

Article

Rhombohedral $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, a new pyro-biophase formed in the ash of the desert spoon (*Dasyllirion wheeleri*) from the Sonoran Desert

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Abstract

Terrestrial vascular plants affect Earth's long-term geological processes, contributing to carbon cycling, chemical weathering and soil formation. Plants transport elements from the soil to their above-ground structures, accumulating a range of macroelements including Na, K, Mg, Ca, Si, S, P and Cl. Wildfire combustion concentrates these macroelements into inorganic ash. This ash is dominated by oxides, carbonates, halides, sulfates and phosphates of Na, K, Mg and Ca. This work describes $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, which occurs abundantly in the ash of the desert spoon (*Dasyllirion wheeleri*), a plant native to the Sonoran Desert. Electron microprobe analysis, powder X-ray diffraction Rietveld refinement and Raman spectroscopy confirm that this phase matches synthetic rhombohedral (R3) $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$. This phase forms during the smouldering combustion of *D. wheeleri* trunks, producing friable, decimetre-sized, porous, ash lumps that pseudo-morphically preserve the plant's fibrous structure. This ash occurs as glassy, sintered, porous aggregates, dominated by $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, with sylvite, calcite, fairchildite, arcanite and minor hydroxyapatite and periclase. Several double K–Ca carbonates form under surficial pressures and temperatures below $\sim 800^\circ\text{C}$, including $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, and bütschliite ($\text{K}_2\text{Ca}(\text{CO}_3)_2$) and its dimorph, fairchildite. The occurrence of rhombohedral $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and fairchildite are consistent with smouldering between 518 and 780°C . Upon exposure to water, $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ rapidly decomposes, leaving calcite. The occurrence of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ as a major phase in the plant ash expands our understanding of Earth's mineral diversity, provides new insights into the widespread geological process of wildfire ash formation and highlights the role that these fires play in forming mineral phases that are rare in other geological settings. Though $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ was first identified in *Dasyllirion wheeleri*, this phase probably forms in other fire-adapted plant species. The occurrence of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ in plant ash is an example of an inorganic phase that bridges the gap between biomineralisation and geological mineral formation.

Keywords: rhombohedral double carbonate; wildfire; ash; $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$; pyro-biophase; electron microprobe analysis; powder X-ray diffraction Rietveld refinement; Raman spectroscopy

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Introduction

Terrestrial vascular plants play a key role in Earth's long-term geological processes, influencing and contributing to, for example, carbon cycling, chemical weathering and soil formation. These plants inhabit the subaerial and subterranean environment simultaneously, where they continuously transport elements from the shallow soil environment to above-ground organic structures. Concomitant with this life process is the sequestration of atmospheric CO_2 into the organic architecture. Plants contain a wide range of macroelements translocated from the soil environment to their above-ground structures, most notably Na, K, Ca, Si, S, P and Cl. These elements can reach concentrations of 1000 to 10,000 ppm

levels or higher in the dried plant material (Calva-Vázquez *et al.*, 2006; Garvie, 2016; Ramírez *et al.*, 2006; Ramírez-Orduña *et al.*, 2005; Zárubová *et al.*, 2015). Calcium occupies a special role in plants as it concentrates in the biominerals weddellite and whewellite, which can themselves concentrate to high levels. For example, a large saguaro cactus (*Carnegiea gigantea*) contains on the order of 1×10^5 g of the Ca oxalate weddellite (Garvie, 2006): the Ca is translocated from the soil in water taken up by the roots of the rhizosphere (White and Broadley, 2003). The fate of the macroelements in plants can depend on the manner of their demise. During aerobic decay, plant carbon is largely emitted back into the atmosphere because of decomposition by bacteria and fungi. Whereas the fate of the macroelements during aerobic decay is less well understood, they are probably solubilised and returned to the soil. In contrast, combustion converts many of a plant's macroelements into an inorganic ash that accumulates on the soil surface and is emitted into the atmosphere in smoke.

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Wildfire is a geological process that influences widespread surficial mineral formation, erosion patterns, sediment transport, soil formation, and the shaping of vegetation patterns over geological time periods (Galloway and Lindström, 2023; Rengers and McGuire, 2021). The immediate aftermath of a wildfire is charred plants and an inorganic ash residue. This residue is primarily inorganic (e.g. Anca-Couce *et al.*, 2012; Bodí *et al.*, 2014; Carvalho *et al.*, 2002; Daouk *et al.*, 2015; Garvie, 2016), produced by a self-sustaining smouldering process, a form of non-flaming combustion. Smouldering is a complex physico-chemical process that generates a thermal wave that involves dehydration (<100°C), oxidation and pyrolysis (<400°C), leading to the formation of char (Anca-Couce *et al.*, 2012; Ohlemiller, 1985). In most self-sustaining smouldering reactions, char oxidation serves as the primary heat source that drives the lower-temperature dehydration, oxidation and pyrolysis of wood. Char oxidation temperatures typically range from 400 to 700°C, with the formation of an inorganic residue of ash.

Plant ash formed by wildfires contains a wide range of minerals and bio-pyrophases, e.g. Vassilev *et al.* (2013). The mineralogy of ash is influenced by the concentration of plant macroelements, most commonly Na, K, Mg, Ca, Si, S and Cl, along with factors including oxygen availability, combustion temperature, type of fuel, and environmental conditions (Garvie, 2016; Liodakis *et al.*, 2005; Yusiharni and Gilkes, 2012). For instance, the wood of the desert tree *Parkinsonia microphylla* contains significant levels of K, Ca and Mg, resulting in ash dominated by fairchildite ($\text{K}_2\text{Ca}(\text{CO}_3)_2$) and its dimorph bütschliite, calcite (CaCO_3), lime (CaO), and periclase (MgO), with trace amounts of K-bearing salts (Garvie, 2016). In the same region, the wood of the desert tree *Prosopis juliflora* is rich in K, Ca and Cl, with ash dominated by sylvite (KCl) and calcite (Garvie *et al.*, 2015). Similarly, ash from Australian native plants contains a variety of minerals, including calcite, fairchildite, nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$), and sylvite (Yusiharni and Gilkes, 2012). The mineralogy of the ash is also influenced by burn conditions. For example, Liodakis *et al.* (2005) examined the ash of six Greek forest species at combustion temperatures of 600, 800 and 1000°C. At 1000°C, the ash is dominated by simple oxides, carbonates and sulfates of Ca, Mg and K, such as lime, periclase, K_2SO_4 , and K_2CO_3 . At 600°C, the ash contained these same phases together with calcite, $(\text{Ca,Mg})\text{CO}_3$, and $\text{Ca}(\text{OH})_2$, and the double carbonates fairchildite and $\text{K}_2\text{Ca}(\text{CO}_3)_2$. These studies illustrate the mineralogical diversity of plant ash.

Three K–Ca carbonates are expected at surficial pressures and below ~700°C, i.e. bütschliite $\text{K}_2\text{Ca}(\text{CO}_3)_2$ and its dimorph fairchildite, and $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (Arceo and Glasser, 1995; Arefiev *et al.*, 2019a; Arefiev *et al.*, 2019b; Winbo *et al.*, 1997). Fairchildite is widely reported in plant ash (Englis and Day, 1929; Garvie, 2016; Humphreys *et al.*, 2004; Milton and Axelrod, 1947), with masses of a “hundred pounds or more” (Milton and Axelrod, 1947). These large masses form clinkers within burning trees through a process called pyro-biomineralisation (Humphreys *et al.*, 2003). Clinkers from several locations have similar compositions, being dominated by fairchildite (Milton and Axelrod, 1947) and calcite (Humphreys *et al.*, 2004). Though less widely described, bütschliite is also found in ash (Dawson and Sabina, 1957; Mandarino and Harris, 1965). The experiments of (Pabst, 1974) show the formation of bütschliite as a reaction product of heating K_2CO_3 and CaCO_3 at 420°C and 505°C. No reaction took place at 340°C, whereas fairchildite formed at 585°C. Depending on temperature and composition in the K_2CO_3 – CaCO_3 system, experiments at room pressure produce various proportions of K_2CO_3 , calcite, fairchildite, bütschliite,

and the double carbonate $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (Arceo and Glasser, 1995; Arefiev *et al.*, 2019a; Kröger *et al.*, 1943). The double carbonate $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ crystallises in space group *R*3 with unit cell dimensions $a = 13.010(4)$ Å, $c = 8.615(3)$ Å, $V = 1262.9(9)$ Å³, $Z = 6$ (Winbo *et al.*, 1997). To date, $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ has not been described as a mineral, though Winbo *et al.* (1997) suggested that it “should occur in combustion products [of plant materials]”.

Here is described the double carbonate, $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, a new ash bio-pyrophase that occurs in the ash of the desert spoon plant (*Dasyllirion wheeleri*) from the Sonoran Desert. Electron microprobe analysis, powder X-ray diffraction Rietveld refinement and Raman spectroscopy confirm that this phase matches synthetic rhombohedral (*R*3) $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$. Note, though the description of the rhombohedral $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ was submitted to the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association as a new mineral (IMA2022-037a), the proposal was rejected. The rejection was based on the fact that a human cause for the ignition of the 180,757-acre Telegraph wildfire could not be unequivocally ruled out, and there is no consensus as to whether ‘wildfire’ constitutes a geological process. Because of this lack of consensus, the mineral status of inorganic materials formed by wildfires acting on plant matter remains uncertain.

Materials and methods

Field ash

Ash from *Dasyllirion wheeleri* plants was collected at 33°15'7.62" N, 111°7'0.40" W, near the small town of Superior, Arizona, USA, following the Telegraph Fire in June 2021. Samples were taken from eight burnt *D. wheeleri* plants and stored in a dry nitrogen atmosphere to prevent moisture exposure. Many minerals in the ash, including $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, are sensitive to moisture. The samples studied here were collected within a few days of having formed during the Telegraph Fire. In addition, all sample preparation, such as grinding and polishing, required the use of non-polar solvents, as well as storage of samples in a dry atmosphere.

Powder X-ray diffraction and Rietveld refinement

Powder X-ray diffraction (XRD) patterns were acquired with a Rigaku MiniFlex 600 diffractometer. This diffractometer is operated with $\text{CuK}\alpha$ radiation and is equipped with an automatic divergence slit system and post-diffraction graphite monochromator. Data were acquired from 2 to 65°2 θ at 0.02° steps and 30 s/step. The diffractometer was aligned with the Si powder standard (NBS 6d), and the experimental pattern was further corrected by adding the NDS Si powder as an internal standard. XRD samples were prepared from ~50 mg fragments of ash. Fragments were crushed and lightly ground to a fine powder and mixed with a few millilitres of toluene. The resulting slurry was pipetted and spread into a thin, smooth film on a low-background, single-crystal, quartz plate. This slurry was dried rapidly (~5 s) under flowing warm air, forming a thin film on the quartz plate.

Refinement of the powder XRD pattern was undertaken with Profex 5.3, which is a graphical user interface to the Rietveld refinement program BGMN (Döbelin and Kleeberg, 2015). The refinement pattern was acquired from 10 to 75°2 θ at 0.01° steps and 25 s/step. The following structure files were used for the refinement: fairchildite (Pertlik, 1981); $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (Winbo *et al.*, 1997); calcite (Sitepu, 2009); arcanite (Ojima *et al.*, 1995); sylvite (Walker

et al., 2004); hydroxylapatite (Wilson *et al.*, 1999); and periclase (Hazen, 1976).

Elemental analysis and imaging

Fragments of the ash were embedded in epoxy. The 1"-round sections were dry cut and dry ground down to 1200 grit and then polished for ~20 s with a 1-micron diamond suspended in mineral oil on lapping felt. The sample was then washed with toluene. Quantitative elemental microanalyses using wavelength dispersive spectroscopy (WDS) were acquired at the University of Arizona's Michael J. Drake Electron Microprobe Lab with a CAMECA SX100 electron microprobe (15 kV and 6 nA, 10 mm beam). Ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ damages rapidly, even with a 10 μm beam. This damage was mitigated during the ~3 minute WDS acquisition by continuously moving the sample under the beam during the analysis – this movement was possible by simultaneously observing the crystal with an attached optical microscope while acquiring the WDS data. Element-distribution maps were acquired with the Zeiss Auriga high-resolution field emission scanning electron microscopy (SEM) equipped with an Oxford X-Max energy dispersive X-ray Spectrometer (EDS) at the John M. Cowley Center for High Resolution Electron Microscopy at Arizona State University.

Raman microscopy

Raman spectra were acquired with the XploRA PLUS microRaman spectrometer microscope with a 532 nm solid-state laser using a Plan N100x objective. Ash was lightly ground in toluene, and

a few ml was dried on a polished stainless steel planchette. The spectra were recorded with a beam power of 17 mW on the sample. Counting times ranged from 50 to 500 s for the 10–2000 cm^{-1} spectral range. Spectral resolution of ~1 cm^{-1} was achieved using an 1800 mm^{-1} grating.

Study site and plant

On June 4th, 2021, the Telegraph wildfire ignited near Superior, Arizona, burning 180,757 acres of native xeric wildlands. The cause of the Telegraph wildfire remains unproven; while human activity is a possibility, a natural origin cannot be ruled out. The fire swept through the Arizona Upland subdivision of the Sonoran Desert, the highest and coolest part of the desert, dominated by the 'saguaro-paloverde forest' plant community. Common in the burn area is *Dasyllirion wheeleri* (Walker, 2020), also known as desert spoon or sotol, which is a medium-sized evergreen xeric monocot shrub with an unbranched trunk, common in the Chihuahuan and Sonoran Deserts.

D. wheeleri is a monocotyledon with a trunk anatomically similar to other monocots, such as palms (Fathi *et al.*, 2014; Parthasarathy and Klotz, 1976). Its trunk consists of a fibrous network of tangled primary vascular bundles embedded in lighter-coloured parenchymatous ground tissue (Fig. 1A). Powder XRD analysis of these vascular bundles shows reflections from whewellite, set against a broad background from scattering by the organic woody material. When a piece of trunk dominated by vascular bundles was submerged in sodium hypochlorite solution, the organic matter dissolved, leaving behind a white sediment

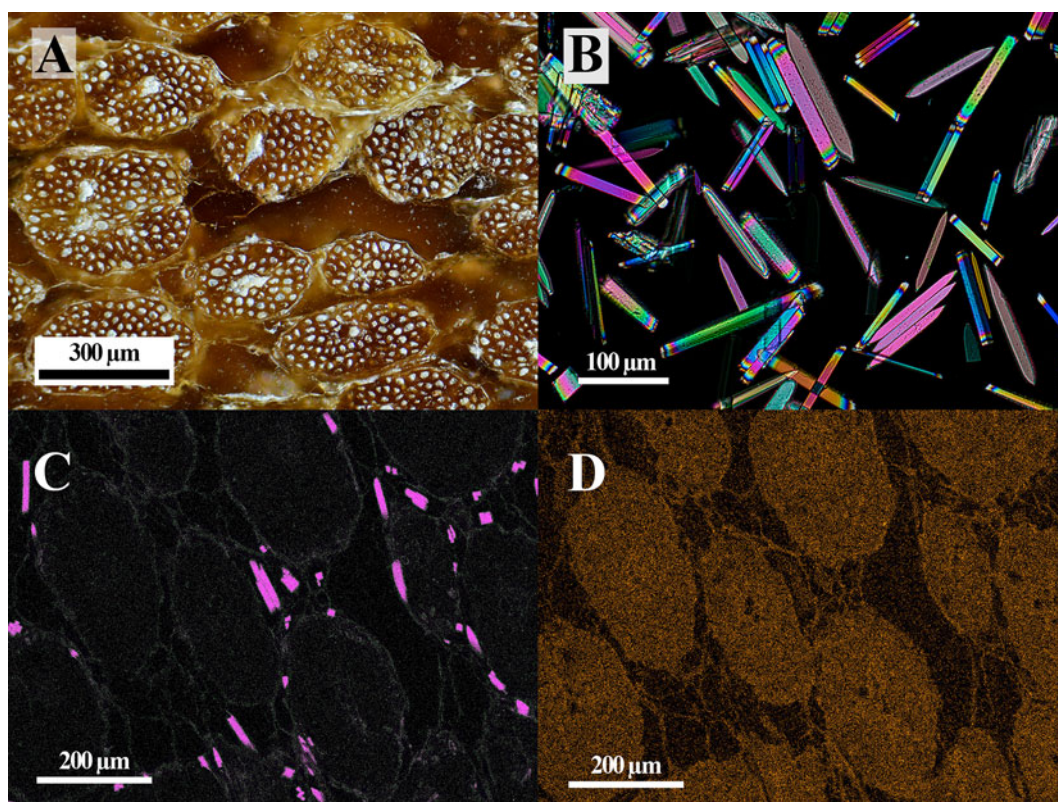


Figure 1. (A) Reflected-light optical photograph of a polished section of unburnt *Dasyllirion* stem wood. (B) Whewellite crystals extracted from the stem wood viewed under cross-polarised light. (C) Calcium and (D) potassium EDS element-distribution maps showing the distribution of whewellite (pink) crystals in the wood.

composed of euhedral raphids (Fig. 1B). The powder XRD pattern of this sediment matches whewellite.

The EDS spectroscopy of the vascular bundles shows prominent peaks for K and Cl, along with less intense peaks for Ca, Mg, S, Na, Si and P (Supplementary Fig. S1). The qualitative EDS analysis suggests the following (wt.% and at.%) averaged over a 1×0.75 mm area of the wood: 2 and 0.6 K; 1 and 0.37 Cl; 0.6 and 0.2 Ca; 0.3 and 0.12 S; and 0.1 and 0.05 Mg. Element-distribution imaging using EDS shows that whewellite is present within the parenchymatous tissue surrounding the vascular bundles (Fig. 1C), whereas the other macroelements, such as K (Fig. 1D), are more uniformly distributed throughout the organic material.

Ash results

The *D. wheeleri* ash logs consist of friable, decimetre-sized, porous, white to grey sintered masses (Fig. 2). Photographs of the char from the partially burnt trunk show interconnected tangles of the vascular bundles with an abundance of 200 μ m long colourless, white crystals (Fig. S2). Powder XRD patterns of the char show Bragg reflections for calcite and minor whewellite sitting on the broad scattering maximum from the charred organic material. Char oxidation caused by the smouldering leaves sintered masses

of inorganic ash that pseudomorphically preserves the fibrous structure of the original plant (Fig. 2B).

Powder XRD patterns of the ash logs show reflections that are dominated by reflections for $K_2Ca_2(CO_3)_3$ (Winbo *et al.*, 1997) and fairchildite (Fig. S3), lesser sylvite, calcite and arcanite, and minor hydroxylapatite and periclase. Multiple samples and areas of ash were sampled by XRD. Single-crystal X-ray studies could not be undertaken for the ash $K_2Ca_2(CO_3)_3$ because of its intimate association with the other minerals and because of the polycrystalline nature of the grains. The latter was confirmed by viewing the grains under crossed-polarised transmitted light. The structural identity of $K_2Ca_2(CO_3)_3$ in the ash was determined by Rietveld refinement (Fig. 3). The powder XRD pattern that showed the ash $K_2Ca_2(CO_3)_3$ phase was refined with a final $\chi^2 = 1.58$ ($R_p = 3.49\%$, $R_{wp} = 3.97\%$, $R_{exp} = 3.16\%$, $GoF = 1.18$, Durbin-Watson $d = 0.62$), for 6501 measured points, 465 peaks and 368 parameters (Fig. 3, Supplementary Table S1 and Supplementary CIF and checkcif files). The $K_2Ca_2(CO_3)_3$ is associated intimately with the other minerals, and so all minerals in the ash were refined (Table 1). The

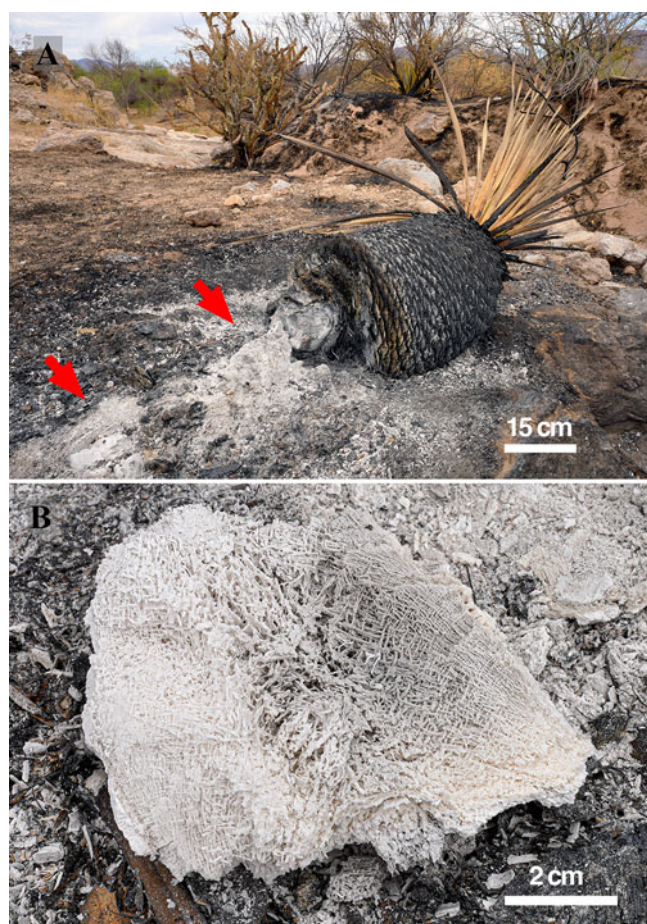


Figure 2. Photograph of a burnt *Dasylirion wheeleri* plant following the wildfire combustion. (A) The recumbent trunk has smouldered, leaving large chunks of white inorganic ash (red arrows). (B) Close-up photo of an ash chunk that preserves the fibrous nature of the plant.

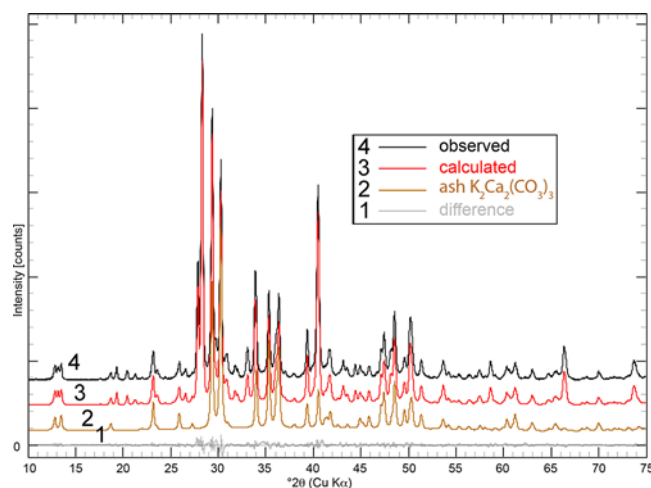


Figure 3. Rietveld refinement of the *Dasylirion wheeleri* ash showing the observed pattern (black), calculated profile (red), refined pattern for the ash $K_2Ca_2(CO_3)_3$ (tan), and the difference pattern (grey). The calculated pattern refines with 56.1% $K_2Ca_2(CO_3)_3$ + 17.6% sylvite, + 13.5% fairchildite, 7.5% calcite, 2.8% arcanite, 1.8% hydroxylapatite and 0.7% periclase. The patterns are shifted along the y-axis for clarity.

Table 1. Cell parameters and phase fractions determined by Rietveld refinement for the minerals in the wildfire ash

Mineral	R_{phase} (%)	Refined cell parameters (Å)	Refined fraction (%)
Ash $K_2Ca_2(CO_3)_3$	3.67	$a = 13.0564(2)$ $c = 8.6369(2)$	56.1
Sylvite	2.72	$a = 6.2941(1)$	17.6
Fairchildite	4.14	$a = 5.2879(1)$ $c = 13.3962(6)$	13.5
Calcite	3.09	$a = 4.9915(2)$ $c = 17.045(1)$	7.5
Arcanite	4.13	$a = 5.7727(9)$ $b = 10.060(3)$ $c = 7.4906(9)$	2.8
Hydroxylapatite	4.06	$a = 9.4034(7)$ $c = 6.9307(8)$	1.8
Periclase	3.84	$a = 4.2143(4)$	0.7

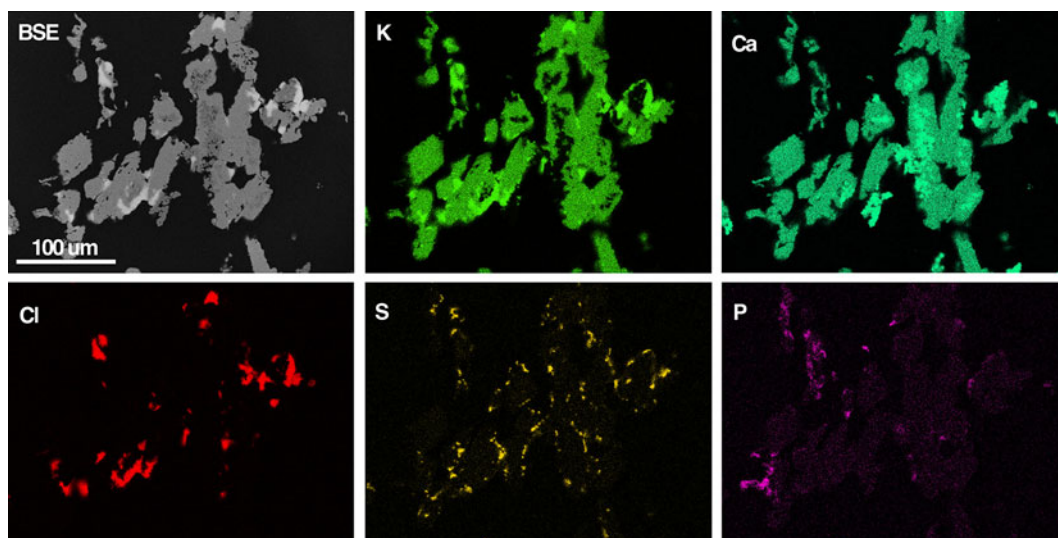


Figure 4. BSE-SEM image of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ -bearing ash (grey) and coloured EDS element-distribution maps for K, Ca, Cl, S and P. The Cl map shows the location of sylvite, the S map for arcanite, and the P map the location of hydroxylapatite. Calcite is visible as the brighter signal in the Ca map, which is dark in the K map. Most of the green signal in the Ca map corresponds to ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, and small regions of fairchildite show a less intense green signal.

ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ is trigonal, R3 (#146), and Rietveld refinement gives $a = 13.0564(2) \text{ \AA}$, $c = 8.6369(2) \text{ \AA}$, $V = 1275.07(6) \text{ \AA}^3$ and $Z = 6$.

The structure of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ comprises two crystallographically distinct carbonate ions, positioned in columns around the three-fold axes, where 25% of the cations (one Ca^{2+} and one K^+) are located. The remaining cations are situated in general positions between the carbonate columns. There are two distinct cation sites: Ca(1) and K(1) are positioned on a three-fold axis in the special position 'a', while Ca(2) and K(2) occupy general positions between the three-fold axes. Each O atom is shared between a C atom and either three or four cations. Tables S2a to S2f show selected interatomic distances and angles. In many common trigonal and orthorhombic carbonates, the carbonate groups are orientated parallel in planes, resulting in layered structures. In contrast, in $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, the carbonate groups are inclined relative to the principal axes. The structure of synthetic $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ is described in detail in Winbo *et al.* (1997).

In ash containing a range of minerals, the ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ is most easily recognised in the powder XRD patterns by the two reflections between 12 and $14^\circ 2\theta$ (CuK α) at 6.8639 (101) and 6.5288 (110, $\bar{1}\bar{2}0$) $\text{\AA}$ (Fig. S4). The 002 reflection for fairchildite occurs between the two ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ reflections forming a triplet. As this region of the diffraction pattern contains relatively few reflections from the other ash components, the presence of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and fairchildite can be readily determined in complex mineral mixtures.

Back-scattered electron (BSE) SEM images (Fig. 4) show aggregates with a branching architecture composed of intimately associated $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, fairchildite, calcite, sylvite and minor hydroxylapatite. $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ occurs as anhedral grains to 200 μm across in the aggregates, though polarised-light microscopy shows these grains to be polycrystalline at the micron scale. The ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ is colourless and transparent, with a vitreous lustre: no fluorescence was noted at either short- or long-wave UV. Aggregates are brittle and give a white streak.

Electron microprobe data were acquired by WDS (Table 2). The composition of the ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ determined by WDS analy-

Table 2. Composition data (in wt.%) for the ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ determined by WDS

Area	K ₂ O	CaO	P ₂ O ₅	SO ₂	CO ₂ *
1	27.32	32.84	0.02	0.04	39.71
2	27.49	33.39	0.04	0.01	39.00
3	28.46	32.00	0.08	0.07	39.29
4	27.23	32.72	0.11	0.04	39.87
5	27.85	32.58	0.07	0.02	39.41
6	27.69	32.99	0.07	0.05	39.10
7	27.68	32.91	0.08	0.17	39.07
8	27.55	33.38	0.12	0.08	38.81
9	27.80	32.76	0.07	0.05	39.17
10	26.84	33.72	0.14	0.07	39.18
11	27.65	32.02	0.07	0.12	40.04
12	27.69	31.91	0.10	0.11	40.07
13	27.42	32.68	0.11	0.08	39.62
14	27.83	33.14	0.08	0.07	38.74
15	28.19	32.50	0.43	0.78	38.01
Mean	27.65	32.77	0.11	0.12	39.27
S.D.	0.39	0.53	0.10	0.19	0.55

Notes: CO₂* – determined by the stoichiometry. S.D. – standard deviation. Note, the minor P and S probably derive from the hydroxylapatite and arcanite, respectively, which are ubiquitous in the grains (see Fig. 4).

sis is (wt.%, $n = 15$) K₂O 27.65 ± 0.39 and CaO 32.77 ± 0.53 , with CO₂ determined by stoichiometry of 39.27 wt.%. The empirical formula (based on 16 atoms pfu) and normalised to 9 oxygen atoms is $\text{K}_{2.01}\text{Ca}_{2.00}\text{C}_{3.00}\text{O}_9$. The ideal formula is $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, which requires (wt.%) K₂O 27.84, CaO 33.14, CO₂ 39.02. The elements Na, Si, Mg, Al, Fe, Mn, P and S were near or below the detection limit and totalled <0.16 wt.%, so they were not included in the table or empirical formula. Only P and S were regularly above detection limits with average P₂O₅ and SO₂ at 0.11 and 0.12 wt.%, respectively. The intimate association of ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ with fairchildite and calcite prevented direct determination of the CO₂ content. The CO₂ concentration was calculated in the stoichiometry.

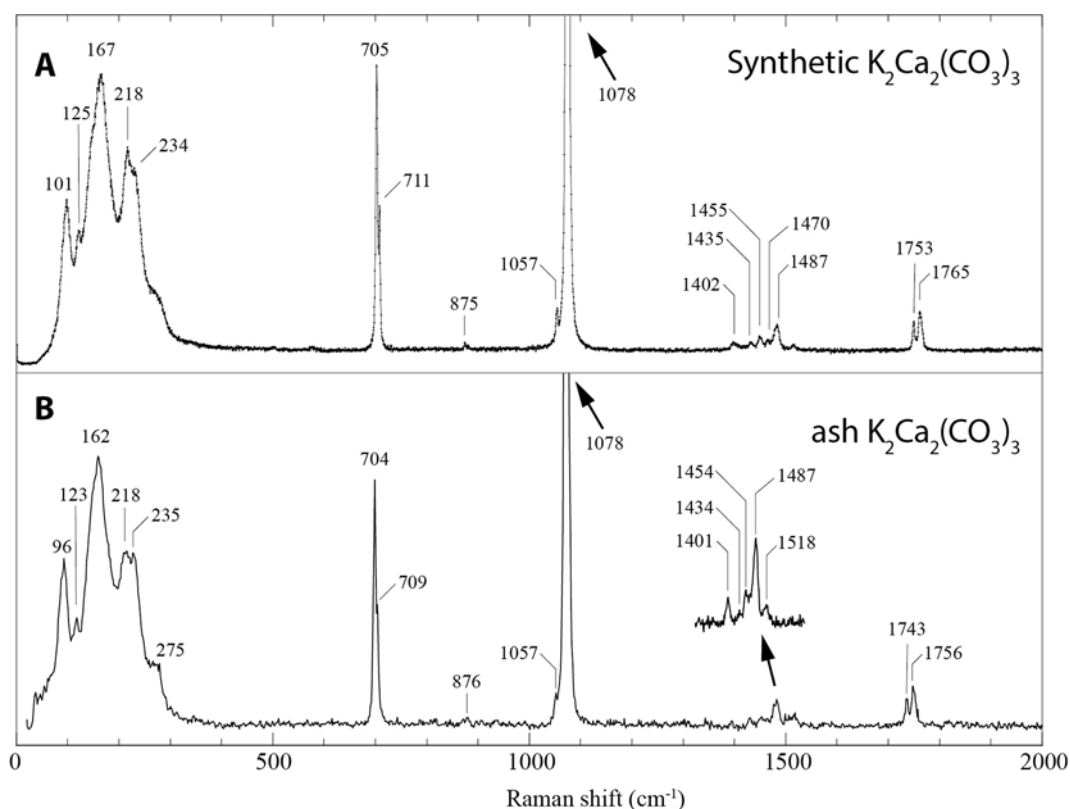


Figure 5. Raman spectrum of (A) synthetic $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (from Arefiev *et al.*, 2019b) compared with (B) ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$. The spectrum was acquired in high-resolution mode (slit = 50 μm , pinhole = 100 μm and 500 s acquisition), except for the inset region between 1400 to 1500 cm^{-1} which was acquired with a slit = 100 μm , pinhole = 500 μm and ten 50 s spectra summed.

The Raman spectrum of ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (Fig. 5) matches that of synthetic $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ (Arefiev *et al.*, 2019a; Arefiev *et al.*, 2019b). The spectrum is dominated by two intense but overlapping bands in the region of symmetric stretching C-O vibrations $\nu_1(\text{CO}_3^{2-})$ at 1078 and 1076 cm^{-1} , and low-frequency bands ascribed to lattice vibrations. This double band dominates the intensity of the Raman spectrum, with the next most intense band at 162 cm^{-1} only 7% of its intensity. The region attributed to $\nu_4(\text{CO}_3^{2-})$ asymmetric in-plane bending shows two sharp resolved bands at 704 and 709 cm^{-1} . In addition to these intense vibrations from the CO_3^{2-} groups, the following bands and assignments are present: weak band at 876 cm^{-1} corresponding to the symmetric out-of-plane mode $\nu_2(\text{CO}_3^{2-})$; several bands between 1400 and 1500 cm^{-1} corresponding to the asymmetric stretching $\nu_3(\text{CO}_3^{2-})$ vibrations; and two bands at 1743 and 1756 cm^{-1} corresponding to the combination vibrations $\nu_1 + \nu_4$.

The ash minerals, including ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$, are stable in the air under normal laboratory low-humidity conditions. However, washing the ash with water leaves a residue of calcite, hydroxylapatite and minor periclase.

Discussion

Within the temperature range produced during smouldering, i.e. 400 to 700°C and at atmospheric pressure, the K_2CO_3 – CaCO_3 phase diagram contains several K, Ca and K–Ca carbonates, with compositions dependent on the K to Ca ratio and temperature (Arefiev *et al.*, 2019a; 2019b). Above 50 mol.% K_2CO_3 and below 520°C, the system is dominated by K_2CO_3 and bütschliite, and

above this temperature K_2CO_3 and fairchildite. Bütschliite and $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ form below 518°C and between 50 and 33 mol.% K_2CO_3 , whereas $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and fairchildite form between 518°C and 780°C. In addition, the presence and stability of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and fairchildite in biomass fuels are governed by the temperature and p_{CO_2} of the combustion atmosphere (Winbo *et al.*, 1998). The thermoanalytical study of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ suggests that it can form during the combustion of biomass, where $p_{\text{CO}_2} = 0.10$ to 0.15 bar, and between 530–790°C (Winbo *et al.*, 1998). The published experimental data on the K_2CO_3 – CaCO_3 system, together with the observed mineralogy, constrain the smouldering temperatures and are consistent with the following processes during ash formation in *D. wheeleri*: (1) Below ~400°C, dehydration, oxidation and pyrolysis of the wood produce char enriched in minor elements (detected by EDS), most notably K, Ca, Mg, Si, P, S and Cl. During this stage, the abundant whewellite concentrates as the wood dehydrates and decreases in volume. (2) Calcite is formed from whewellite above 480°C in the char as a result of the smouldering of the wood. Calcite is absent in uncharred wood and forms from the decomposition of whewellite, which occurs near 479°C through a series of intermediate Ca oxalate compounds (Frost and Weier, 2004; Izatulina *et al.*, 2018). (3) There is combustion and formation of K_2CO_3 from K-rich char during oxidation above ~500°C. (4) The macroelements K–Ca–Mg–Cl are concentrated in the wood during combustion above 518°C, together with the reaction of K_2CO_3 with calcite to form $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and $\text{K}_2\text{Ca}(\text{CO}_3)_2$ (fairchildite).

Different areas of the ash log show variable amounts of ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ + fairchildite + calcite + sylvite. Some areas are

dominated by calcite, sylvite and ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$. It is speculated that during char oxidation, K_2CO_3 is formed, which then reacts with the abundant calcite, forming the K–Ca double carbonates. The presence of ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ + fairchildite, instead of ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ + bütschliite, is consistent with char oxidation above 520°C (Arefiev *et al.*, 2019a). The cation and Cl ratios in the wood give insights into the final minerals that form in the ash. For example, the following atom% for the general areal of the wood (Fig. S1) gives 0.6 K, 0.37 Cl, 0.2 Ca, 0.12 S and 0.05 Mg averaged over a 1×0.75 mm area. Given that K and Cl form KCl, this leaves the remaining K to react with Ca to form $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ /fairchildite, and the remaining minerals found in the ash. Though ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ and fairchildite concentrations vary from different areas, calcite and sylvite are always present. The variations in mineral concentrations are probably governed, in part, by the local concentration of whewellite raphids.

Conclusions

Wildfire is an important geological process as it influences bulk, widespread surficial mineral formation, erosion patterns, sediment transport, soil formation and atmospheric chemistry. Thus, in this broader, time-scale perspective, wildfires are part of the geological processes that shape the Earth's surface. In addition, the inorganic phases in the ash are minerals. The ash $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ phase is probably widespread in wildland fire ash but is up-to-now unreported. A difficulty in identifying and studying the K–Ca double carbonates stems from their moisture instability, all of which readily decompose to calcite and presumably a soluble K salt in water.

The discovery of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ as an abundant phase in the ash of the *D. wheeleri* plant expands our understanding and knowledge of Earth's mineral diversity, especially concerning the widespread geological process of wildfire ash formation. In addition, the occurrence of $\text{K}_2\text{Ca}_2(\text{CO}_3)_3$ in plant ash is an example of an inorganic phase that bridges the gap between biomineralisation and geological mineral formation.

Supplementary material. The supplementary material for this article can be found at <https://doi.org/10.1180/mgm.2025.10098>.

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