

Soil minerals recover after they are damaged by bushfires

Emielda Yusiharni^{A, B} and Robert J. Gilkes^B

^ADepartment of Forestry, Faculty of Agriculture, University of Mataram, Lombok, Indonesia, Email yusihb01@student.uwa.edu.au

^BSchool of Earth and Environment, The University of Western Australia, Perth, 6009, Australia, Email b.gilkes@cyllene.uwa.edu.au

Abstract

We studied the impact of bushfires on soil minerals and the recovery of minerals under wet conditions. Samples were taken shortly after a bushfire from under and adjacent to burnt logs. Kaolinite, goethite and gibbsite were dehydroxylated by the bushfire. Pure minerals were also investigated to determine how heating affects soil minerals and their recovery by rehydroxylation at 55 and 95°C. Rehydroxylation of heated gibbsite was extensive during hydrothermal treatment at 95°C and after 14 days had formed boehmite, bayerite and gibbsite. The process was much slower at lower temperatures. On heating metakaolinite formed from kaolinite and hematite formed from goethite. These minerals showed no change in XRD patterns after hydrothermal treatment but TGA weight loss did increase substantially for metakaolinite. SSA for all three dehydroxylated minerals increased substantially with period of hydrothermal treatment. These results suggest that dehydroxylated minerals and their partly rehydroxylated forms will exist in heated soils and may affect the chemical behaviour of soils.

Key Words

Reversion, rehydroxylation and dehydroxylation

Introduction

Australia has a history of severe forest and bushfires for diverse vegetation and fire regimes (FRA 2000). Fire was used as a powerful land-use tool by indigenous Australians to manage grasslands, forest and fauna (Gill and Moore 1990). The nature of the Australian environment, which is generally hot, dry and prone to drought and the volatile natural vegetation, causes Australian vegetation to be particularly vulnerable to fire.

Heating during a fire which burns litter and both fallen and standing timber may impose significant impacts on soil properties (Raison 1979). Increases in soil fertility and elevated plant nutrient concentrations in regrowth occurred after a single fire (Christensen 1994). These effects occur for both surface and lower soil horizons for high intensity fires. The effect of heating on soil mineralogy has not been extensively studied although modest (200–600°C) temperatures cause mineral transformations (Ketterings *et al.* 2000). Kaolinite decomposes at temperatures between 500°C and 700°C (Richardson 1972) losing lattice water. Metakaolinite forms in the temperature range from 450°C to 600°C. Gibbsite alters to an amorphous phase on heating at 200°C (Rooksby 1972), and goethite is transformed to hematite at ≈300°C (Cornell and Schwertmann 1996). The persistence of the dehydroxylated compounds in heated soils is unknown and is the subject of this investigation.

Methods

We investigated how bushfire and laboratory heating of soil affects soil minerals and their recovery by rehydroxylation at 55 and 95°C.

Soil samples burnt in a forest fire

Samples were obtained from soils that had been heated under a burning log or litter. Samples were removed as a 1cm thick layer from under burnt Eucalyptus and grass tree (*Xanthorrhoea pressii*) logs from up-slope and down slope sites with a lateritic colluvium soil. Sampling took place shortly after a fire at Wundowie in the Darling Range, Western Australia in early March 2009. Samples were taken from a 10cm strip below a burnt log (0-10cm laterally) and 10-20cm and 20-30cm away from the log. The nomenclature for heated soil from under burnt Eucalyptus and grass tree logs from up-slope (US) and down slope (DS) sites at Wundowie bush fire site are as follow: DS Unburnt (unburnt soil 0-10cm depth from down slope), DS 0-10 cm (heated soil from down slope, 0-10cm from log), DS 10-20 cm (heated soil from down slope, 10-20cm from log), DS 20-30 cm (heated soil from down slope, 20-30cm from log), DS Unburnt (unburnt soil 0-10cm depth from Up slope), DS 0-10 cm (heated soil from up slope, 0-10cm from log), DS 10-20 cm (heated soil from up slope, 10-20cm from log), and DS 20-30 cm (heated soil from up slope, 20-30cm from log). The soils are very gravelly and were sieved to obtain the <2mm fraction for analysis.

Heated pure minerals

Gibbsite was obtained from Alcoa Alumina, Western Australia. Kaolinite from Mc Namee Pit, Bath, South Carolina, United States. Goethite from a lateritic Ni deposit, Koniambo, New Caledonia. The minerals were heated for 1 hour at temperatures above and below DTA dehydroxylation maxima. Gibbsite was heated at 250°C, 300°C and 350°C. Kaolinite at 500°C, 550°C and 600°C. Goethite at 250°C, 300°C and 350°C. For the rehydroxylation experiment, 6.5g of the heated mineral was mixed with 26cm³ of water then heated in closed containers in an oven for 0, 14, 70, and 200 days at two temperatures (55 and 95°C).

Analytical techniques

Materials were analyzed by XRD on a Philips PW3020 diffractometer, thermal gravimetric analysis (TGA) on a STA 6000 instrument (Perkin-Elmer, Norwalk, CT, USA), transmission electron microscopy (TEM) on a JEOL 3000 FEG electron microscope equipped with an Oxford Instruments INCA 200 Energy Dispersive Spectrometer (EDS). Specific surface area (SSA) was measured using a Micrometrics Gemini 2375 instrument with VacPrep 061 using a 5 point BET method with N₂ as the absorbate. The pH and EC of the materials was determined in a 1:5 deionised water extract. Forms of Fe, Al and Si were determined using the specific extractants: dithionite-citrate-bicarbonate, ammonium oxalate and sodium pyrophosphate (Rayment and Higginson 1992) and with analysis by an inductively coupled plasma with optical emission spectroscopy (ICP-OES) (Perkin-Elmer).

Results

Soil heated by forest fires

The XRD patterns of heated and unheated soil from the Wundowie bushfire show the effect of fire. The main crystalline compounds of unheated soil are quartz, gibbsite, kaolinite, and goethite. At the largest distance (20-30cm) from the burnt log, all the four minerals persisted and calcite occurred as it is a common constituent of plant ash (Harper *et al.* 1982). Closer to the burnt log, gibbsite and goethite XRD intensities decreased as did the kaolinite intensity directly below the burnt log (0-10cm), these minerals had been dehydroxylated.

Table 1. Effect of heating on soil extractable Al, Fe and Si of 0-1cm depth soil at two distances from burnt grass tree (GT) and eucalyptus (EU) logs. DS: down slope, and US: up slope.

Samples	Oxalate			Na pyrophosphate			DCB		
	Al	Fe	Si	Al	Fe	Si	Al	Fe	Si
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
GT DS Unburnt	1353	452	110	1684	513	264	1161	3358	14
GT DS 0-10cm	7591	2373	2383	3617	620	356	5428	8467	941
GT DS 10-20cm	5199	1860	1128	3932	945	382	4116	10194	545
GT DS 20-30cm	4581	1574	1443	3137	651	371	3312	7337	607
GT US Unburnt	5153	2283	481	4593	1391	614	4751	17583	335
GT US 0-10cm	16958	4157	5230	9370	334	484	17230	9568	2093
GT US 10-20cm	15007	4288	2762	9276	1605	431	16842	24996	1701
GT US 20-30cm	10331	3011	2030	6948	1225	457	9672	17044	1109
EU DS Unburnt	2078	1035	194	1256	557	322	1686	7223	137
EU DS 0-10cm	12621	4068	5092	3493	522	354	4109	5678	802
EU DS 10-20cm	7045	2346	1640	3462	731	344	7123	16259	1082
EU DS 20-30cm	4112	1497	710	2750	613	436	4948	14287	637
EU US Unburnt	1260	748	1307	1461	706	210	3432	5468	265
EU US 0-10cm	8411	3291	1983	4617	964	299	6676	12515	921
EU US 10-20cm	5022	2090	1841	2756	711	363	3572	7955	849
EU US 20-30cm	4950	2105	1634	2859	740	360	5294	13901	1033

Ash from bushfire considerably increased the pH and EC of all soil samples relative to the original. The increases in EC simply reflect the addition to the soil of soluble salts in plant ash (Harper *et al.* 1982). The extractable Al, Fe and Si values (Table 1) for GT DS, GT US, EU DS and EU US also increased substantially after the bushfire with values for the heated soil being considerably higher than for unburnt soil and the values are mostly higher directly under burnt logs. These poorly ordered soluble forms of Al, Fe and Si minerals had been formed by dehydroxylation of the parent crystalline minerals.

Dehydroxylation and rehydroxylation of pure minerals

Dehydroxylation of kaolinite, goethite and gibbsite caused slight to moderate increases in their specific surface area (SSA). All three minerals had lost most structural water during heating but had clearly acquired structural water (we define this as water lost at $T > 110^{\circ}\text{C}$) during the rehydroxylation treatment (Figure 1). XRD indicated that the metakaolinite formed from kaolinite heated at 600°C showed no change in structure for wet incubation times up to 200 days. Hematite formed from goethite at 350°C also experienced no change in structure. XRD showed that rehydroxylation of heated gibbsite (initially boehmite and amorphous material) was extensive at 95°C and after 14 days, additional boehmite (Bo), bayerite (Ba) and gibbsite (Gi) had formed (Figure 2). The process was much slower at 55°C . TGA results for heated kaolinite and to a lesser extent for heated goethite showed considerable structural water was acquired during rehydroxylation with most water being lost over a range of temperatures rather than a specific temperature as occurred for the unheated mineral (Figure 1).

Gibbsite heated to 350°C had a microporous, granular appearance, consistent with SSA results (Figure 3A). After incubation for 14 days at 95°C complex intergrowths of hexagonal crystals had formed (Figure 3.B) which is consistent with XRD results (Figure 2) that show that boehmite, bayerite and gibbsite had formed.

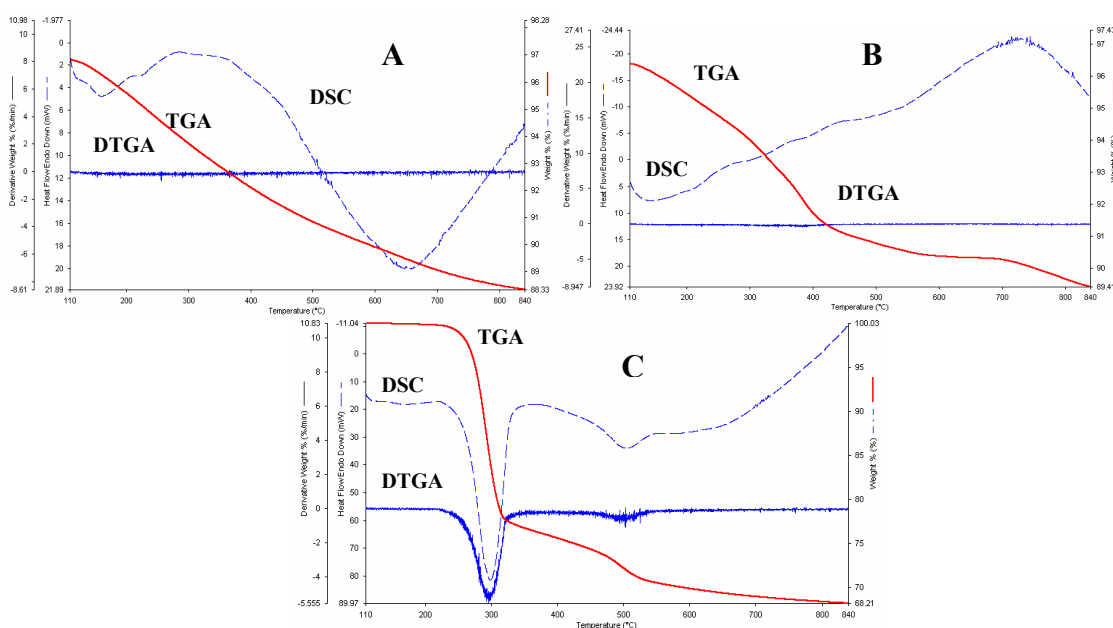


Figure 1. TGA results for rehydroxylated heated kaolinite (A), goethite (B) and gibbsite (C): 95°C , 200 days, wet incubated at $55/95^{\circ}\text{C}$, 0-200 days.

Conclusion

Gibbsite, goethite and kaolinite are dehydroxylated by heating in bushfires. Laboratory dehydroxylation of kaolinite, goethite and gibbsite caused structural changes and slight to moderate increased in SSA. Rehydroxylation of 350°C heated gibbsite was extensive during hydrothermal treatment at 95°C and after 14 days boehmite, bayerite and gibbsite had formed, the process was slower at 55°C . We propose that the process occurs in soils but at present remain unreported.

Metakaolinite and hematite showed no change in XRD patterns due to rehydroxylation but structural water content increased substantially for metakaolinite. These results suggest that dehydroxylated minerals and their rehydroxylated forms must be present in naturally heated soils and may exert significant effects on the chemical behavior of the soil.

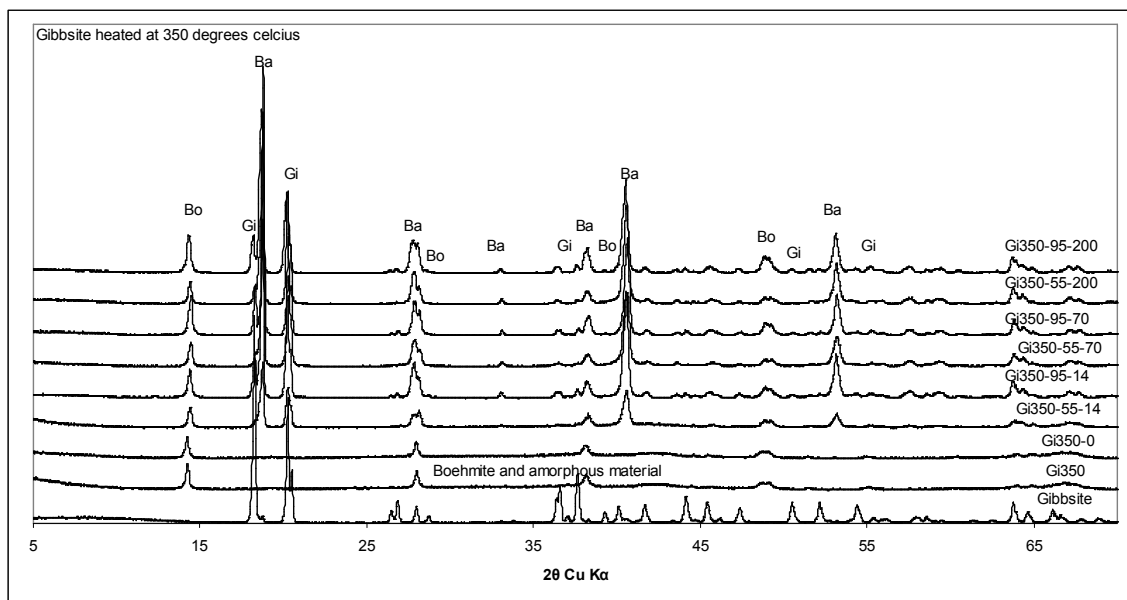


Figure 2. XRD patterns for heated gibbsite, wet incubated at 55/95°C, 0-200 days.

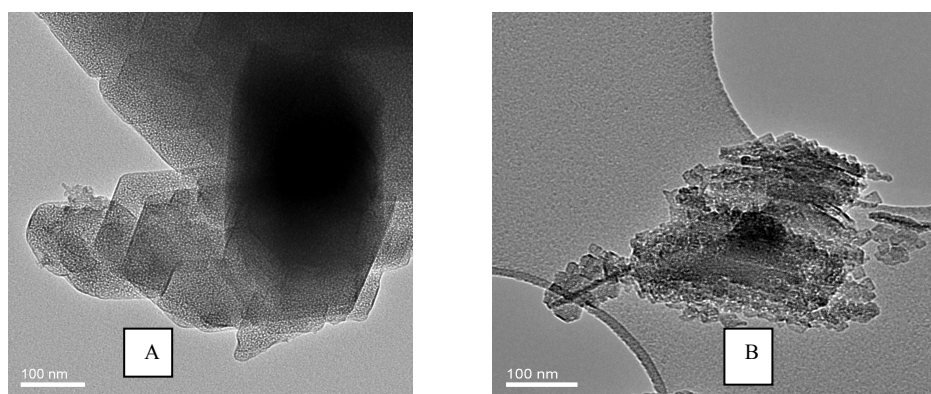


Figure 3. Electron micrographs of original gibbsite heated at 350°C (A), gibbsite dehydroxylated at 350°C then incubated for 14 days at 95°C (B).

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