species adsorb effectively to various Fe-(hydr)oxides (Bolan et al., 2013; Burton et al., 2009; Dixit and Hering, 2003) and may form inner-sphere complexes with maghemite (Morin et al., 2008), As(III) species are generally more prone to desorption (Fendorf et al., 2010b; Herbel and Fendorf, 2006).

Although $\text{As(III)}_{\text{aq}}$ was positively correlated with solid-phase As(III) determined by XANES, the behaviour of $\text{As(III)}_{\text{aq}}$ was complex and non-linear with respect to temperature and heating duration. This complexity may reflect varying degrees and modes of As species incorporation / retention in char residue (Vithanage et al., 2017), in combination with competing interactions between solid-phase As(III) formation (maximum at $\sim 300\text{--}400^\circ\text{C}$ and shorter heating durations) and As_{Ex} formation (maximum at $700\text{--}800^\circ\text{C}$ and longer heating durations). Recent work also suggests that biochars formed by organic matter pyrolysis between $400\text{--}600^\circ\text{C}$ may mediate abiotic electron transfer far more effectively than previously thought (Prévost et al., 2016). Hence, it is conceivable that $\text{As(III)}_{\text{aq}}$ formation may also have been influenced by some electron transfer from the biochar residues during the 1 h water extraction process.

For the 800°C treatment, the mobilisation of proportionally more As(V) in water closely reflects the observed changes in solid-phase As speciation. Although the pH of water extracts generally increased with increasing loss of carbon and is likely connected with ash production (Certini, 2005), pH itself had no discernible systematic ($P > 0.1$) influence on mobilisation of $\text{As(III)}_{\text{aq}}$ in these samples (Fig. SI15).

These observations have important implications for seasonal, fire-prone ASS landscapes. They indicate that *fire alone* in an organic-rich soil containing As(V) -schwertmannite, may be sufficient to enhance As(III) mobilisation into surface waters upon initial rainfall or surface re-flooding. Importantly, As may be mobilised *prior* to the onset of Fe(III) -reducing conditions that are more generally regarded as a typical trigger for As mobilisation in such systems (Burton et al., 2008a; Burton et al., 2011; Burton et al., 2014; Johnston et al., 2010).

4.5 Environmental implications and further research

This study demonstrates that heating and combustion of organic-rich soil containing As(V) -bearing schwertmannite can cause electron transfer from organic material to both As(V) and Fe(III) , thereby forming considerable As(III) and Fe(II) . This in turn triggered enhanced As(III)

mobility in water immediately upon re-wetting of soil. Consequently, in iron- and arsenic-rich ASS landscapes, surface water quality may be negatively impacted following rainfall after wildfire. The temperatures and time-frames required for As(III) formation are relatively modest (90% As(III) in 10 min at $\sim 400^{\circ}\text{C}$), and are likely to occur in topsoil during many wildfires (Blake et al., 2012; Certini, 2005). However, a converse finding is that hotter fires, or those with a longer duration of burning, may partially re-oxidise As(III) to As(V), thereby partly mitigating subsequent impacts on water quality. Our findings have heightened relevance given predictions of increasing wildfire risk in much of Australia due to future climate change (Clarke et al., 2016).

It is possible, perhaps even likely, that there are differences in pyrolysis products (and thus experimental outcomes) resulting from heating samples in a temperature controlled oven when compared to natural combustion of organic-rich soil during a wildfire. In addition, during a natural fire, considerable vertical gradients in soil temperature (and O_2) are likely to develop at a centimeter scale (Certini, 2005). Hence, while this study demonstrates the potential for rapid As(III) formation, there is a need to verify these observations in a field setting. In particular, further work is required to assess the magnitude of the likely effects on surface water quality in the context of other environmental variables (i.e. fire intensity / duration, depth of heat penetration, As content, natural schwertmannite content).

Other common Fe-(hydr)oxide minerals, including ferrihydrite and goethite, are also known to be effective host-phases for As(V) and As(III) species (Ona-Nguema et al., 2005; Sherman and Randall, 2003; Waychunas et al., 1995). An obvious topic for further research is to explore whether heating As(V)-bearing ferrihydrite or goethite in an organic-rich soil matrix leads to similar effects as described here. If this is demonstrated to be the case, then the environmental relevance of the processes and findings described here may extend to a much broader range of environments than ASS landscapes.

There is an additional, although openly speculative, potential environmental implication that is

worthy of consideration. Arsenic in groundwater is a major human health issue (Smedley and Kinniburgh, 2002), particularly in some important rice growing regions of the world (Islam et al., 2016). Rice straw and stubble is often burnt in many rice growing regions, with an estimated 13.9 Tg of rice straw subject to open field burning in India alone (Gadde et al., 2009). Rice plants and rice straw also contain As, especially when irrigated with As-bearing groundwater (Dittmar et al., 2010; Islam et al., 2016; Seyfferth et al., 2014). Fe(III) minerals such as goethite and ferrihydrite commonly play a critical role in hosting As in rice paddy soils, both in soil aggregates and as plaques around shallow rice roots (Frommer et al., 2011; Seyfferth et al., 2010). The formation of more mobile $\text{As(III)}_{(\text{aq})}$ species and reduction of As-bearing Fe-oxides in soil during rice-paddy flooding are regarded as critical pathways for As mobilisation in surface waters (Roberts et al., 2010) and promote uptake of As by rice (Wang et al., 2015).

The findings of this study raise an intriguing question, i.e. *"Can burning of rice stubble also promote the formation of As(III) species by thermally altering As-bearing Fe(III)(hydr)oxide minerals in near-surface soil?"*. If so, then burning rice stubble may represent another, as yet unexplored, pathway influencing As behavior / cycling and contribute to As mobility in rice-based agricultural systems. Although high temperatures induced by rice stubble/straw fires are unlikely to last long, nor penetrate very far into the underlying soil (Bento-Gonçalves et al., 2012), generation of any additional As(III) may have cumulative effects, especially given that stubble and straw burning occurs annually. Given the human health significance of arsenic contamination of groundwater in some rice growing regions (Smedley and Kinniburgh, 2002), the potential for such an effect is worthy of investigation.

5. CONCLUSIONS

This study demonstrates that heating As(V)-schwertmannite in an organic-rich soil matrix, as may occur during a wildfire, can generate substantial As(III) and greatly increase As(III) mobility immediately on re-wetting. The fact that maximum As(III) was generated at relatively modest temperatures ($\sim 300\text{--}400^\circ\text{C}$) and short heating times (10 min), has implications for As cycling and

water quality in fire-prone ASS landscapes - although the observations reported here would greatly benefit from additional support via field-based verification. Further research is warranted to examine whether similar processes may occur with other common Fe (hydr)oxide minerals (i.e. ferrihydrite and goethite).

APPENDIX A. SUPPLEMENTARY MATERIAL

Supplementary data associated with this article can be found, in the online version, at <https://>

ACKNOWLEDGMENTS

Arsenic XAS was conducted at the Australian Synchrotron, Melbourne (grant no. AS171/XAS/11609) and we thank Peter Kappen and Chris Glover for assistance and advice with collection of XAS data. Additional arsenic XAS was conducted at the National Synchrotron Radiation Research Centre (NSRRC) in Taiwan. Research expenses and salary support for Scott Johnston was provided by the Australian Research Council (grant nos. FT110100130 and LP120100238), Great Lakes Council and Port Macquarie Hastings Council. Research expenses and salary support for William Bennett was provided by the Australian Research Council (DE140100056). We thank Roz Hagan for her thorough and diligent work in the laboratory and for being a particularly awesome all-round Technician. We thank Don Brushett for HPLC-ICP-MS analysis that was possible due to Australian Research Council LIEF grant (LE150100007). This research was supported by the Environmental Analysis Laboratory (EAL) which is a Southern Cross University NATA accredited research support facility.

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Fig. 1: Proportion of solid-phase As(III) species in relation to a) temperature and varying carbon content (2 h combustion time) and b) combustion time and temperature (medium carbon content); concentrations of $\text{Fe(II)}_{\text{HCl}}$ in relation c) temperature and varying carbon content (2 h combustion time) and d) combustion time and temperature (medium carbon content). As(III) determined by linear combination fits of As K-edge XANES spectra. Error bars for As K-edge XANES are $\pm 5\%$.

Fig. 2: As K-edge XANES spectra of a) low carbon (~9%), b) medium carbon (~22%) and c) high carbon (~44%) soil:schwertmannite mixtures after heating at 200, 300, 400, 500, 600, 700 and 800 °C for 2 h and; medium carbon soil:schwertmannite mixtures after heating at d) 200 °C, e) 400 °C, and f) 600 °C for various times (5, 10, 30, 60 and 120 minutes). Dashed lines are reference spectra for As(III) and As(V).

Fig. 3: Fitted ^{57}Fe Mössbauer spectra (292 K) for medium carbon treatments, 2 h heating duration. d and s denote doublets and sextets respectively.

Fig. 4: Fitted ^{57}Fe Mössbauer spectra (292 K) for medium carbon treatments, 5, 10, 30 and 60 minutes heating duration at 600°C. d and s denote doublets and sextets respectively.

Fig. 5: $^{57}\text{Mössbauer}$ derived estimates of Fe(II) in soil:schwertmannite treatments in relation to a) temperature and varying carbon content (2 h combustion time) and b) temperature and combustion time (medium carbon content). Error bars for Fe(II) are $\pm 2\%$.

Fig. 6: Bivariate relationship between As(III) species in all soil:schwertmannite treatments and a) concentration of $\text{Fe(II)}_{\text{HCl}}$ and b) $^{57}\text{Mössbauer}$ derived Fe(II). As(III) determined by linear combination fits of As K-edge XANES spectra.

Fig. 7: X-ray diffractograms of medium carbon soil:schwertmannite mixtures after heating at 600°C for 10 min and 2 h. Mg = magnetite; Mh = maghemite; H = hematite; Q = quartz.

Fig. 8: Qualitative estimates of changes in relative abundance of a) maghemite and b) hematite in relation to heating temperature and carbon content (2 h combustion time). Based on normalised X-ray diffraction peak integral intensity (Maghemite-220; Hematite-104) derived from Fig. 8.

Fig. 9: Mobilisation of $As(III)_{aq}$ and $As(V)_{aq}$ species in 1:5 water extracts of soil:schwertmannite mixtures in relation to a), b), c) combustion temperature and carbon content (2 h combustion time) and d), e) and f) combustion time and combustion temperature (medium carbon content).

Fig. 10: $\text{As(III)}_{\text{aq}}$ in 1:5 water extracts in relation to solid-phase As(III) in soil:schwertmannite treatments with respect to a) varying carbon content and temperature (2 h combustion time) and b) combustion time and temperature (medium carbon content). As(III) determined by linear combination fits of As K-edge XANES spectra.

Table 1

Characteristics of soil:schwertmannite mixtures. All concentrations are in $\mu\text{mol g}^{-1}$ except organic carbon and $^{57}\text{Mössbauer Fe(II) (%)}$.

Carbon treatment	Temp. (C) / combustion time	Organic carbon (%)	$^{57}\text{Mössbauer Fe(II) (%)}$	Fe_{Tot}	As_{Tot}	$\text{Fe(II)}_{\text{HCl}}$	As_{Ex}	pH (1:5 water)
Low	None	9.1	0.94	2353	4.74	21	0.03	3.26
	200 / 2h	8.4	1.12	2202	4.75	156	0.06	3.12
	300 / 2h	6.9	2.63	2425	5.09	215	0.18	2.78
	400 / 2h	5.2	10.6	3206	6.90	112	0.42	3.49
	500 / 2h	4.1	10.6	2876	5.48	76	1.28	3.32
	600 / 2h	3.5	8.88	2631	4.81	65	1.51	3.41
	700 / 2h	1.9	7.03	2399	5.04	101	1.91	3.62
	800 / 2h	0.9	10.5	2125	4.48	19	1.89	3.65
Medium	None	22.0	0.97	2096	4.76	37	0.03	3.45
	200 / 2h	18.3	6.81	2434	5.89	188	0.06	3.64
	300 / 2h	17.2	16.2	2681	6.14	547	0.38	3.36
	400 / 2h	13.5	14.6	3064	6.98	411	1.02	3.95
	500 / 2h	10.7	10.3	2909	6.49	178	1.46	3.65
	600 / 2h	9.2	11.6	2959	6.30	112	1.84	3.57
	700 / 2h	5.7	11.7	2593	6.32	146	3.73	3.66
	800 / 2h	4.9	11.8	2761	6.26	93	2.75	4.12
High	None	44.2	3.99	2123	5.39	61	0.04	3.70
	200 / 2h	40.0	3.49	2118	5.06	242	0.03	4.99
	300 / 2h	36.4	20.4	2131	6.06	551	0.54	3.85
	400 / 2h	38.5	21.3	3044	8.58	603	1.15	5.18
	500 / 2h	33.9	7.24	3219	8.32	161	1.57	5.91
	600 / 2h	32.1	5.18	2702	5.73	105	1.89	5.99
	700 / 2h	32.9	4.46	2917	7.84	82	3.92	5.89
	800 / 2h	19.5	4.11	2758	8.25	142	5.51	6.75
Medium	200 / 5 min	21.1	1.06	2114	4.92	241	0.04	3.43
	200 / 10 min	21.0	1.38	2053	4.85	251	0.03	3.62
	200 / 30 min	20.8	3.49	2191	5.18	301	0.08	3.86
	200 / 60 min	20.0	3.59	2242	5.15	223	0.06	3.85
	400 / 5 min	20.8	12.3	2554	5.83	452	0.15	3.86
	400 / 10 min	20.6	31.1	2477	6.16	984	0.61	4.47
	400 / 30 min	19.1	44.4	2605	6.22	1345	0.44	4.62
	400 / 60 min	16.0	36.5	2482	5.48	1200	0.75	5.13
	600 / 5 min	16.2	38.5	2606	6.03	1499	0.66	6.09
	600 / 10 min	16.4	40.7	3003	6.76	1361	1.07	6.44
	600 / 30 min	17.5	36.3	2619	5.23	922	1.16	6.09
	600 / 60 min	12.1	23.6	2973	6.08	293	1.58	4.61

Accepted Manuscript

Rapid arsenic(V)-reduction by fire in schwertmannite-rich soil enhances arsenic mobilisation

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PII: S0016-7037(18)30050-4
DOI: <https://doi.org/10.1016/j.gca.2018.01.031>
Reference: GCA 10634

To appear in: *Geochimica et Cosmochimica Acta*

Received Date: 18 November 2017

Accepted Date: 21 January 2018

Please cite this article as: Johnston, S.G., Bennett, W.W., Burton, E.D., Hockmann, K., Dawson, N., Karimian, N., Rapid arsenic(V)-reduction by fire in schwertmannite-rich soil enhances arsenic mobilisation, *Geochimica et Cosmochimica Acta* (2018), doi: <https://doi.org/10.1016/j.gca.2018.01.031>

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