

Wood-ash stone in *Angophora costata* (Gaertn.) J.Britt. following Sydney bushfires

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Summary

Wood-ash stone, consisting of lumps of carbonate several cubic centimetres in size, were found in the burnt portion of a stump and a trunk (burnt on the ground) of a common Sydney sandstone tree, *Angophora costata*, following the 2002 new-year fires in the Lane Cove valley. It appears to result from the fusion and crystallisation of the ash at temperatures <1000°C. The study material is composed mostly of calcite, as determined by X-ray diffraction and petrological analysis, and in comparison to other examples it contains higher concentrations of Ca and Mg but much lower levels of K, Na and P. This composition probably accounts for the absence of rare potassium carbonates that are reported in other studies. This is the second known occurrence of wood-ash stone in Australia and outside North America.

Keywords: wood ash; mineralization; chemical composition; forest fires; trees; burning; *Angophora costata*

Introduction

Under certain conditions the burning of trees results in the production of copious amounts of carbonate minerals such as calcite and rare potassium carbonates. Known as 'wood-ash stone' or 'fused wood-ash stone', it is thought to result from the fusion and recrystallisation of ash within the trunks of large standing trees that caught fire higher up the trunk and slowly burnt downwards. This burn pattern appears to favour the conversion of wood to ash concentrated in alkali and alkaline-earth metals and thence to wood-ash stone under a slow-burning regime. Wood-ash stone was first reported from North America in several conifers including *Abies concolor*, *A. grandis*, *A. procera*, *Pseudotsuga taxifolia*, *Thuja plicata* and *Tsuga heterophylla*, and possibly *Pinus monticola* (Englis and Day 1929; Kienholz 1929; Milton 1944; Milton and Axelrod 1947), and deciduous angiosperms including *Betula* sp., *Carya* sp. and *Quercus prinus* (Dawson and Sabina 1958; Mandarino and Harris 1965; Dietrich 1971). It was first reported in Australia in *Angophora costata* (Myrtaceae), a prominent evergreen tree species in the Sydney area, by Humphreys and Hunt (1979) and Humphreys *et al.* (1987). This represented the first report of wood-ash stone outside North America. All these records refer to the natural occurrence of wood-ash stone. Somewhat related materials occur in combustion furnaces and boiler fire boxes as a type of slag or clinker where biomass fuels such as sawdust, straw, wood-chips and wood-ash

are used (e.g. Kienholz 1929; Thy *et al.* 2000). The purpose of this note is to report the second known occurrence of wood-ash stone in Australia, which differs in form, composition and distribution from other known examples.

The setting

The wood-ash stone was found in the burnt standing and fallen trunk of a sizeable smooth-barked apple, *Angophora costata* (Gaertn.) J.Britt., in Hawkesbury Sandstone terrain of the Lane Cove valley (33°45.712S, 151°6.972E), some 2 km south-east of the previous record (Humphreys *et al.* 1987) (Fig. 1). The study tree is positioned at the junction of a short debris slope and footslope well above waterways and was first noticed on 30 January 2002. It is presumed to have caught fire during 1–3 January when a wildfire occurred in the catchment. The remains of the tree consist of a standing trunk 2.75–3.5 m high and an unburnt portion of upper trunk and branches, 15–16 m long, lying on the ground directly downslope of the standing trunk (Fig. 2). A cavity 0.75 m deep, lined by charred wood and partly filled with water, occurred in the top of the standing trunk. This part of the tree had a wider girth than the trunk below (478 cm versus 280 cm at its smallest girth 1.3 m above ground level). Four protuberances from the trunk occurred below the breakage line. These varied from 20 to 70 cm wide (across the trunk), 20–80 cm long (down the trunk) and 10–20 cm deep so that the tops formed a gently sloping step back onto the trunk. Epicormic shoots sprouted from one of the larger protuberances within 3–4 months of the fire.

Separated from the trunk and the fallen portion of the tree there was a strip (trace) of ash and wood-ash stone that extended 3.5 m from the start of the charred end back towards the standing trunk (Fig. 1). This is interpreted as part of the original fallen tree that continued to burn whilst on the ground. From these observations the following burn history of the tree is deduced.

- The tree caught fire about 3 m above ground level some time between 1 and 3 January 2002, possibly starting where hot embers were trapped on a protuberance.
- The fire burnt deep into the tree at about this height, leading to toppling of the upper 20 m or so some time after the main fire passed, as all the ground cover and shrub understorey were burnt but not the fallen upper branches and leaves.

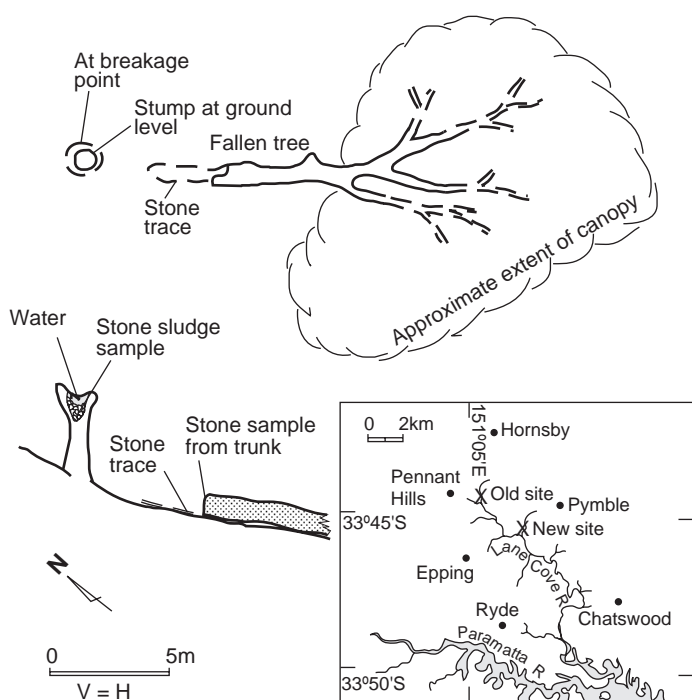


Figure 1. Position of trunk in relation to tree in plan and vertical view. Inset of Lane Cove valley and location of two sites.

- The upper part of the standing trunk possibly continued to burn or smoulder to create or enlarge the bowl, which subsequently filled with rainwater.
- The fallen tree continued to burn, leading to consumption of 3.5 m of trunk.
- The actual period of burning was probably less than one week as a significant shower occurred on 6–7 January (24.5 mm was recorded at Macquarie University automatic weather station which is located <1 km to the south).

Methods

Three wood-ash stone samples were selected for analysis: (i) from the standing trunk, (ii) from the trace of the trunk burnt on the ground, and (iii) from within the on-ground portion of the trunk. Major elements were determined by Energy-Dispersive Polarised X-Ray Fluorescence (EDPXRf) on a SPECTRO X-Lab 2000 X-Ray Spectrometer. This analysis was undertaken on crushed (TEMA tungsten carbide mill) samples (0.3–0.4 g) fused with lithium tetraborate/metaborate flux at 1050°C and set in a carbon die to form glass discs. Loss on ignition was measured by heating samples in a muffle furnace at 1000°C for 4 h. Mineralogy was determined using X-ray diffraction (XRD) with a Philips PW1800 microprocessor and Co K α radiation, a variable divergence slit and a graphite monochromator. The diffraction patterns were analysed using the commercial software package XPLOR (CSIRO Land and Water). Thin sections were prepared from impregnated (araldite) undisturbed samples and were examined under a petrological microscope.

Results

Characteristics of the stone

The appearance of the wood-ash stone varied over the site. Material from within the hollow consisted of a mixture of whitish calcareous sludge and larger lumps, often >2–6 cm long and wide, of wood-ash stone, charcoal and charred wood. Some smaller discrete lumps, about 1 cm, were positioned on the rim of the water-filled cavity. The sample material was obtained as blind grab samples and hence larger but fragile lumps may have been present. Though lumps of charcoal of similar size were present, it was not possible to observe the contact between the wood, charcoal and stone. In appearance this stone was porous, with an elongated structure resembling wood. No good examples of flow structures were noted. In contrast, the trace material formed a mat about 50 cm wide and about 1 cm thick, positioned along the apparent central axis of the burnt trunk. The mat consisted of randomly oriented splinters of whitish carbonate that formed a loose mesh directly on the sandy mineral soil surface and, in places, welded portions with smooth flow features that indicated a molten phase (Fig. 3). The fragility of the mat was apparent on handling, which resulted in broken segments 5–10 cm long and about 5 cm wide. Little charcoal was present as this section of the trunk had been mostly consumed. The stone from the on-ground tree was more powdery and easily crumbled in the hand, and sand grains could be detected. This material extended to within 2–5 cm of the edge of the trunk but penetrated only 10–15 cm into the trunk. The contact between the stone and the tree consisted of charcoal 1–3 cm thick, thence burned wood of a similar thickness and thence unburned wood. This burn pattern probably indicates slow uniform burning. These three stone materials had also been affected differently in the post-fire period. The bowl material was immersed in water and the trace material was affected by rain splash and possibly runoff as the slope displayed numerous erosional and depositional features such as pedestals, litterdams and



Figure 2. The burnt *Angophora costata* showing the standing trunk, the fallen trunk and upper canopy. The pale patch extending from the burnt end of the fallen trunk back towards the standing trunk represents the remains of the burnt trunk. Photo date: 16 June 2002.

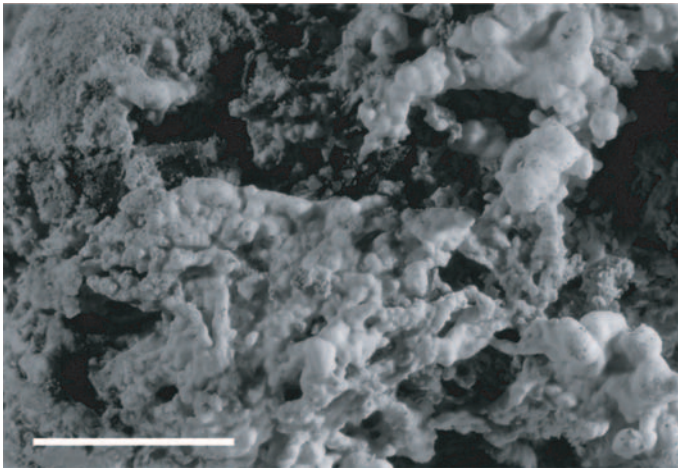


Figure 3. Close up of ‘trace’ (sample No. 1298) wood-ash stone. Note the small patches of smooth globular lumps, which suggest flowage during fusion. Bar length: 5 mm.

microterraces (e.g. Mitchell and Humphreys 1987; Zierholz *et al.* 1995). In contrast, the stone from the on-ground tree was partly sheltered from direct rainfall. Nevertheless, at the time of initial observation, the stone was ‘protected’ by a rim of the outer trunk, 5 cm wide. This probably implies that an equivalent thickness of stone had been dislodged by rain splash since the fire. Overall, the amount of stone produced is conservatively estimated to be about 20 kg dry weight.

Elemental composition

The elemental composition of the wood-ash stone from the recently-sampled tree, together with all other known records, is given in Table 1. Notwithstanding the different morphologies and post-burn histories, the compositions of the three samples from the present study are very similar if the amount of silica is ignored (Table 1). Calcium dominates, followed by Mg, K and Na with very small amounts of Al, Fe, Mn, P, S and Ti. The silica is probably quartz and is unlikely to be a constituent of wood-ash stone (see next section). The older Lane Cove valley sample is also dominated by Ca, but K replaces Mg in relative importance. The North American samples contain more K than Ca. The western hemlock samples contain modest levels of P, Mg and Na and, in one sample, Mn. These data therefore indicate both compositional variation between species and between individuals even when they are from similar sites.

Mineralogy

The XRD analysis indicates the dominance of calcite in all three samples from the new wood-ash stone (Fig. 4). In addition, the on-ground tree sample contained some quartz. An examination of this material in thin section as well as the trace material revealed the presence of sand-sized quartz as infillings in burrow features (pedotubes), 3–5 mm in diameter. These pedotubules resemble termite infillings found in soils and tree/shrub stems (Lee and Wood 1971; Humphreys 1994) and may indicate the presence of ‘mud-gut’ in this tree, though none was detected in the unburnt

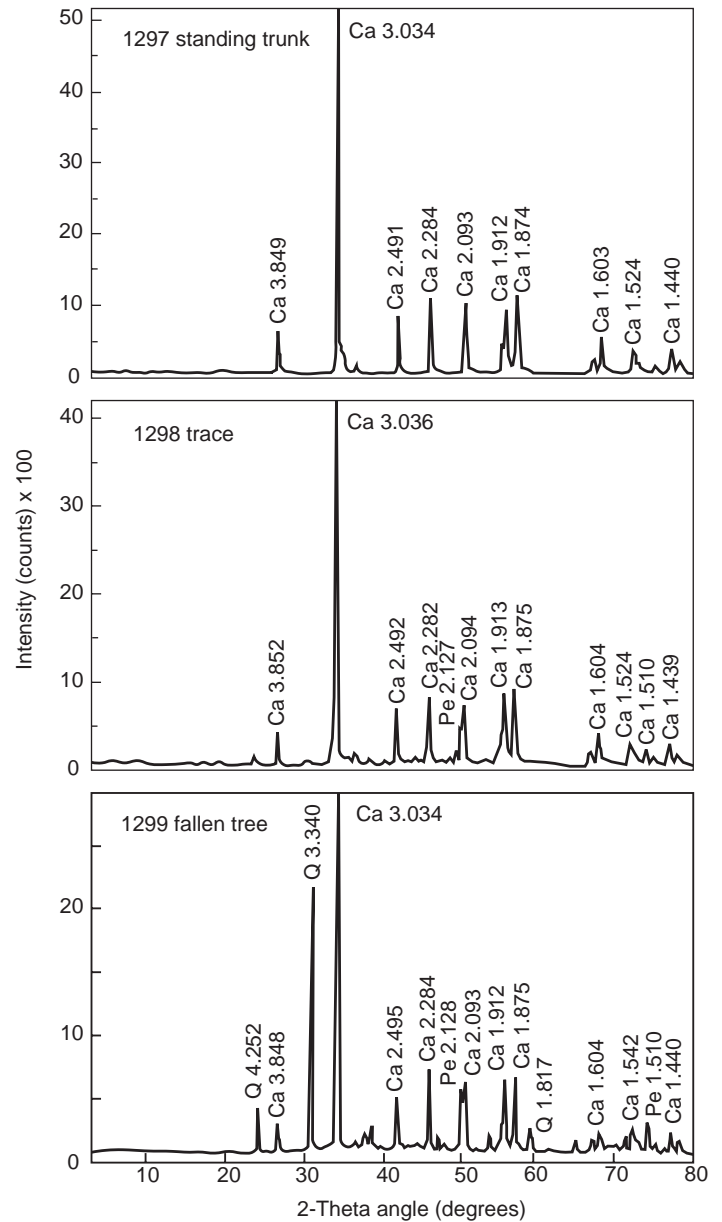


Figure 4. XRD traces of three samples: No. 1297 from standing trunk, No. 1298 from trace of remnant burnt trunk, No. 1299 from remains of fallen tree. The peaks of calcite (Ca), quartz (Q) and periclase (Pe) are indicated.

portion of the tree. It is also possible that some of the Si might be in the form of opal phytolith ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) which is often deposited between and within plant cells (Hart 1990). In detail the XRD traces indicate minor substitution of Mg /Fe in the calcite and the possible presence of small amounts of periclase (native magnesia) and possibly dolomite and aragonite. The potassium carbonates kalicinite, buetschliite and fairchildite noted by others (e.g. Milton and Axelrod 1947; Dietrich 1971) were not identified. Also a metastable, unidentified tri-carbonate mineral (modal composition of 40% CaO, 23% K_2O and 6% Na_2O) reported by Humphreys *et al.* (1987) was not detected. The absence of these rare potassium carbonates is not surprising given the relatively low concentration of potassium in the XRF analysis (Table 1).

Table 1. Elemental composition of fused wood-ash stones (%)

Component	Australia				North America					Ratio of oxides ^f
	Smooth-barked apple				Western hemlock			Fir tree ^d	Oak tree ^e	
	Tree 1 ^a	Trace1 ^a	Trunk 1 ^a	Tree 2 ^b	Tree 1 ^c	Tree 2 ^c	Tree 3 ^c			
CaO	32.36	32.79	26.61	25.69	22.02	21.90	21.79	18.50	16.20	2.25
K ₂ O	3.59	4.83	2.48	13.28	25.01	24.54	30.42	23.60	40.40	12.04
MgO	13.07	11.69	8.31	7.45	6.28	4.48	4.06	2.3	0.51	1.58
Na ₂ O	1.42	1.52	0.72	2.60	5.31	2.06	4.20	10.7	1.75	5.40
SiO ₂	1.05	8.96	28.22	1.62	0.32	0.38	0.41	nd	0.43	nd
Al ₂ O ₃	0.16	0.48	1.24	0.41	1.68	0.99	0.34	1.0	0.19	nd
Fe ₂ O ₃	0.08	0.10	0.21	0.11					0.15	9.42
P ₂ O ₅	0.52	0.16	0.16	0.08	6.96	6.58	5.47	nd	1.96	17.51
MnO	0.33	0.28	0.23	0.06	1.13	1.23	6.67	nd	0.22	2.54
TiO ₂	0.01	0.11	0.32	0.01	nd	nd	nd	nd	tr	nd
S	0.018	0.084	0.017	nd	tr	tr	0.27	0.28	nd	nd
CO ₂	nd	nd	nd	nd	19.67	25.47	nd	nd	35.34	nd
LOI	47.23	38.98	31.59	49.64	nd	nd	nd	nd	nd	2.33
Total	99.83	99.98	100.1	100.9	nd	nd	nd	nd	101.6	
^g (Ca+Mg)/(Na+K)	14.77	11.54	17.94	3.51	1.56	1.71	1.25	0.91	0.66	

LOI = loss on ignition

nd = not determined

tr = trace

^aSmooth-barked apple, *A. costata*: tree 1, standing trunk (sample No. 1297); trace 1 (sample No. 1298); trunk 1, on-ground tree (sample No. 1299).^bSmooth-barked apple, *A. costata*: tree 2 — Lane Cove valley, NSW (Humphreys *et al.* 1987)^cWestern hemlock, *Tsuga heterophylla*: trees 1 and 2 — Kaniksu National Forest, Idaho (Englis and Day 1929); tree 3 — Wind River, Washington (Englis and Day 1929).^dWhite fir, *Abies concolor*: Grand Canyon National Park, Arizona (Milton and Axelrod 1947).^eChestnut oak, *Quercus prinus*: Long Shop, Virginia (Dietrich 1971).^fRatio of average tree wood to stone composition of *A. costata* (average of tree 1, trace 1 and trunk 1) assuming ratio of sapwood to heartwood of 0.575:0.425, 47 kg of dry ash produced from about 2.1 m³ of burnt wood, and dry ash content of 1.455% and 2.635% for sapwood and heartwood respectively. Wood analysis as per Humphreys *et al.* (1987). Values >1 indicate that there is sufficient of the element in the estimated dry ash to account for the composition of the stone.^gMolar ratio.

Discussion

Despite various studies, the formation of wood-ash stone remains poorly understood except in very general terms (Humphreys *et al.* 1987). Nevertheless, the presence of lumps of carbonate, some showing evidence of flowage, indicates the fusion of elements at temperatures <1000°C since CaCO₃ decomposes at about 900°C. This situation may be best achieved where a tree burns slowly downwards especially, it seems, if the centre of the trunk has been subjected to decay (e.g. Kienholz 1929; Milton and Axelrod 1947). Fire moving up the tree is likely to achieve higher temperatures and hence no carbonate. This scenario accounts for the presence of a wood-ash stone in standing burnt trunks rather than in logs and trunks on the ground. However, the present study indicates that on-ground formation can occur too, but this would seem to be possible only if temperatures remained less than 900°C. The small amount of trace stone may indicate that lower temperatures conducive to carbonate formation developed only where the trunk was in contact with the ground (since the ground is a poor conductor and hence acts as a cooling medium) and/or towards the end of the pyrolysis event.

Wood-ash stone is quite unlike the appearance and description of other calcite 'stones' that develop as a secretion around injured parts of some tropical species, especially *Chlorophora excelsa*

and *Millettia* sp. (Campbell and Fisher 1932; Harris 1933; Plancquaert 1946; Carozzi 1967). It is also unlikely that the wood-ash stone calcite developed from the pyrolysis of calcium oxalate crystals, a transition that occurs at temperatures of 430–510°C (Pobeguain 1943; Brochier *pers. com.*), since the typical micritic microstructure that the calcite crystals develop by this route (Brochier and Thion 2003) is very different from the calcite found in wood-ash stone.

In comparison to North American samples, the Australian material is relatively enriched with Ca and Mg and deficient in K and Na. A possible explanation for this is the expected greater levels of leaching in the Australian examples, which were exposed to rain in various ways. Another possible reason for the difference may relate to the nutrient status of the growing medium. It is well known that Hawkesbury Sandstone soils are nutrient poor and deficient in many essential plant nutrients (e.g. Beadle 1954; Chapman and Murphy 1989). This may explain the low values of some elements such as P, but it does not readily account for all of the differences noted above. Previously Humphreys *et al.* (1987) suggested that a reasonable supply of K, Na, Mg, Fe and especially Al and Si could be obtained from Hawkesbury Sandstone rock minerals of quartz, kaolinite, illite mixed-layer clays, feldspar, biotite and siderite, even though some of these (especially K, Na and Mg) are not retained in the soil. However, the composition of the rock

or the soil does not easily account for the amount of Ca. This provides a clear indication that there is either another source of some elements or that the biogeochemical cycling may be quite complex and/or operate over long periods of time. Nevertheless, regardless of the soil/rock nutrient level, the composition of wood from *A. costata* growing on Hawkesbury Sandstone shows that there is enough of all elements to account for the composition and mass of wood-ash stone (Table 1, last column; Humphreys *et al.* 1987). In this case about 47 kg of dry ash is estimated to have been produced from 2.1 m³ of consumed trunk to yield about 20 kg of wood-ash stone, and the ratio for each major element between the dry ash and wood-ash stone is >1. It is also possible that the variable composition might relate to the pyrolysis temperatures achieved during fusion. For example Thy *et al.* (2000) note that initial heating of straw wood-ash leads to a partial loss of K and Na (i.e. alkali metals) in contrast to Ca and Mg (alkaline-earth metals) and to a lesser extent P. Hence a higher ratio of Ca or Mg to Na or K would imply relatively higher temperatures. This effect is explored by using the molar ratio of Ca + Mg to Na + K (Table 1). Studies demonstrating the presence of potassium carbonates exhibit ratios of 0.66 to 0.91, whereas the present study with calcite as the dominant mineral has the highest ratios of 11.5 to 17.9. An intermediate value of 3.51 for the older *A. costata* sample would seem to reflect the dominance of calcite and the unidentified tri-carbonate mineral noted above. If valid this index indicates that the temperature was highest in the recent example and lowest in the North American examples.

As noted above this is the second find of wood-ash stone in Australia and outside North America. but there appear to have been no new finds from the latter region for over 30 years. This is somewhat surprising given the greater awareness of forest fires not only on both continents, but globally. Thus, the occurrence of wood-ash stone must be considered quite rare. Yet, given the needs to better utilise forest products, there remains a demand for knowledge of the changes induced when burning biomass. This need is well recognised where wood is used as a fuel and where the by products of combustion are considered in terms of fertilisers and other useful materials and/or where these products reduce thermal efficiency in power plants (e.g. Thy *et al.* 2000).

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