



# Minerals in the ash of Australian native plants

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## ABSTRACT

This study characterized the ash of several Australian native plant species (silver wattle (*Acacia retinodes*), prickly moses (*Acacia pulchella*), wandoo/white gum (*Eucalyptus wandoo*), red gum or marri (*Corymbia calophylla*), grass tree (*Xanthorrhoea preissii*), jarrah (*Eucalyptus marginata*) and harsh hakea (*Hakea prostrata*)) and investigated the reactions of ash with soil. The ashes were alkaline with pH ranging from 12.3 to 13.8, and contained substantial amounts of plant nutrients. Amounts of calcium, magnesium, sodium or silicon varied depending on plant species and plant part. Many minor elements were also present including elements with no biological function. Available phosphorous (Colwell–P) in the ashes ranged from 30 to 199 mg/kg. All elements were mostly present in crystalline compounds which were identified using XRD and SEM. Minerals present in ash included calcite ( $\text{CaCO}_3$ ), fairchildite ( $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ), nesquehonite ( $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ ), sylvite (KCl), lime (CaO), scolecite ( $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3(\text{H}_2\text{O})$ ), quartz ( $\text{SiO}_2$ ) (derived from dust), portlandite ( $\text{Ca}(\text{OH})_2$ ), periclase (MgO), and apatite, probably resembling hydroxyl-apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) and wilkeite ( $\text{Ca}_5(\text{P, S, Si})\text{O}_4(\text{OH}, \text{CO}_3)$ ). Ash has important liming and fertilizer values and its effectiveness in these roles is a consequence of the properties of these minerals and their reaction with soil as was demonstrated in an ash plus soil incubation experiment.

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## 1. Introduction

Wild and managed fires burn many thousands of hectares of forest annually and consume some or all of the vegetation and litter (Ulery et al., 1996). The intensity of forest burning is related to weather conditions, amount of fuel available and the condition of the fuel. Fires create ash consisting of organic and inorganic residues from the combustion process (Übeda et al., 2009). Ash may be defined as a complex mixture of charcoal, char and minerals (i.e. inorganic compounds) (Scott, 2010). The characteristics and the amount of forest plant ash produced under natural or controlled conditions depend on several factors, including the species and the part of plant that was combusted (leaves, fruit, bark or wood), plant age and combustion degree (Clapham and Zibilske, 1992; Demeyer et al., 2001; Ulery et al., 1993; Vance and Mitchell 2000).

Most elements in plants are retained in the ash with most N and some S being lost (Perkiomaki, 2004). Consequently the N content in ash is usually small, particularly where fuels are completely combusted (Khanna et al., 1994). The carbon (C) content of ash varies with combustion degree, with C remaining as unburnt plant material, charcoal and carbonate minerals (Vance and Mitchell, 2000). The color of ash varies from black through grey, brown to white with the type of plant and combustion process influencing ash color. Dark colored (black) ash contains higher amounts of charred organic material compared to the light colored ash that is mostly composed of

crystalline or amorphous inorganic compounds (Knicker, 2007). Recent studies have proposed that ash color could be used as an indicator of fire severity (Bodí et al., 2011; Keeley, 2009; Pereira et al., 2011) but the nature and amount of inorganic compounds need to be considered and differ with vegetation type. Several laboratory studies have examined the relationship between ash color and fire severity for various biomass types and combustion temperatures (Liodakis et al., 2005; Liodakis et al., 2009; Misra et al., 1993). For combustion at 600 °C,  $\text{CaCO}_3$  and  $\text{K}_2\text{Ca}(\text{CO}_3)_2$  were present while for 1300 °C combustion, CaO and MgO were the dominant compounds (Misra et al., 1993). However, in general the nature of minerals in plant ash is poorly understood and is the subject of this paper.

Ash is generally an alkaline material with pH ranging from 9.0 to 13.5 (Khanna et al., 1994; Liodakis et al., 2005) and ash has been used as a combined liming agent and nutrient source (Etiegni and Campbell, 1991; Yusiharni et al., 2007). For example, application of ash to an acid soil increased soil pH, and levels of extractable Ca, Mg and  $\text{SO}_4$  (Voundi Nkana et al., 2002). Ash generally contains significant amounts of most plant nutrient elements and thus can be regarded as a multi nutrient fertilizer (Vance and Mitchell, 2000). Furthermore addition of ash to soil may increase the availability of some soil nutrients to plants because of exchange with ions dissolved from ash (Voundi Nkana et al., 2002).

Several studies have investigated the physical and chemical properties of ash from diverse plant species (Etiegni and Campbell, 1991; Gabet and Bookter, 2011; Khanna et al., 1994; Übeda et al., 2009). However, the forms of plant nutrients in ash including the forms of water-soluble elements and their interactions with soils have

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**Table 1**

The nomenclature for plant ash and some properties of the ash. SSA = specific surface area (m<sup>2</sup>/g), EC = electrical conductivity (mS/cm), Bic P = bicarbonate P (mg/kg).

Key	Species and plant material	Ash %	Ash Color	SSA (m <sup>2</sup> /g)	pH (1:5)	EC (1:5) (mS/cm)	Bic P (mg/kg)
SW	Silver wattle wood	1.72	G1 8/N	5.8	13.8	18.9	145
SL	Silver wattle leaf	3.39	G1 5/N	4.2	12.8	13.9	198
PM	Prickly moses leaf and twig	2.81	G1 4/N	8.3	13.1	8.5	199
WW	Wandoo wood	3.07	2.5Y 7/2	9.2	13.6	15.1	176
WL	Wandoo leaf	3.02	G1 5/N	2.4	13.3	14.3	32
RW	Red gum wood	4.71	G1 7/N	2.4	13.8	23.2	183
RL	Red gum leaf	4.07	G1 6/N	2.5	13.4	18.4	30
GT	Grass tree leaf	3.40	G1 3/N	2.7	13.5	22.9	145
JL	Jarrah leaf	3.27	2.5Y 6/2	2.9	13.2	18.9	196
HH	Harsh hakea leaf and twig	4.01	G1 4/N	7.7	12.3	16.3	164

received little attention. The research described in this paper determined the amounts and mineral forms of elements in ash derived from several Australian native plant species and evaluated the reactions of plant ash with heated and unheated soil.

## 2. Material and methods

### 2.1. Ash preparation

The five Australian native plants used for the study are major constituents of forest vegetation at Bakers Hills, Darling Range, Western Australia: silver wattle (*Acacia retinodes*), prickly moses (*Acacia pulchella*), wandoo/white gum (*Eucalyptus wandoo*), red gum or marri (*Corymbia calophylla*), grass tree (*Xanthorrhoea preissii*), jarrah (*Eucalyptus marginata*) and harsh hakea (*Hakea prostrata*). The leaves and wood samples were dried in an oven at 60 °C until the weight was constant (up to 7 days) and then cut to 1–2 cm to made the sample homogenous. A subsample of approximately 50 g then placed in an aluminum oven tray and burned in

open air for about 15 min with agitation to maximize burning, to simulate combustion in a forest fire in the field. Temperature was not recorded during the combustion process. Combustion was almost complete for each material with only small amounts of charcoal remaining in the ash. A key to the materials investigated and the abbreviations used to identify these materials are given in Table 1.

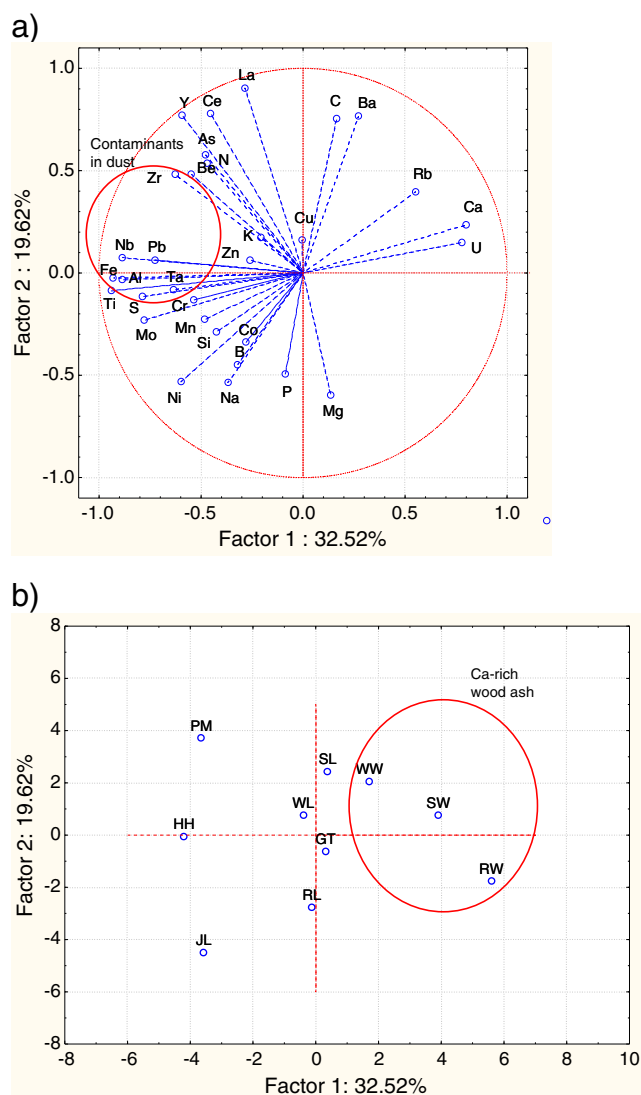
### 2.2. Characterization of the ash

Ash color was classified using a Munsell Color Chart (Munsell Color Co., 1998). Specific surface area (SSA) was measured using a Micrometrics Gemini 2375 instrument with VacPrep 061 using a five point BET method with N<sub>2</sub> as the absorbate. The pH of the ash was determined in a 1:5 deionized water extract. The samples were analyzed for bicarbonate extractable P (Bic P) (Colwell, 1963). Total carbon and nitrogen were determined on an Elementar CNS (Vario Macro) analyzer. Water-soluble elements in ash were determined using Association of Official Analytical Chemistry (AOAC) standard methods (AOAC, 1990). 0.5 g of ash was mixed with 100 ml of DI

**Table 2**

Total element concentrations in plant ash (mg/kg). Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

Element (mg/kg)	Ash Type									
	SW	SL	PM	WW	WL	RW	RL	GT	JL	HH
Al	1014	1802	3499	2028	1375	840	2540	1085	3689	6091
As	3	5	4	3	2	0	0	1	3	5
B	242	282	164	197	1215	153	657	135	936	248
Ba	494	372	1092	913	842	169	149	561	55	60
Be	0.2	0.4	0.3	0.3	0.5	0.1	0.1	0.1	0.3	0.2
Ca	289,300	206,800	134,200	248,300	177,600	219,400	147,900	162,801	149,800	158,600
Ce	6	27	51	43	23	4	6	11	9	15
Co	3	2	3	1	1	2	6	2	3	2
Cr	42	24	44	18	41	11	30	131	62	45
Cu	122	453	92	71	104	97	97	88	131	99
Fe	2688	4098	13,792	4067	2920	1518	4473	4177	14,850	22,870
K	32,370	41,660	37,400	29,380	42,110	32,660	35,810	45,790	33,000	34,080
La	6	30	58	31	15	2	4	10	3	8
Mg	58,670	76,801	21,570	49,760	60,940	43,420	66,990	69,610	111,300	33,920
Mn	387	1005	522	2998	3150	694	822	890	3494	3955
Mo	1	1	3	1	1	1	1	4	3	4
Na	1792	10,080	6319	26,520	92,980	24,340	60,220	9406	83,140	47,990
Nb	5	5	8	5	5	3	5	4	8	8
Ni	7	9	15	8	20	10	16	30	35	14
P	4986	11,190	6097	2649	7715	9940	13,470	10,750	8867	7074
Pb	3	3	23	14	5	0	13	21	35	8
Rb	148	210	179	187	170	205	196	229	92	107
S	1842	6046	5086	2437	5490	2121	5489	8738	6454	23820
Si	5610	10,010	15,870	11,450	9140	9090	18,300	10,600	17,220	7010
Ta	26	23	26	28	23	22	22	23	32	35
Ti	168	291	764	242	226	119	375	206	887	706
U	16	11	8	13	9	13	9	10	9	9
Y	1	8	17	6	6	1	1	3	2	7
Zn	61	322	273	92	1039	292	335	149	131	317
Zr	4	5	12	3	4	3	5	4	3	7



**Fig. 1.** Principal component analysis of log total element concentration for native plant ash, variables (a) and plant material (b). Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

water and placed on a mechanical shaker for 24 h. Extracts were then filtered through a 0.22  $\mu\text{m}$  Millipore filter. Water-soluble elements were then measured using an inductively coupled plasma optical emission spectrometer (ICP-OES) (Perkin-Elmer, Norwalk, CT, USA). Ash content of plant material was determined by a separate dry combustion in a muffle furnace at 550  $^{\circ}\text{C}$  for 2 h (Rayment and Higginson, 1992).

Total elements were determined in duplicate with a model PE ELAN 600 inductively coupled plasma-atomic emission spectroscopy (ICP-OES) instrument (Perkin-Elmer, Norwalk, CT, USA) after concentrated perchloric acid digestion of the ash (Rayment and Higginson, 1992). Conventional XRD of the ash was conducted on a Philips PW3020 diffractometer with a diffracted beam monochromator ( $\text{CuK}\alpha$ , 50 kV, 20 mA). Powder samples were scanned from 4 to 70 $^{\circ}$  2 $\theta$ , using a step size of 0.02 $^{\circ}$  2 $\theta$  and a scan speed of 0.04 $^{\circ}$  2 $\theta$  s $^{-1}$ . Synchrotron XRD (SXRD) analysis was performed at the Australian Synchrotron where powder samples were mounted into glass capillaries with a 1.0  $\text{\AA}$  wavelength set for this analysis in order to provide a high peak/background and adequate resolution for identifying minor constituents. The composition and morphology of the plant ash was examined by scanning electron microscopy (SEM)

and energy dispersive X-ray spectrometry (EDS) using a JEOL 6400 instrument. Samples for SEM analysis were placed on metal stubs and carbon coated before analysis. Principal component analysis was carried out on the bulk chemical data and on element concentrations of ash particles derived from SEM EDS spectra using STATISTICA (STATISTICA, 2011).

### 2.3. Incubation of ash–soil mixture

Topsoil (0–10 cm) from Bakers Hills, (Yalanbee soil, a lateritic podzolic soil, which is an Alfisol (USDA, 2010)) was used in the incubation study. The same acid sandy, highly P-deficient soil had been used in a study of the P fertilizer value of chicken litter ash by Yusiharni et al. (2007). Soil properties (<2 mm fraction) are as follow; pH (1:5  $\text{H}_2\text{O}$ ) 4.5, Electrical conductivity (EC) (1:5  $\text{H}_2\text{O}$ ) 0.04 mS/cm, total P 0.25%, bicarbonate extractable P 0.49 ppm (Colwell 1963), total carbon 1.64%, total nitrogen 0.08%, clay, silt and sand were 4%, 6%, and 90% respectively (Yusiharni et al., 2007). Subsamples of unheated soil were air dried and passed through a 2 mm sieve for use in the incubation experiment and for chemical analysis, while other soil subsamples were first heated at 200  $^{\circ}\text{C}$  in a muffle furnace for one hour to simulate heating in a bushfire. 100 g of unheated and heated soil were thoroughly mixed with each ash (SW, SL, PM, WW, WL, RW, RL, GT, JL and HH) in vials at rates of 0 and 1 g/100 g soil. Each mixture was replicated two times, wetted to about 20% water content with addition of toluene as a microbial inhibitor. The tops were firmly screwed onto the vials, which were placed in the dark at 20  $^{\circ}\text{C}$  for 0, 1 and 5 weeks. After each incubation period a subsample was removed for analysis for Bic-P, EC and pH as described above.

**Table 3**

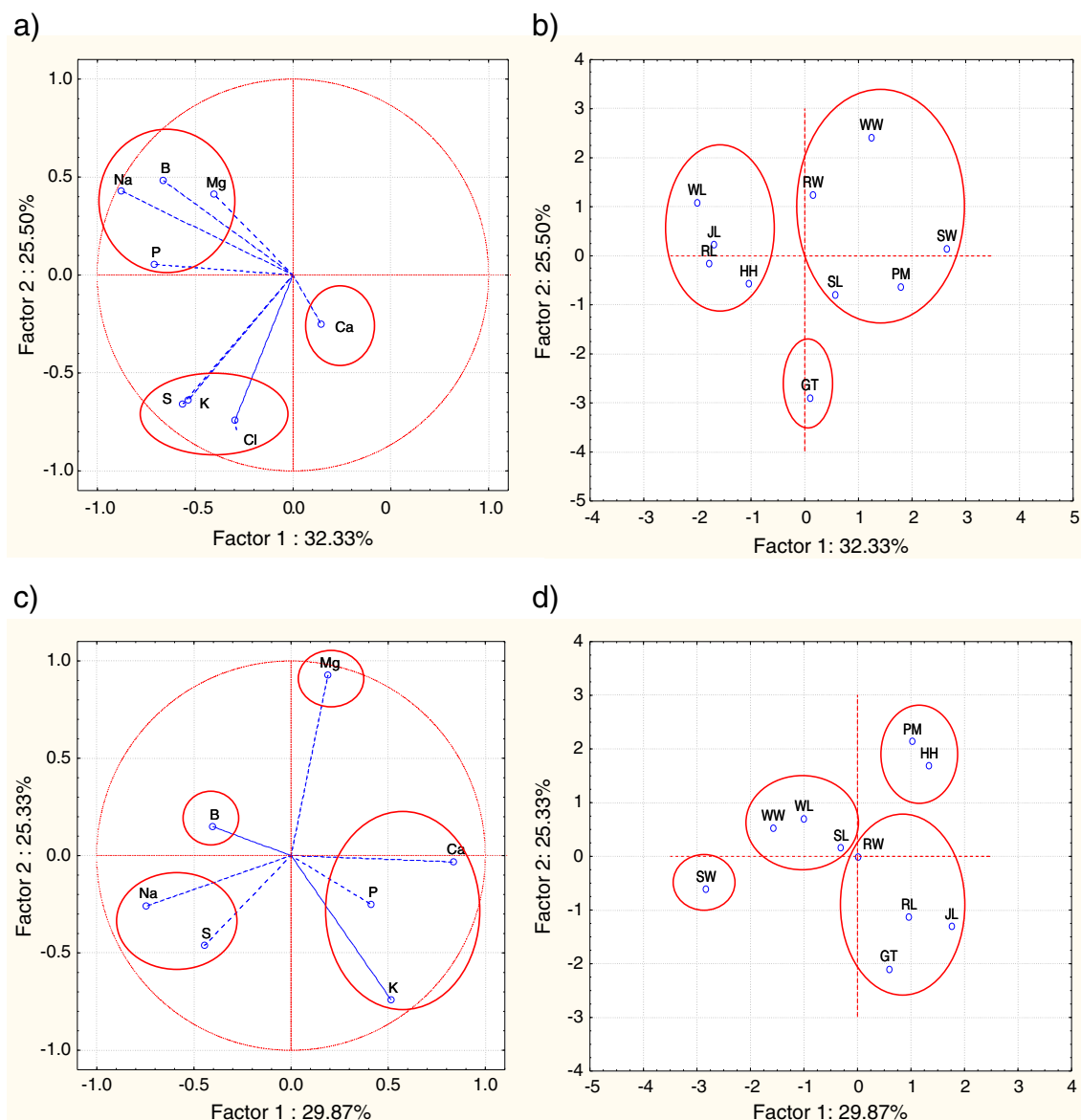
(a) Concentration of water-soluble elements in plant ash. Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

Ash type	Water soluble element concentration (mg/kg)							
	Na	Mg	K	Ca	P	S	B	Cl
SW	1100	3500	7217	25,990	5	54	22	3600
SL	1629	6332	11,330	22,700	13	150	20	11,290
PM	892	5500	6195	38,650	17	132	16	6607
WW	5103	4137	4680	23,320	63	64	32	200
WL	15,020	6581	8666	16,510	52	148	163	15,370
RW	4655	6429	11,810	25,980	185	52	17	717
RL	10,080	4650	16,180	31,830	221	143	85	4670
GT	1733	2545	20,131	26,250	129	234	10	14,410
JL	12,600	5800	12,730	37,550	166	164	74	2997
HH	8658	6650	9410	23,430	57	303	18	9226

(b) Proportion of element in plant ash that is water-soluble\*

Ash type	Proportion of element that is water soluble						
	Na	Mg	K	Ca	P	S	B
SW	0.61	0.06	0.22	0.09	0.001	0.03	0.09
SL	0.16	0.08	0.27	0.11	0.001	0.02	0.07
PM	0.14	0.25	0.17	0.29	0.003	0.03	0.10
WW	0.19	0.08	0.16	0.09	0.024	0.03	0.16
WL	0.16	0.11	0.21	0.09	0.007	0.03	0.13
RW	0.19	0.15	0.36	0.12	0.019	0.02	0.11
RL	0.17	0.07	0.45	0.22	0.016	0.03	0.13
GT	0.18	0.04	0.44	0.16	0.012	0.03	0.07
JL	0.15	0.05	0.39	0.25	0.019	0.03	0.08
HH	0.18	0.20	0.28	0.15	0.008	0.01	0.07

\* The proportion of water soluble Cl could not be calculated as no total Cl values are available due to use of perchloric acid dissolution.



**Fig. 2.** Principal component analysis of log water soluble element concentrations, variables (a) and cases (b) and log proportion that is water soluble, variables (c) and plant material (d) for native plant ash. Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

### 3. Results and discussion

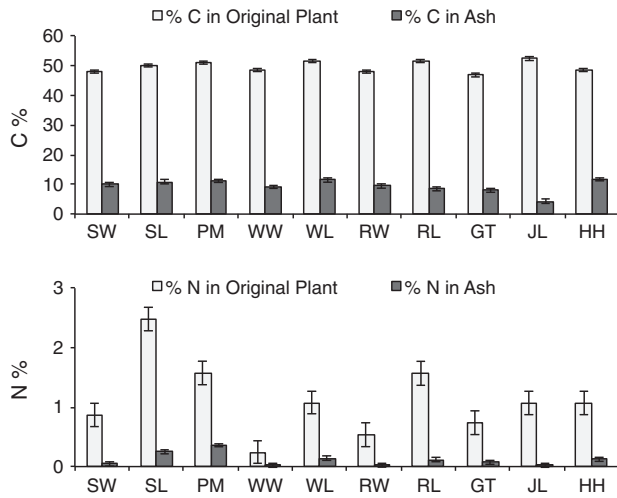
#### 3.1. Characteristics of the ashes

The ash content of the plant materials as the result of furnace burning ranged from 1.7 to 4.7%. Properties of plant ash produced by open-air burning are shown in Table 1. Ash was white (G1 8/N, G1 7/N, G1 6/N, G1 5/N, or G1 4/N) and grey (G1 3/N, 2.5Y 7/2 or 2.5Y 6/2). Grey ash contains more carbon (charred organic material) than white ash possibly reflecting differences in the intensity of combustion (Khanna et al., 1994; Lentile et al., 2006; Neary et al., 1999; Roy et al., 2010). White ash generally contains abundant calcite ( $\text{CaCO}_3$ ) (Ulery and Graham, 1993) as will be discussed subsequently.

All the ashes were alkaline with pH ranging from 12.3 to 13.8. These high values are associated with the presence of carbonates, oxides and hydroxides of base cations in ash (Ulery et al., 1993). The electrical conductivity of the ash extracts (1:5) was high, indicating that the ash contains considerable amounts of soluble salts, with

red gum wood ash containing the highest amount (23.2 mS/cm) and prickly moses leaf/twig ash the least (8.5 mS/cm). Other workers have made similar observations (Badía and Martí, 2003; Iglesias et al., 1997; Kutiel and Naveh, 1987). The specific surface area of the ashes ranges from 2 to 9 m<sup>2</sup>/g indicating that ash particles (crystals) are very small (micron size) and are thus likely to be quite reactive. Amounts of available phosphorous (P) in the ash ranged from 29 to 198 mg/kg reflecting the combustion of organic P and the presence of partly soluble P minerals in ash (Galang et al., 2010; Kutiel and Shaviv, 1989).

The ash produced by open-air combustion in this study may not be identical to ash produced during wildfires, prescribed fires or ash derived from laboratory ignition at controlled temperatures. Raison (1979) mentioned that ash generated in a muffle furnace would be different from ash produced during a wildland fire. Bodí et al. (2011) also found in their recent study that ash derived at several temperatures in a laboratory study may not have effectively replicated ash created by a bushfire.

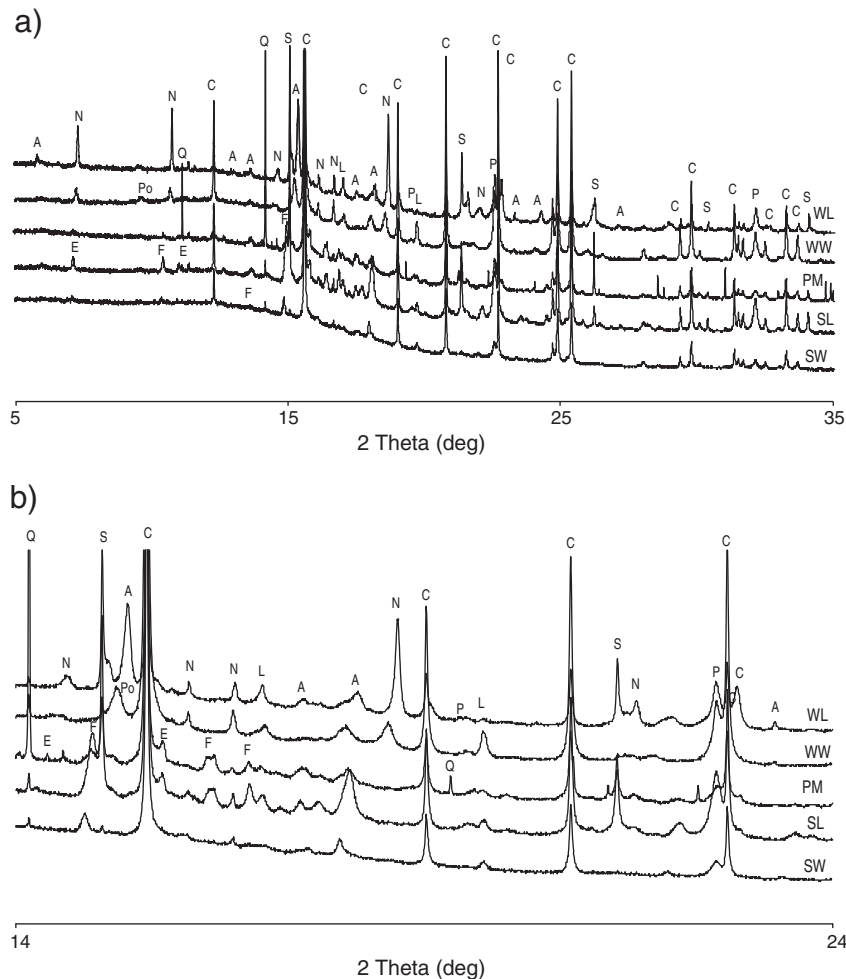


**Fig. 3.** Mean ( $n = 3$ ) values of carbon (C) and nitrogen (N) concentrations (%) for native plant materials (original and ash). Silver wattle wood (SW), silver wattle leaf (SL), prickly moose leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

### 3.2. Total, water extractable element, carbon and nitrogen concentrations

Table 2 lists the mean element concentrations for the ashes. Plant ash contains most plant nutrient elements and many other elements (Khanna et al., 1994). The most abundant elements in these ash samples were Ca, K, Mg, P, S, Fe, Mn, Na, and Si, which is in agreement with other work (Etiegni and Campbell, 1991; Gabet and Bookter, 2011; Misra et al., 1993).

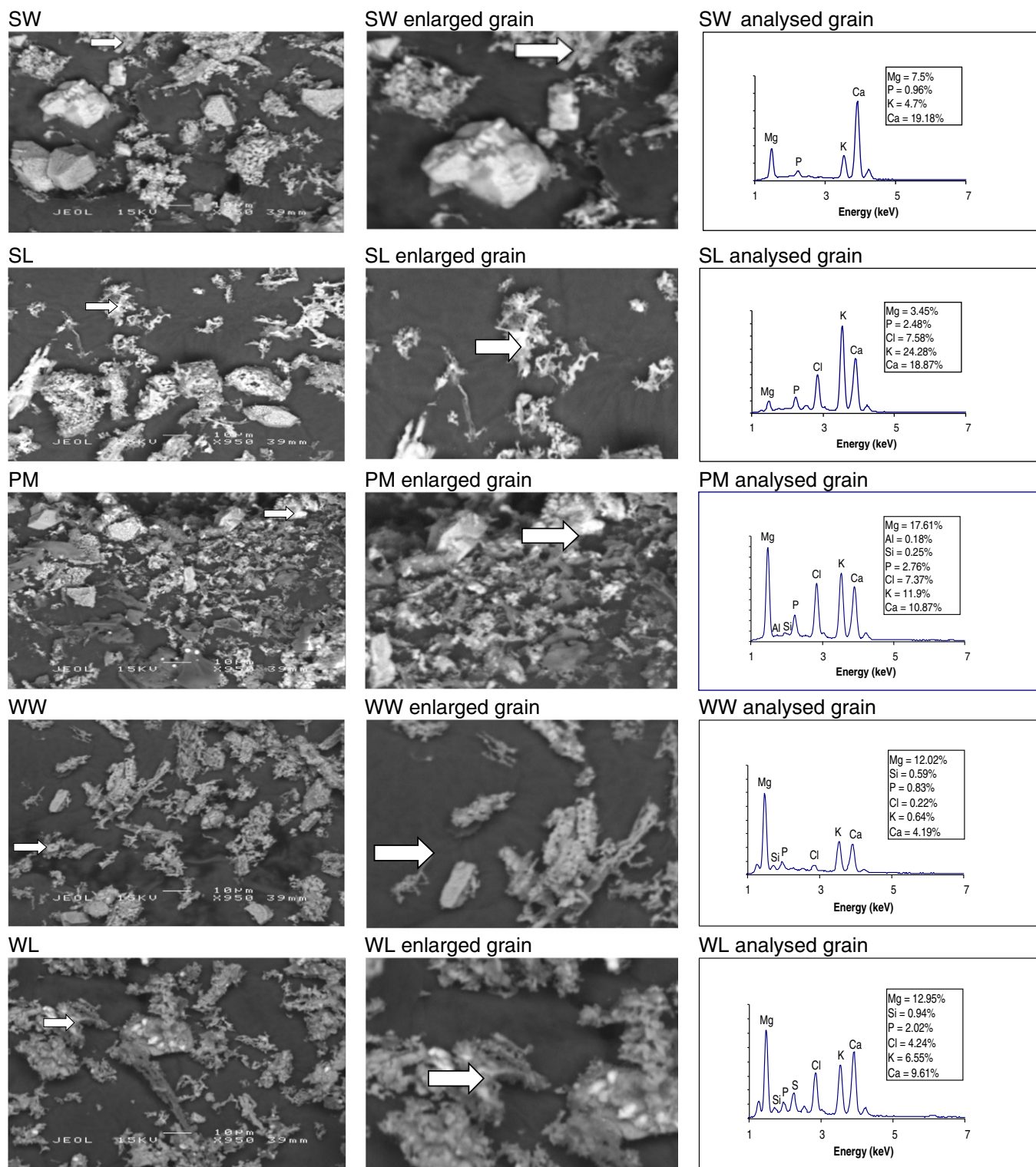
Total element concentrations in ash differed substantially between plant materials as has been reported by Khanna et al. (1994) and Liodakis et al. (2009). The chemical composition of ash is highly dependent upon the fuel (e.g. wood and leaf proportions) and the combustion degree (Khanna et al., 1994). Silver wattle wood ash (SW) had the highest concentration of calcium (289,300 mg/kg), jarrah leaf ash (JL) had the highest concentration of magnesium (111,300 mg/kg) and grass tree ash (GT) had the highest concentration of potassium (45,700 mg/kg). The calcium concentration is generally higher for wood and twig ash compared to leaf ash, concentrations of magnesium and potassium were higher in leaf ash than in wood ash (Table 2 and Fig. 1). Other elements are present at relatively small concentrations in ash, with some elements being most likely present in minerals derived from soil/dust contaminating the plant materials (i.e. Ti, Al, Zr, Pb) (Fig. 1) (Ludwig et al., 2005). The plant samples were not washed prior to burning as this would remove soluble elements and in addition soil and dust minerals and their thermal reaction products would be present in natural ash.



**Fig. 4.** (a) Synchrotron XRD patterns for SW, SL, PM, WW and WL. (b) Enlargements of part of the SXRD patterns (F = fairchildite ( $K_2Ca(CO_3)_2$ ), N = nesquehonite ( $MgCO_3 \cdot H_2O$ ), C = calcite ( $CaCO_3$ ), S = sylvite (KCl), A = apatite ( $Ca_5(PO_4)_3(OH)$ ), L = lime (CaO), E = scolecite ( $CaAl_2Si_3O_{10} \cdot 3(H_2O)$ ), Q = quartz ( $SiO_2$ ), Po = portlandite ( $Ca(OH)_2$  and P = periclase ( $MgO$ )).





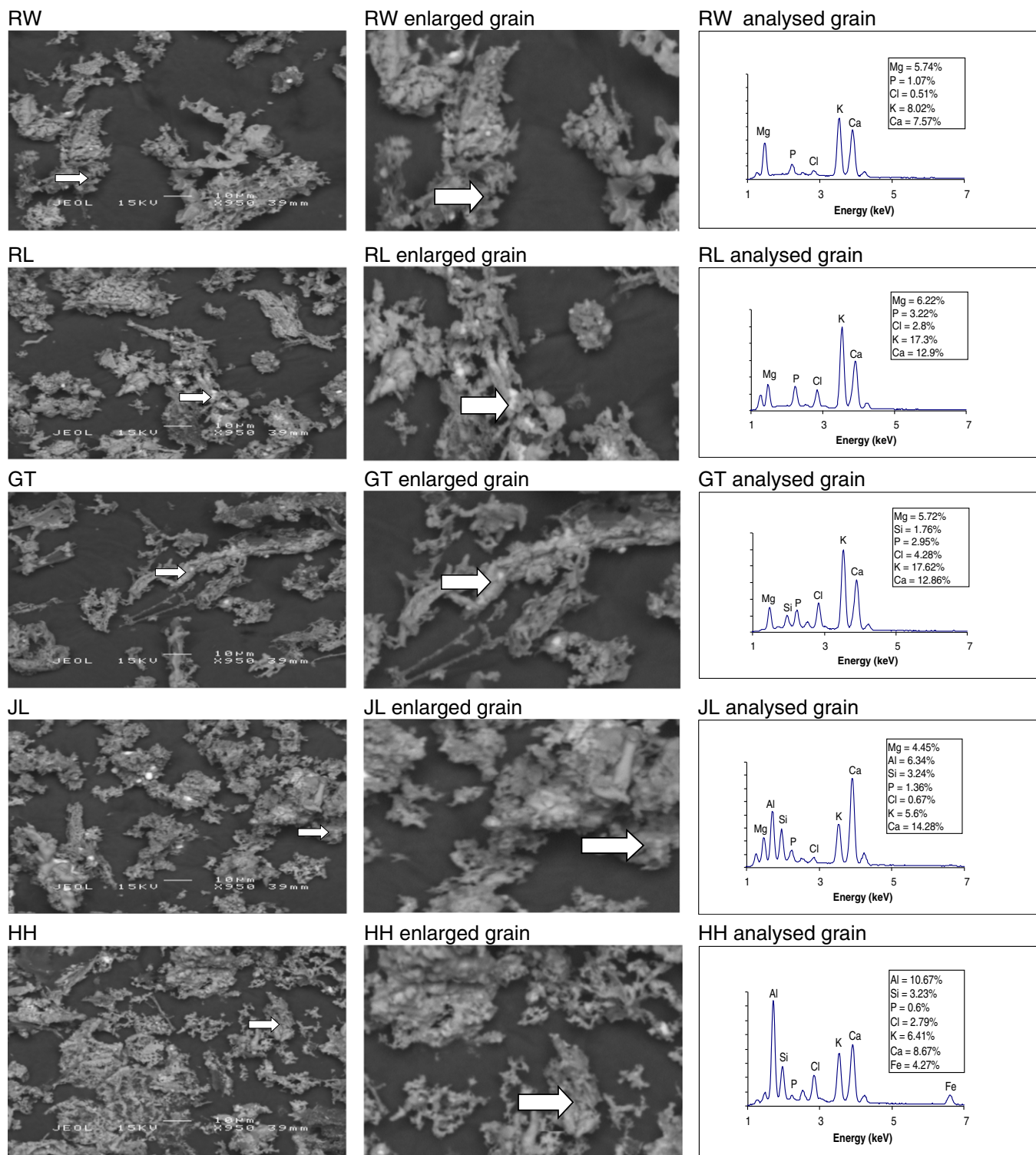


**Fig. 6.** Scanning electron micrograph (SEM) and X-ray spectra of the indicated ash particles for SW, SL, PM, WW and WL ash. Calcite crystal ( $\text{CaCO}_3$ ), microcrystalline hydroxyl apatite and mixed potassium, magnesium and calcium salts are present.

original plant materials were not washed to remove dust as we wished to simulate natural conditions during forest fires. We considered that some of the crystalline compounds in ash might be due to plant constituents chemically reacting with dust/soil constituents during combustion.

Principal component analysis for the concentration of elements soluble in water including their solubility as a proportion of total element concentrations is illustrated in Fig. 2a, b, c and d. Water-soluble

calcium is well separated from other elements and it is more strongly associated with wood ash (RW, WW and SW) and also PM and SL ash. The association of water-soluble P, Mg, Na and B is mostly related to leaf ash materials (WL, JL and RL). Water soluble Cl, K and S are associated and are relatively abundant in grass tree ash. Quite distinct groupings (e.g. Ca, K, P) occur when elements are expressed as log proportion of total element soluble in water (Fig. 2c and d). Explanation for these groupings will be provided by the XRD and SEM/EDS results



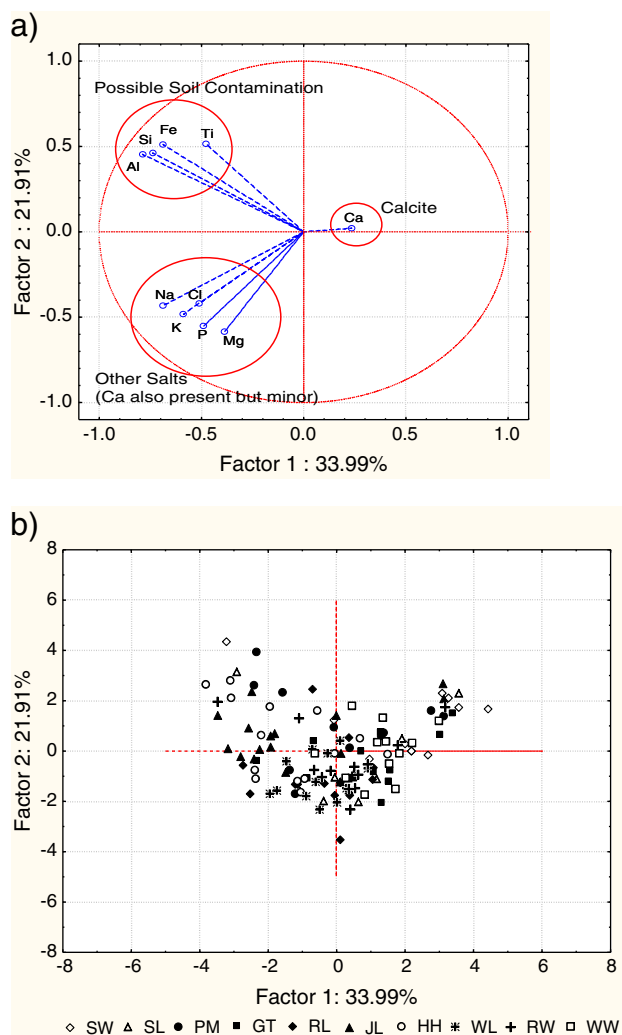
**Fig. 7.** Scanning electron micrograph (SEM) and X-ray spectra of the indicated ash particles for RW, RL, GT, JL, and HH ash. Calcite crystal ( $\text{CaCO}_3$ ), microcrystalline hydroxyl apatite and mixed potassium, magnesium and calcium salts are present.

discussed below. Several studies have observed that water-soluble element concentrations varied according to plant species and combustion temperature (Gray and Dighton, 2006; Pereira et al., 2009). A recent study by Pereira et al. (2011) of ash from cork oak (*Quercus suber*) observed substantial water soluble Ca, Mg, Na, Si and S in the ash.

Mean values of total carbon and nitrogen concentrations in raw plant materials and ash are presented in Fig. 3. Total carbon was

above 40% for all the raw plant materials and decreased to below 10% for their ash. Total carbon concentrations are similar for all the plant samples. The reduced concentrations of total carbon in plant ash are due to the almost complete removal of organic material from the ash with remaining carbon being mostly present as carbonates (Gabet and Bookter, 2011; Misra et al., 1993). Wandoo leaf ash (WL) and harsh hakea ash (HH) had the highest total carbon and





**Fig. 8.** Principal component analyses of log SEM EDS elemental analyses results for native plant ash particles. Variables (a) and plant material (b). Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

their ash color was considered to be white (G1 5/N and G1 4/N respectively) rather than grey. Burning plant materials greatly reduced the nitrogen concentration in the ashes. Almost complete loss of N occurs where combustion of the fuel is nearly complete (Khanna et al., 1994; Raison et al., 1985). The N content of ash produced at temperatures above 600 °C is normally low, which is presumably due to the conversion of most plant nitrogen to  $\text{NH}_3$ ,  $\text{NO}_x$  and  $\text{N}_2$  gases during the combustion process (Misra et al., 1993).

### 3.3. Mineralogy and Morphology of ash (XRD and SEM)

Conventional XRD patterns of SW, SL, PM, WW, WL, RW, RL, GT, JL and HH ash showed that the major compounds present in the ashes are calcite, apatite and quartz (data not shown here). Harper et al. (1982) also found that calcite, apatite and quartz were present in the ash of plant materials where quartz was identified as being an impurity from dust or soil. Ulerý et al. (1993) observed calcite and some minor unidentified peaks in plant ash. The sensitivity of conventional XRD is insufficient to identify trace amounts of minerals, therefore synchrotron XRD (SXRD) patterns of ashes (Figs. 4a, b and

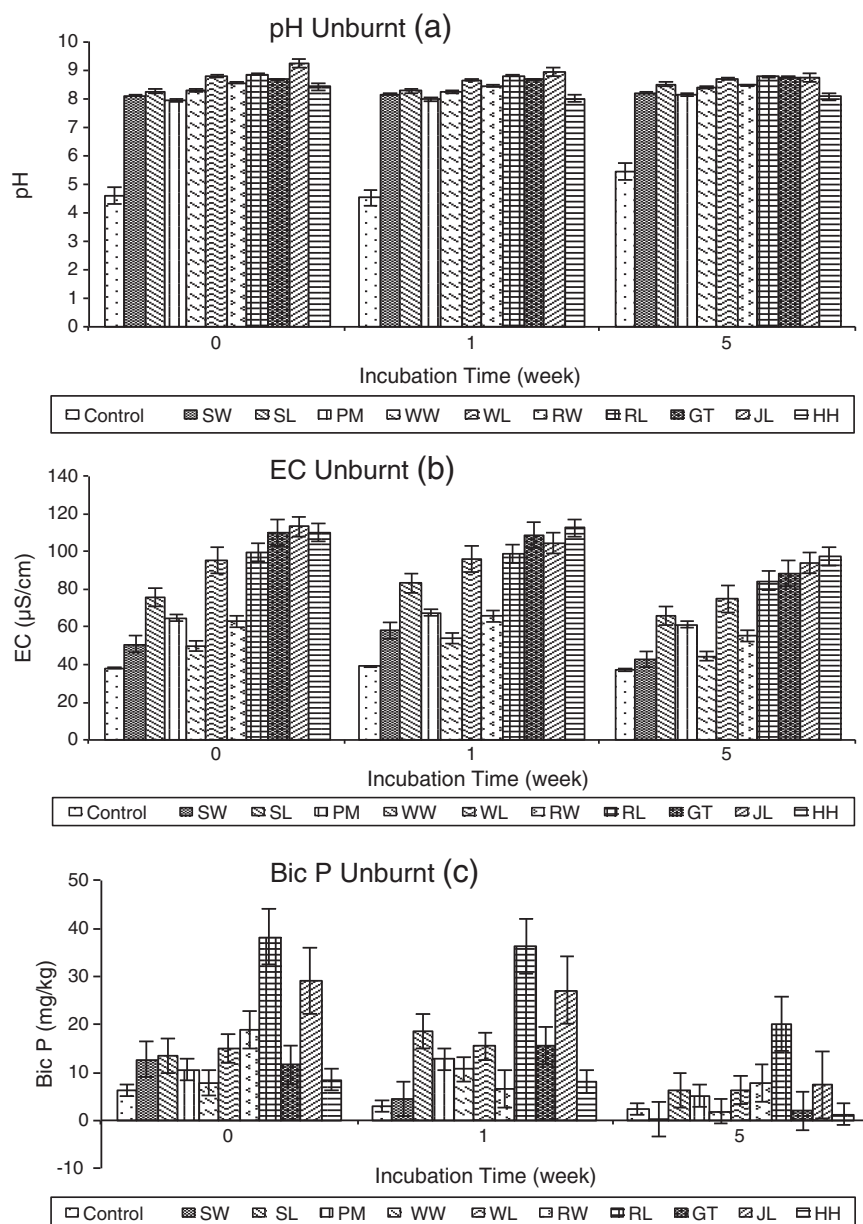
5a, b) in a glass capillary were also obtained. These patterns offer better detection and resolution of weak and adjacent reflections than is provided by conventional XRD (Williams et al., 2003). However the glass of the capillary contributes to the broad background scattering seen in Figs. 4 and 5 so that amorphous silica (e.g. phytoliths) can not be detected.

The main compounds identified by SXRD in the plant ashes were various oxides, carbonates and hydroxides of Ca, Mg and K as has also been reported by Misra et al. (1993). The minerals present were fairchildite ( $\text{K}_2\text{Ca}(\text{CO}_3)_2$ ), nesquehonite ( $\text{MgCO}_3 \cdot \text{H}_2\text{O}$ ), calcite ( $\text{CaCO}_3$ ), sylvite (KCl), lime (CaO), scolecite ( $\text{CaAl}_2\text{Si}_3\text{O}_{10} \cdot 3(\text{H}_2\text{O})$ ), portlandite ( $\text{Ca}(\text{OH})_2$ ), periclase (MgO), apatite group minerals probably resembling hydroxyl-apatite ( $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ ) and wilkeite ( $\text{Ca}_5(\text{P, S, Si})\text{O}_4(\text{OH, CO}_3)$ ) and quartz ( $\text{SiO}_2$  (Table 4). Fairchildite, nesquehonite, scolecite, portlandite and periclase were not identified using conventional XRD. As discussed above, the proportion of water-soluble elements in ash (Table 3.b) is low, which may be attributed to the presence of these mostly poorly soluble minerals. Hydroxide minerals form when the ash is exposed to air as oxides of Ca, Mg and K react with atmospheric water (Misra et al. 1993). Liodakis et al. (2005) detected periclase (MgO), lime (CaO) and portlandite ( $\text{Ca}(\text{OH})_2$ ) in wood ash prepared at 600 °C. Reaction of these oxides with atmospheric carbon dioxide results in the formation of calcite and other carbonates. However, carbonates also form during combustion. Periclase and lime probably formed directly via the combustion of magnesium- and calcium-containing organic matter rather than via decomposition of  $\text{MgCO}_3$  and  $\text{CaCO}_3$  (Liodakis et al., 2005).

SXRD could not detect the present of halite (sodium chloride) in the ash, even though ICPO-ES data showed abundant sodium (up to 93,000 mg/kg of total Na) and chloride (up to 15370 mg/kg water soluble Cl) in the ash so these ions may not be present as halite. This interpretation is consistent with the low proportion (0.15–0.29) of total Na that was soluble in water (Table 3b).

Scanning electron microscopy of particles and associated EDS X-ray spectra for all the ashes show that diverse particle sizes, shapes and compositions occur (Figs. 6 and 7). Ash contains particles with sizes ranging from  $<1 \mu\text{m}$  to  $100 \mu\text{m}$ . Apart from distinct mostly prismatic, large calcite crystals, most grains seen in the micrographs are K- and Mg-rich aggregates of very small particles often containing Cl and they commonly contain little P, Fe, S and Si. The sensitivity of EDS for Na is extremely poor, so that Na peak is not visible in EDS spectra. Liodakis et al. (2009) found that SEM spectra of particles of plant ash contained lines due to Ca, Mg, K, P and Si as observed in this work. The present results indicate the complex nature of ash, with a high diversity of composition, shape and size of particles.

The EDS spectra and XRD results indicate that grains are mostly complex mixture of extremely small crystals including calcite, fairchildite, nesquehonite, sylvite, lime, scolecite, quartz, portlandite, periclase, apatite (hydroxyl-apatite and wilkeite). Principal component analysis of log element concentrations derived from SEM-EDS spectra of ash particles (Fig. 8a, b) is helpful in determining the underlying associations of elements in ash particles. Calcium was quite well separated from other elements presumably representing particles of calcite, lime or portlandite, while P, Mg, K, Cl and Na are grouped representing the various halide, phosphate and mixed cation carbonates that are present. The grouping of Al, Fe, Si and Ti probably represent impurity particles derived from dust and these include the soil minerals quartz ( $\text{SiO}_2$ ), anatase ( $\text{TiO}_2$ ), kaolin ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ), goethite ( $\text{FeOOH}$ ) and hematite ( $\text{Fe}_2\text{O}_3$ ). Leaf and twig ash contains more of these contaminating minerals than wood ash as a consequence of the greater surface area of these plant materials. Some Si also occurs as amorphous silica within plant materials, as it is a structural constituent of many grasses, prickly shrubs, etc (Lanning et al., 1958). The plant ash materials are not tightly grouped in Fig. 8b due to the diversity of minerals present and the various concentrations of the impurity minerals.



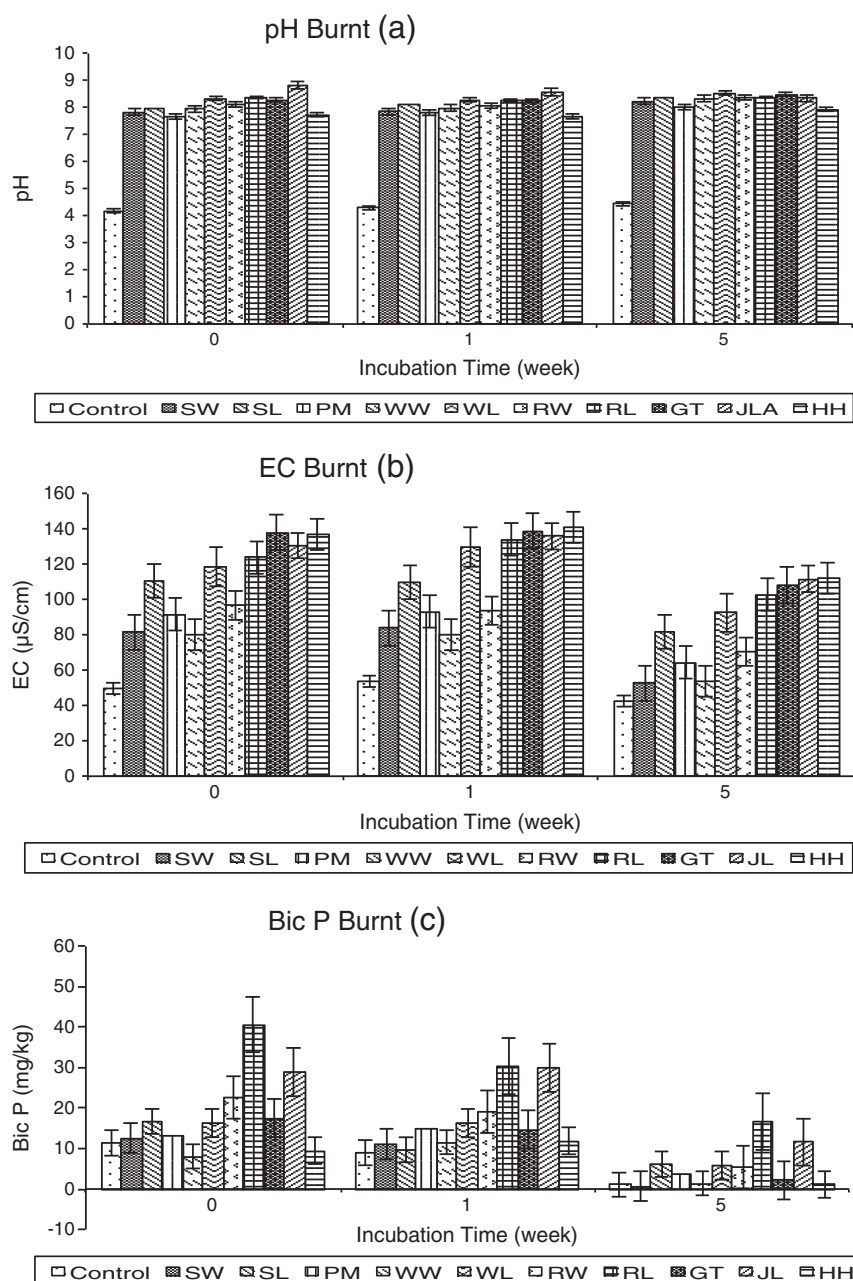
**Fig. 9.** Mean ( $n=3$ ) values of pH (a), EC (b) and bicarbonate P (c) for unburnt soil incubated with native plant ash. Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

### 3.4. Ash and soil incubation

The effects on pH, EC and Bic P of the addition of ash to unburnt and burnt soil are illustrated in Figs. 9 and 10. The soil had an original pH of 4.5, which was not affected by heating but pH increased substantially when ash was added to both the unburnt and burnt soil. The addition of all ashes increased soil pH by about 3 units, with wandoo leaf ash (WL) increasing the pH of unburnt and burnt soil by about 4 units. The EC of burnt soil was more than for unburnt soil and was greatly increased by the addition of ash. EC decreased slightly after 5 weeks of incubation. The increases of pH and EC for soil plus ash are due to the dissolution of salts include carbonates in the ash. Differences in EC values for different ashes reflect the different amounts of soluble halides, carbonates, hydroxides and oxides present in the various ash materials (Goforth et al., 2005; Terefe et al., 2008). The decrease of EC for the 5 week incubation for burnt and unburnt soil plus ash possibly reflects the crystallization of less soluble minerals during incubation (Kutiel and Shaviv, 1992).

The amount of plant-available P (bicarbonate soluble P) in burnt soil increased relative to unburnt soil and increased substantially with addition of ash for 0 and 1 weeks of incubation. Values had decreased after 5 weeks incubation time presumably due to P-fixation. The increase in Bic P for burnt soil reflects the combustion of organic P compounds in the soil (Galang et al., 2010), with a possible contribution from the transformation of soil minerals. The addition of substantial amount of P to the soil in ash, which contains apatite and wilkeite clearly increased the available P in the soil (Kutiel and Shaviv, 1992).

The considerable amounts of plant nutrient elements in plant ash can be used to improve soil fertility. The understanding of mineralogical and morphological properties of ash provided by this research helps explain and predict some effects of ash on soil fertility. A major finding is that some compounds in ash are sparingly soluble in water so that plant nutrient elements (e.g. P in apatite) are not readily released to soil solution.



**Fig. 10.** Mean ( $n = 3$ ) values of pH (a), EC (b) and bicarbonate P (c) for burnt soil incubated with native plant ash. Silver wattle wood (SW), silver wattle leaf (SL), prickly moses leaf and twig (PM), wandoo wood (WW), wandoo leaf (WL), red gum wood (RW), red gum leaf (RL), grass tree leaf (GT), jarrah leaf (JL), and harsh hakea leaf and twig (HH).

Ash deposited during wildfire and prescribed fires contains diverse compounds that will variously affect soil properties, especially for acid soils. Addition of ash to heated and unheated acid soil during the incubation study increased the pH and EC values due to dissolution of the salts in the ash. The different pH and EC values for each ash are explained by the different amounts and occurrences of carbonates and other salts in ash. The increased amount of plant available phosphate in soil to which ash has been added is at least partly due to dissolution of the apatite in ash.

#### 4. Conclusions

The ash of these native plant species has diverse chemical, mineralogical and morphological properties and differs in solubility, depending on plant species and plant part. Compounds in the ash include fairchildite ( $K_2Ca(CO_3)_2$ ), nesquehonite ( $MgCO_3 \cdot H_2O$ ), calcite

( $CaCO_3$ ), sylvite (KCl), lime (CaO), scolecite ( $CaAl_2Si_3O_{10} \cdot 3(H_2O)$ ), quartz ( $SiO_2$ ), portlandite ( $Ca(OH)_2$ ), periclase (MgO). Much of the P in ashes is present as the mineral apatite. These compounds are more soluble when applied to acid soil where they could provide substantial amount of P for plants whereas P in apatite may be much less available if the ash is deposited on naturally alkaline soil or on a soil that has been raised to a high pH value due to the liming action of ash. These effects will occur in the field for prescribed or wild fires and their magnitude will presumably vary with the duration and intensity of fire, the type and abundance of fuel and soil type. These topics deserve further investigation.

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