Irreversible clay mineral transformations from bushfires in acid sulfate soils: An indicator of soil processes involved in climate variability and climate change

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Abstract

In this paper, we present work on the influence of heat in bushfires and in controlled laboratory experiments, to provide a better understanding of some aspects of the unresolved mineral transformations from bushfires in acid sulfate soils (ASS). The mineralogy using conventional laboratory and synchrotron X-ray diffraction (XRD) analyses of layer silicate minerals, iron oxides, oxyhydroxides and salt efflorescences provided evidence of the irreversible processes that have contributed to their formation. A conceptual model is presented for using the field morphological, mineralogical, and magnetic properties of unburnt and burnt ASS with sulfuric material (pH <4) at Jury Swamp in the lower Murray-Darling Basin to explain irreversible mineralogical transformations as a consequence of drying (droughts and climate change) and subsequent bushfire burning. The conceptual model characterised the known lateral and vertical changes to the various ASS layers, horizons and materials, which included the burned reddened and yellowish soils as well as the relatively unburned blackened soil layers and salt efflorescences.

Keywords: Bushfire burning, X-ray diffraction, phyllosilicates, iron oxides, salt efflorescences

Introduction

Fire severity and the degree of "soil change" depends on fire behaviour and temperatures reached in soil, the residence time, and other biophysical variables (ecosystem type, fuel characteristics, topography, weather, etc.). Field and mineralogical studies in South Africa (Fitzpatrick, 1980) and Australia (Yusiharni and Gilkes 2012) have identified the loss of kaolinite in surface soils after burning. In Australia, Grogan *et al*. (2003) identified maghemite formation in burnt plant litter from an acid sulfate soil at East Trinity, North Queensland. Thermally induced collapse and decomposition of phyllosilicates and the formation of new iron oxide minerals is likely to have important implications for chemical and physical processes in acid sulfate soils (ASS). While predictions of fire-induced mineral transformations can be made based on laboratory experiments, few field investigations have been conducted to check them in ASS occurring in inland wetland systems. Little if any attempts appear to have been made to study the thermal transformations of phyllosilicates, iron oxides-oxyhydroxides and salt efflorescence in ASS formed after wetland drying during extreme drought periods (Fitzpatrick, Shand and Merry 2009) and to use this information for the estimation of burning temperature of past fire events. The ultimate aim of this work is to: (a) determine the effects of fire on mineral transformations in ASS during extreme drought conditions in the Murray Darling Basin and (b) estimate burning temperatures by analyzing the presence of specific phyllosilicates, iron oxides-oxyhydroxides and salt efflorescences in order to understand irreversible mineral transformations from bushfires during extreme drought periods.

Materials and Methods

From 2007 to 2009, Australia's largest river catchment system, the Murray–Darling, experienced record low flows due to rainfall reductions and water over allocation in the Murray–Darling Basin. This led to a major decline in water levels in the whole lower Murray River system in South Australia and the extreme drying of wetlands and lakes. In the wetlands between Lock 1 (upstream from Mannum at Blanchetown) and Wellington near the entrance to Lake Alexandrina, the combination of decreasing water levels and gently sloping near-shore beds caused large expanses of previously inundated sediments and subaqueous soils to be exposed (Fitzpatrick *et al*. 2009; 2011). These extremely low water levels also led to large areas of river sediments and subaqueous soils being exposed for the first time in a long period (>>100 years) and these submerged soil/sediment layers contained large amounts of sulfidic (i.e. pH>4) material, which then oxidised to sulfuric (pH<4) material (Fitzpatrick et al. 2009). As a consequence when the surface soil layer (0 to 50 cm) of Jury Swamp had completely dried, the dry vegetation (stands of willows, Phragmites and other dead reeds and rushes) and peaty materials were burned (Figures 1 and 2). The dried reeds and willow trees were up to 2 to 3 metres high when the burning occurred. With such a tremendous fuel load, the fires caused temperatures thought to exceed 500° C.

A conceptual model was constructed to characterise the known specific lateral and vertical changes to the ASS layers, horizons, materials and other features caused by drying (droughts) and subsequent burning at Jury Swamp (Figures 1 and 2). A severely burned location in Jury Swamp was identified by reddened surface soils, loss of organic matter, and white to gray ash on top of the soil. The reddened surface soil layer ranged in thickness from 1 to 10 cm and was underlain by a relatively unburned blackened soil layer (JUR-B) 10 to 20 cm thick (Figure 2). Two burned samples including a reddened (JUR-R) and a yellowish (JUR-Y) soil was collected from the site. Two unburned samples with blackened soil layer (JUR-B) and with salt efflorescences (JUR-S) were collected (Figure 2). Dried samples were ground using an agate mortar and pestle before lightly front pressing the powder onto silicon low background holders for conventional XRD analysis using a PANalytical X'Pert Pro Multi-purpose Diffractometer with iron filtered Co Kα radiation, automatic divergence slit and X'Celerator Si strip detector. Mineralogical analysis was also conducted on samples using synchrotron XRD (Fitzpatrick et al. 2011) (Table 1). Mass magnetic susceptibility was measured at low (0.46 kHz; χ_{LF}) and high frequencies (4.6 kHz; χ_{HF}) using a Bartington magnetic susceptibility meter model MS2 (Thompson and Oldfield, 1986) (Table 2).

Table 1. Mineralogical composition of burnt and unburnt samples from conventional X-ray diffraction (***Lab XRD***) and synchrotron XRD (***Synchrotron***) analyses

Sample	Qz	Fd	Gyp	Kn	Mi	St	Ht	Gt	Mh	Ha	Bl	Tsch	Th	Other
Lab XRD														
JUR-B	CD	M	T	CD	CD	CD		T						
JUR-Y	CD	M	M		CD	M			T					
JUR-R	D	M	T		M		M		T					
JUR-S	T		M							CD	CD	M	T	
Synchrotron														
JUR-B	CD	M	T	CD	CD	CD								
JUR-Y	CD	M	M	CD	CD	M								
JUR-R	D	M	T		M		M							
JUR-S	T		T							D	M	M	T	Kn: SD Hx: T Lw: T

Where: D – Dominant (>60%), CD – Co-dominant (sum of components >60%), SD – Sub-dominant (20-60%), M-Minor (5-20%), T-Trace (<5%); Where: Qz = Quartz; Fd = Feldspar; Gyp = Gypsum; Kn = Kaolin; Mi = Mica; St = Smectite; Ht = Hematite; Gt = Goethite; Mh = Maghemite; Ha = Halite; Bl = Bloedite; Tsch = Tschermigite; Th = Thenardite. Other: Kn - Konyaite [$Na_2Mg(SO_4)_2 \bullet 5H_2O$]; Hx – Hexahydrite; Lw – Loweite [$Na_{12}Mg_7(SO_4)_{13} \bullet 15(H_2O)$]; Tsch = Tschermigite [$(NH_4)Al(SO_4)_2 \bullet 12(H_2O)$] ; Burnt samples: reddened (JUR-R) and a yellowish (JUR-Y) soil materials; Unburnt samples: blackened soil material (JUR-B) and salt efflorescences (JUR-S)

Results and discussion

The severely burned location in Jury Swamp (Figures 1 and 2, see 3 photographs in top right hand corner) has a distinctive reddish colour on the soil surface with loss of organic matter, and sometimes white to gray ash on top of the soil. The reddened surface soil layer ranged in thickness from 1 to 10 cm and was underlain by a blackened soil layer 10 to 20 cm thick (Figure 2). The high fuel load from the 2 to 3 metres high dried reeds and willow trees resulted in high temperatures (>500° C) when it caught fire. The topsoil between 0 and 20 cm was transformed irreversibly into reddish hard cemented (fused) ceramic-like, porous fragments or ceramic brick-like soil material. The schematic process model presented in Figure 2, illustrates the unique occurrence, transformation and formation of minerals formed during: (i) drying (i.e. drought conditions) to form the following salt efflorescences: tschermigite, hexahydrite, konyaite, bloedite, loweite, gypsum and thenardite (Table 1), (ii) bushfire activities, which causes the dehydroxylation of kaolin, mica and smectite to form amorphous compounds such as metakaolinite and (iii) bushfire activities, which also causes the dehydroxylation of goethite (or possibly ferrihydrite) to form maghemite and hematite (Tables 1 and 2). In summary, the soil temperatures during the extreme or intense burning at Jury Swamp were high enough to alter, collapse, and decompose soil phyllosilicates (kaolin, mica, smectite) and especially transform goethite to maghemite and hematite. Pyrite (FeS_2) was also likely converted to the iron oxide maghemite (Fe_2O_3), releasing sulfur dioxide gas, but possibly retaining the same pyrite framboid shape. Conditions for maghemite formation were ideal because the pyrite ‘framboids’ were completely coated in organic matter and heated to above 300° Celsius in a carbon reducing atmosphere.

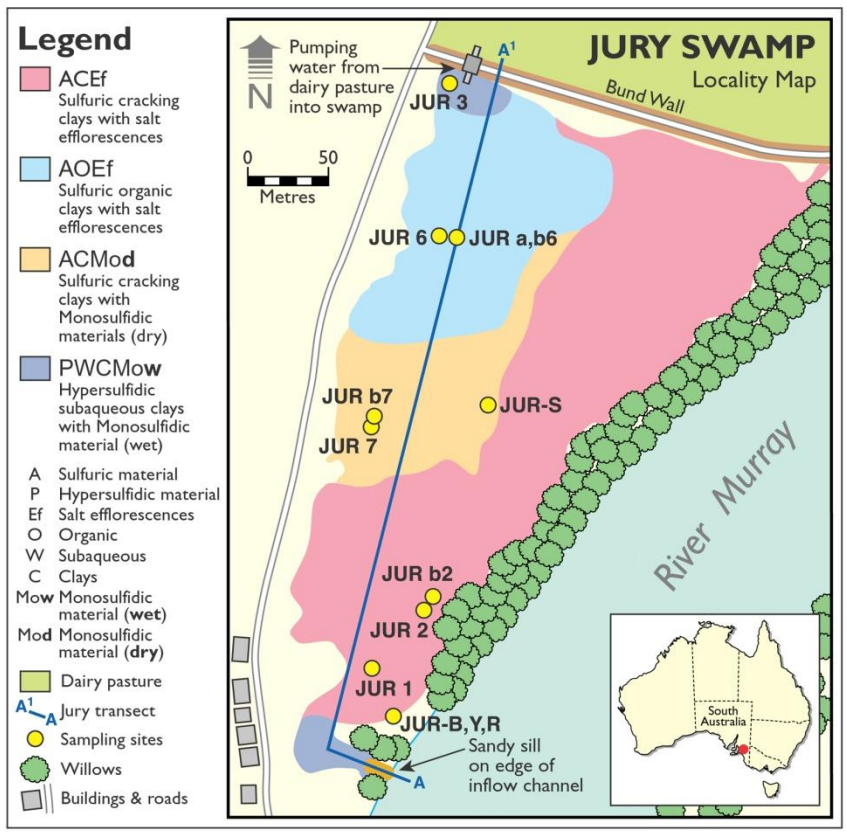

Figure 1. Acid Sulfate Soil map of Jury Swamp showing distribution of the following:

(i) wide range of ASS Subtypes such as Sulfuric cracking clays, Sulfuric organic clays to Hypersulfidic subaqueous clays;

(ii) features such as salt efflorescences and dried & wet monosulfidic material,

(iii) locality of cross section $A–A^1$ across Jury Swamp and

(iv) sampling sites.

(from Fitzpatrick *et al.* 2011)

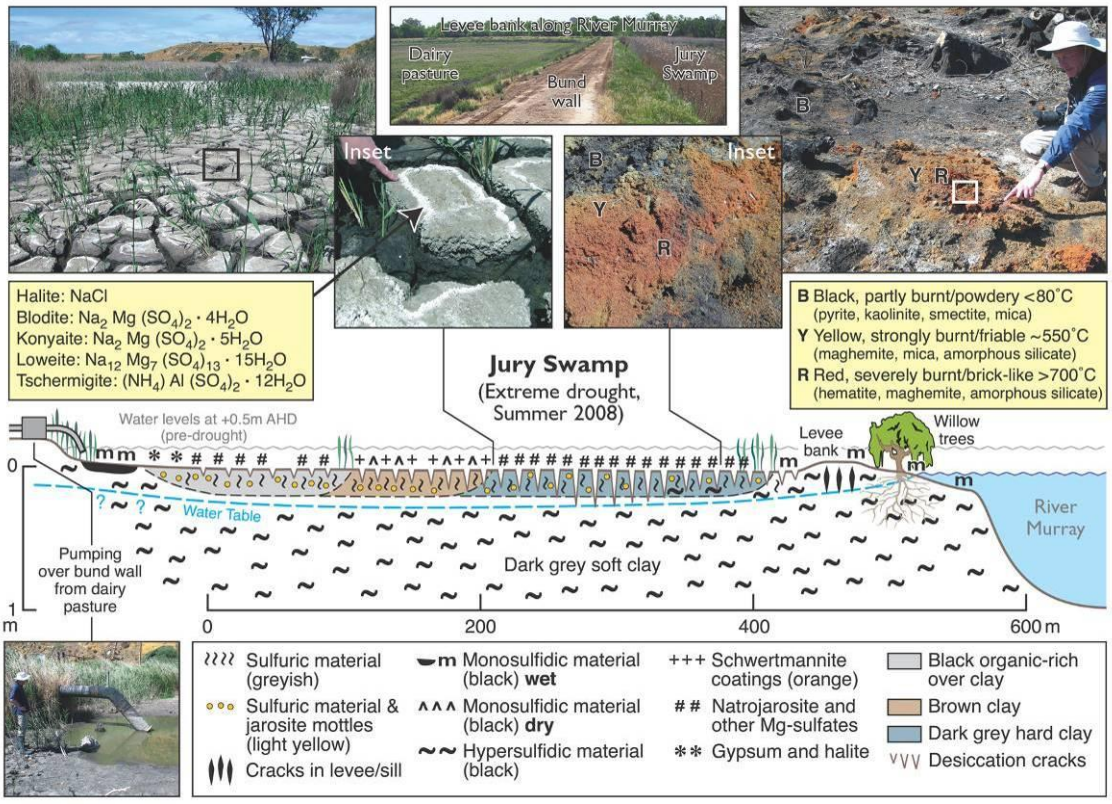

Figure 2. Explanatory soil-regolith model of Jury swamp showing a cross section along transect A^1-A in the Acid Sulfate Soil Map in Figure 1 showing distribution and kinds of salt efflorescences and impacts of degrees of burning (from Fitzpatrick *et al.* 2011).

The likely transformation of the following salt efflorescences will occur during heating, based on the XRD data from the laboratory heating experiment (Table 3), which involved heating the unburnt ASS salt efflorescences sample (JUR-S): (i) Tschermigite and hexahydrite dehydrate to amorphous phases before 100°C; (ii) Konyaite and bloedite dehydrate to loweite, (iii) Loweite possibly recrystallises with other cations and anions around 280-300°C with peaks at approximately 8.4Å, 3.79Å and 3.72Å, (iv) Gypsum dehydrates to bassanite, (v) Thenardite decomposes around 280°C and (vi) Quartz and halite are relatively unchanged up to 300°C.

Table 2: Mass magnetic susceptibility of burnt and unburnt samples measured at low frequency (LF; 0.465 kHz) and high frequency (HF; 4.65 kHz).

	LF	HF	*CFD
Sample name	**χ_m (SI x 10^{-8})**	**χ_m (SI x 10^{-8})**	**(%)**
JUR-B	84	70	16.7
JUR-Y	776	663	14.6
JUR-R	2475	2139	13.6
JUR-S	1.83	1.5	18.0

χ_m is the mass magnetic susceptibility (10^{-8} m^{-3} kg^{-1}) with typical mass magnetic susceptibilities: Magnetite: 40000-70000; Hematite: 120-170; Goethite: 30-70; Bentonite: 3-6; Palygorskite (Attapulgite): 1 to 2; Dolomite: 1; Calcite: -0.5; Quartz: -0.6; Gypsum: -0.5

*CFD(%) = 100 X [χ_m (LF) - χ_m(HF)] /χ_m(LF) where LF and HF are in the ratio 1:10.

Table 3: Mineralogical composition from heating of the unburnt salt efflorescence sample, based on the XRD data from the laboratory heating experiments.

~42°C,	not much has changed
~71°C,	tschermigite peaks dropped to ~20%, konyaite and hexahydrite peaks dropped to ~90%
~100°C,	tschermigite and hexahydrite peaks gone, konyaite peaks dropped to ~10%, gypsum peaks dropped to ~80%, loweite peaks increased ~30%;
~130°C,	konyaite and blodite peaks gone, gypsum peaks dropped to ~30%, loweite peaks increased ~200%, bassanite peaks appear
~158°C,	gypsum peaks gone, loweite peaks unchanged, bassanite peaks doubled in intensity
~188°C,	loweite peaks dropped ~20%
~215°C,	loweite peaks dropped ~90%
~246°C,	loweite peaks gone, new peak at ~3.79Å
~276°C,	thenardite peaks dropped ~30%, halite peaks dropped ~10%, new peak at 3.79Å doubled in intensity
~301°C,	thenardite peaks dropped ~80%, new peaks at 8.4Å, 3.79Å and 3.72Å doubled in intensity

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