Speleothems as Archives for Palaeofire Proxies

Micheline Campbell[1], Liza McDonough[2], Pauline Treble[3], Andy Baker[4], Nevena Kosarac[5], Katie Coleborn[1], Peter Michael Wynn[6], and Axel Schmitt[7]

[1]UNSW Sydney
[2]Unknown
[3]ANSTO
[4]University of New South Wales
[5]UNSW
[6]Lancaster University
[7]University of Heidelberg

November 24, 2022

Abstract

Wildfires affect 40% of the earth's terrestrial biome, but much of our knowledge of wildfire activity is limited to the satellite era. Improved understanding of past fires is necessary to better understand how wildfires might change with future climate change, to understand ecosystem resilience, and to improve data-model comparisons. Environmental proxy archives can extend our knowledge of past fire activity. Speleothems, naturally occurring cave formations, are widely used in palaeoenvironmental research as they are absolutely dateable, occur on every ice-free continent, and include multiple proxies. Recently, speleothems have been shown to record past fire events (McDonough et al., 2022). Here we present a review of this emerging application in speleothem palaeoenvironmental science. We give a concise overview of fire regimes and traditional palaeofire proxies, describe past attempts to use stalagmites to investigate palaeofire, and describe the physical basis though which speleothems can record past fires. We then describe the ideal speleothem sample for palaeofire research and offer a summary of applicable laboratory and statistical methods. Finally, we present four case studies which detail [1] the geochemistry of ash leachates, [2] how sulphur may be a proxy for post fire ecological recovery, [3] how a catastrophic palaeofire was linked to changes in climate and land management, and [4] demonstrate that deep caves can record past fire events. We conclude the paper by suggesting that speleothem $\delta^{18}O$ research may need to consider the impact of fire on $\delta^{18}O$ values, and outline future research directions.

Reviews of Geophysics

Supporting Information for

Speleothems as archives for palaeofire proxies

Micheline Campbell[1], Liza McDonough[2], Pauline Treble[2,1], Andy Baker[1,2], Nevena Kosarac[1], Katie Coleborn[1], Peter Wynn[3], Axel K. Schmitt[4].

[1]School of Biological, Earth and Environmental Science, UNSW Sydney, Sydney, 2052, Australia

[2]ANSTO, Lucas Heights, Sydney 2234, Australia

[3]Lancaster Environment Centre, Lancaster University, Lancaster, United Kingdom

[4]Institute of Earth Sciences, Universität Heidelberg, 69120 Heidelberg, Germany

Corresponding author: Micheline Campbell (micheline.campbell@unsw.edu.au)

Contents of this file

Text S1 to S3

Introduction

The supporting information in S1, S2, and S3 details the field and laboratory methods for three case studies presented in the manuscript 'Speleothems as archives for palaeofire proxies'.

Text S1.

Ash leachates were performed following the United States Geological Survey Field Leach Test, which is a simple and cost-effective method to simulate leaching by water (Hageman, 2007). Deionised water was added to ash at a ratio of 20:1. Samples were mixed thoroughly and allowed to settle for ~10 minutes. Subsamples were collected and filtered with a 0.45 µm nitrocellulose filter. Filtered samples were then analysed and quantified using solution Inductively Coupled Plasma Atomic Emission Spectroscopy and Mass Spectrometry at the Isotope Tracing in Natural Systems laboratory ANSTO, Australia.

Text S2.

Sample collection

The bulk of the dripwater data presented here is published, and full methods for sample collection and analyses can be found in the original publication (Treble *et al.* , 2016). Additional bulk dripwater samples were collected following that same method. Aliquots for SO_4 dual isotope analyses of dripwaters were taken from those bulk samples. Bulk monthly rainfall samples were collected from April 2017 to January 2018 using a rain gauge. Both rain and dripwater samples were filtered using mixed cellulose 0.45 µm membrane filters and refrigerated at 5°C prior to analyses.

Soil samples were collected from the O and A horizons at 4 m intervals along a 20 m transect. Additional vertical samples were taken at 0.4 m and 1.4 m depth at one site. Soil samples were dried at 60 °C for 48 hours and sieved (2 mm) to remove the coarse fraction, roots, and other organic debris. O horizon samples were further separated into the $>$ 0.5 mm and $<$ 0.5 mm fractions. All soil samples were finely crushed using a ring grinder.

Three bedrock samples were collected for SO_4 dual isotopic analyses.

Representative vegetation samples were collected from above Golgotha Cave (minimum three leaves and attached stems, with three replicates for each species). Samples were dried at 60°C for 48 hours and finely ground with a ball grinder. Where possible, leaves were separated from twigs and seeds for ^{34}S analyses.

Speleothem GL-S4 was collected from Golgotha Cave in 2013. The sample is comprised of white porous calcite and has been dated with annual lamina counting via XFM mapping of Sr concentrations (unpublished data).

Sulphate extraction for isotopic analysis

Sulphate was extracted from bedrock samples following the method of Wynn*et al.* (2008). 300 mg aliquots of bedrock sample were dissolved in 1.5 ml of 4M HCl to yield at least 350 µg of $BaSO_4$for both $\delta^{34}S\text{-}SO_4$ and $\delta^{18}O\text{-}SO_{4.}$ The solution was filtered using mixed cellulose 0.45 µm filters into 2 ml Eppendorf polypropylene tubes.

Rainfall and dripwater samples were prepared for analyses following the method in (Wynn *et al.* , 2015). Resin-filled syringes were prepared by mixing a dry resin component with MilliQ water. This uninitialized resin was poured into 5 ml polypropylene syringe tubes. The resin was then initialised by dripping through 10 ml of 1M HCl and then rinsed using 40 ml of MilliQ water. Aliquots of dripwater and rainfall were taken with sufficient to yield 350 µg of $BaSO_4$ for both $\delta^{34}S\text{-}SO_4$ and $\delta^{18}O\text{-}SO_4$. Each aliquot was then passed through a syringe tube filled with 50 W-X8 resin to remove the cations, and through a syringe tube filled with AG2-X8 to load anions from the solution onto the resin. The anion resin was then eluted with three sequential 0.5 ml aliquots of 1M HCl, and the resulting solution collected in 2 ml Eppendorf tubes.

For both bedrock and water samples, 0.2 ml $BaCl_2$ was added to each tube and thoroughly mixed. Solutions were refrigerated for [?] 48 hours to allow the $BaSO_4$ to precipitate. The $BaSO_4$ precipitate was separated from the eluant by centrifuging for 20 minutes at 3500 rpm and rinsed three times with MilliQ water. Once the solution pH was neutral (tested with pH paper), the samples were dried at 40°C for [?] 48 hours to evaporate the remaining water, leaving behind the dried $BaSO_4$ pellet.

Mass spectrometry

$\delta^{34}S$ and $\delta^{18}O$ were analysed using a Pyrocube elemental analyser (Elementar), linked to an Isoprime 100 continuous flow isotope ratio mass spectrometer at Lancaster University, UK, with instrumental set up followed the protocols established in Wynn et al. (2015). For the finely ground soil and vegetation samples, only$^{34}S/^{32}S$ was measured. For the $BaSO_4$ extracted from drip water, rainfall and carbonate bedrock, both $\delta^{34}S$ and $\delta^{18}O$ were analysed.

Combustion of samples within tin capsules in the presence of vanadium pentoxide at 1050°C yielded SO_2 for determination of $\delta^{34}S\text{-}SO_4$ and pyrolysis within silver capsules in the presence of carbon black catalyst at 1450°C yielded CO for determination of $\delta^{18}O\text{-}SO_4$. $\delta^{34}S$ isotopic composition values were corrected against VCDT using within run analyses of international standard NBS-127 and SO5 (assuming $\delta^{34}S$ isotopic composition of +21.1and +0.5isotopic values were corrected to V-SMOW using NBS-127 and NISTSO6, assuming $\delta^{18}O$ values of +9.3 respectively. Within-run standard replication (1 standard deviation) was <0.5and$^{18}O/^{16}O$.

Secondary ion mass spectrometry

Speleothem GL-S4 was analysed for S concentration using CAMECA Secondary Ion Mass Spectrometry (SIMS) 1280-HR ion microprobe at the Heidelberg University Ion Probe (HIP) laboratory. The speleothem sample was mounted in resin and polished using 1 µm diamond and coated in 5 nm gold to make the surface conductive and produce negative secondary ions. Samples were sputtered using Cs ions over an analytical spot size of 10 µm including pre-sputtering for 3 minutes to reduce surface contamination. Masses^{32}S and ^{35}Cl were measured using Faraday cups. Count rates were converted into S and Cl concentration using NIST610 standard offering semi-quantified concentrations owing to the different matrix (glass) versus the $CaCO_3$ sample. The concentrations in the NIST610 were 570 ppm for S (Guillong *et al.* , 2008) and 470 ppm for Cl (Pearce *et al.* , 1997).

Text S3

Stalagmite CRY-S1 was collected from Crystal Cave in southwest Australia in 2008. A thick section was prepared by cutting along the growth axis and mounting the sub-sample in resin, which was then polished to 1 µm. The top ˜15 mm of the sample is presented here.

S-µXFM analyses were conducted at the Australian Synchrotron under experiment 13457, following methods described in (Borsato et al., 2021; McDonough et al., 2022). The Maia 384-element planar detector was used, and resulting spectra were analysed using ImageJ. Sr S-µXFM maps were used to construct a lamina-count chronology following (Faraji et al., 2021), with laminae counted in ImageJ.

Speleothems as archives for palaeofire proxies

Micheline Campbell[1], Liza McDonough[2], Pauline Treble[2,1], Andy Baker[1,2], Nevena Kosarac[1], Katie Coleborn[1], Peter Wynn[3], Axel K. Schmitt[4].

[1]School of Biological, Earth and Environmental Science, UNSW Sydney, Sydney, 2052, Australia

[2]ANSTO, Lucas Heights, Sydney 2234, Australia

[3]Lancaster Environment Centre, Lancaster University, Lancaster, United Kingdom

[4]Institute of Earth Sciences, Universität Heidelberg, 69120 Heidelberg, Germany

Corresponding author: Micheline Campbell (micheline.campbell@unsw.edu.au)

Key Points:

- Wildfires are a serious hazard, and our knowledge is limited by short satellite observational records.
- Cave decorations (speleothems) are a new archive of palaeofire information.
- Both physical and chemical stalagmite features provide palaeofire information

Abstract

Wildfires affect 40% of the earth's terrestrial biome, but much of our knowledge of wildfire activity is limited to the satellite era. Improved understanding of past fires is necessary to better understand how wildfires might change with future climate change, to understand ecosystem resilience, and to improve data-model comparisons. Environmental proxy archives can extend our knowledge of past fire activity. Speleothems, naturally occurring cave formations, are widely used in palaeoenvironmental research as they are absolutely dateable, occur on every ice-free continent, and include multiple proxies. Recently, speleothems have been shown to record past fire events (McDonough et al., 2022). Here we present a review of this emerging application in speleothem palaeoenvironmental science. We give a concise overview of fire regimes and traditional palaeofire proxies, describe past attempts to use stalagmites to investigate palaeofire, and describe the physical basis though which speleothems can record past fires. We then describe the ideal speleothem sample for palaeofire research and offer a summary of applicable laboratory and statistical methods. Finally, we present four case studies which detail [1] the geochemistry of ash leachates, [2] how sulphur may be a proxy for post fire ecological recovery, [3] how a catastrophic palaeofire was linked to changes in climate and land management, and [4] demonstrate that deep caves can record past fire events. We conclude the paper by suggesting that speleothem $\delta^{18}O$ research may need to consider the impact of fire on $\delta^{18}O$ values, and outline future research directions.

Plain Language Summary

Wildfires are a global hazard, and are likely to become larger, more common, and more intense as we feel the effect of climate change. Most of what we know about wildfires come from satellite data, but these datasets are not long enough to fully understand fire behaviour. We can use palaeoclimate data to learn more. Natural cave decorations (stalagmites) form shallow caves have recently been found to include information about fire events. As they grow, stalagmite chemistry changes according to the climate at the time, and recent research has shown that elements from wildfire ash can be incorporated. Here we review the state of the art of knowledge of this new application in palaeofire research. We detail the development of this emerging field, starting with cave dripwater monitoring results, we give an overview of relevant laboratory and statistical methods, and we provide four case studies from southwest Australia investigating ash geochemistry, post-fire changes in sulphur, how intense fires are linked to climate, and how deep cave stalagmites may also record past fires. Longer records of fire activity will help us understand how fire activity might change with climate change, how ecosystems might respond to those changes, and will be used to improve models.

1 Introduction

Wildfires are a significant hazard with ~40% of the Earth's terrestrial surface being fire prone, and about ~3% of the terrestrial surface burning each year (Chapin et al., 2011; Giglio et al., 2010). In many areas, instances of dangerous fire weather are increasing (Jones et al., 2022). In northern California and Oregon, the likelihood of extreme autumn fire weather has increased by 40% (Hawkins et al., 2022), and both the frequency and size of wildfires have increased in the western United States (Abatzoglou and Williams, 2016; Iglesias et al., 2022). A long-term increase in both extreme fire weather and fire season length has been observed in parts of Australia (BOM and CSIRO, 2020), and there has been a global increase in the frequency of compound fire weather and meteorological drought events (Richardson et al., 2022). Over the past three decades, total annual burned area in Australia has increased significantly (Canadell et al., 2021). Additionally, nine of the eleven largest Australian fires on record have occurred since 2000, including 3 of the 4 'forest megafires' observed since 1930 (Canadell et al., 2021). Fire regimes are a function of climate, human activity, and land use (Marlon, 2020). While it can be difficult to ascertain the dominant control, severe fire weather is expected to increase with climate change (Abatzoglou et al., 2019; Di Virgilio et al., 2019). This suggests that it is becoming increasingly important to understand the climatic conditions leading up to catastrophic wildfires to be able to predict and prepare for their occurrence in the future.

Fires play an important role in shaping landscapes (Bowman et al., 2009), and wildfires (or bushfires) have both direct and indirect impacts on the environment and society, including on ecological communities, biogeochemical cycles, hydrology (both surface and sub-surface), erosion rates, and human lives and infrastructure (Bodí et al., 2012; Iglesias et al., 2015; Santín et al., 2012; Woods and Balfour, 2010). The 2018 fires in California, western United States, burned approximately 770 000 ha, or about 2% of California's land area (Wang et al., 2021). The calculated cost (including capital losses, health costs, and indirect losses) of these fires was between US$126.1-192.9 billion (or 1.5% of California's GDP) (Wang et al., 2021). This is similar to the estimated annual cost of bushfires in Australia, which has been given as ~1.3% of Australian GDP (Ashe et al., 2009). The 2019/2020 Australian 'Black Summer' bushfires burned 23% of the temperate forests in southeast Australia (an unprecedented event, both nationally and internationally), and were exacerbated by long term anthropogenically-forced climate trends, and at least two modes of climate variability dominating the fire and pre-fire season (Abram et al., 2021). The Black Summer Australian fire season resulted in 33 deaths, more than 3000 houses destroyed, and around 19 million ha burned, including the World Heritage listed Gondwana rainforest which does not normally experience bushfires (Abram et al., 2021; Filkov et al., 2020; Ward et al., 2020). The economic cost (both tangible and intangible) of the 2019/20 fire season has yet to be fully determined, but some estimates have put it in excess of AUD$200 billion (Read and Denniss, 2020). Two years after the Black Summer bushfires, just 15% of affected Victorian households had rebuilt while after the same period following the catastrophic 2009 'Black Saturday' bushfires, 77% of affected households had rebuilt, were rebuilding, or had bought a new home (May, 2022). A longitudinal study following the Black Saturday bushfires, which had 173 fatalities, found that a small proportion of the population reported post-traumatic stress disorder, depression, psychological distress, and heightened consumption of alcohol years after the event (Bryant et al., 2014).

Our understanding of climate-fire interactions is largely limited to the last few decades, when satellite imagery has been available (Dutta et al., 2016). While the satellite era has enabled us to collect fire data at high spatial and temporal resolutions, it does not capture the full range of natural variability or the transition from Indigenous land management to colonial land management which has occurred since the 17th Century. As a result, proxy studies and, more recently, modelling studies, must be used to fill our gaps in understanding. Earth System Models have only incorporated fire models in the last ~15 years (Li et al., 2013; Liu, 2018; Teixeira et al., 2021), and improvements are needed to resolve vegetation feedbacks and incorporate anthropogenic activity (via fire suppression or promotion) to improve model performance (Brücher et al., 2014; Hanan et al., 2021; Kehrwald et al., 2016). The development of the Global Charcoal Database (now Global Paleofire Database; https://www.paleofire.org/index.php) has been a key step in enabling hypothesis testing, evaluation of climate-fire interactions, and the development of composite charcoal proxy records which can reconstruct fire activity with improved signal to noise ratios (Fohlmeister, 2012; Power et al., 2010). However, some regions (e.g., Africa, Australia, South America) remain under-researched, with poor data density in the database. This leaves a large knowledge gap in the palaeofire community which may be addressed by the development of new proxy archives. Fire proxy archives such as sedimentary charcoal, tree scars, and chemical signals in ice cores have been used to extend the observational record and better understand fire regimes at local to continental scales. Existing proxy archives such as tree scars, sedimentary charcoal, ice cores, and historical records may be biased by survivorship (tree scars), have decadal or longer resolutions (sedimentary charcoal), be resolved only at continental or hemispheric scales (ice cores), and may be too short to capture the full range of natural variability (historical records). Speleothems, secondary cave formations, offer a new archive for fire proxy data, with some advantages over traditional fire proxy archives. They may be absolutely dated using radiometric techniques, have high temporal resolutions, and incorporate a wide range of proxies, allowing for coupled records of climate and fire. Additionally, speleothems may fill key geographical gaps where few tree ring and sediment core records have been developed (e.g., southwest Australia).

Here, we present an overview of the processes which control fire regimes and associated investigative methods, including satellite products and proxy data (Sections 2 and 3). In Section 4, we describe recent advances in the development of speleothems as proxy archives for fire research, and provide an overview of the relevant proxies. We include a summary of the field, laboratory, and statistical methods relevant to constructing speleothem-based palaeofire records (Section 5). In Section 6 we present four case studies that demonstrate how: [1] speleothem trace metals may be used to identify fire events and intensity, [2] sulphate isotopes and speleothem sulphur can be used to understand post-fire recovery, [3] speleothem fabric can be used to identify intense fire events, and [4] the influence of cave depth on the preservation of fire in the speleothem record. The development of speleothems as fire proxy archives is of global significance, as speleothems are found on all continents bar Antarctica, and are already widely used by the palaeoenvironmental community. In this review, we build on recent research in Australia, but the information and case studies presented here identify the processes that will inform proxy response worldwide.

2 Understanding fire regimes

Fire regimes are a function of climate, human activity, and vegetation composition, and may be non-stationary in time and space (Hantson et al., 2016; Marlon, 2020). Fire reconstructions can now be linked to known climate shifts, including the Medieval Climate Anomaly (where warm and dry conditions in North America were accompanied by increased burning, including the highest fire activity in two 3000 year records (Marlon et al., 2012; Swetnam et al., 2009)), and the Little Ice Age, when cooler temperatures in western North America were accompanied by the lowest biomass burning in the late Holocene (Marlon et al., 2012). The relationship between climate and fire is not always geographically consistent. Antecedent drought conditions generally underpin extreme fire years in the northwestern United States (Gedalof et al., 2005), but in the semi-arid regions of Australia high annual precipitation in the preceding year is a key precursor to large fire events due to enhanced fuel loads (van Etten et al., 2021). While global and continental analyses have suggested that climate has been the primary control on fire regimes (Mooney et al., 2011; Pechony and Shindell, 2010; Power et al., 2008), at the regional scale, there is ample evidence that humans have used fire for protection, hunting and gathering, and land management for tens of thousands of years (Fletcher et al., 2021a; Mariani et al., 2022). This suggests that so-called 'natural' fire regimes are modified by human activity, at least at sub-continental scales. Palaeoenvironmental records support this, demonstrated by upticks in fire frequency well-linked to human activity (Fletcher et al., 2021a; Haberle and David, 2004; McDonough et al., 2022; McWethy et al., 2010; Rehn et al., 2021; Wang et al., 2013). Similarly, the more-recent transition from Indigenous (fire-promoting) to colonial (fire suppressing) land management practices has seen associated changes in fire regime (Fletcher et al., 2021a, 2021b; McDonough et al., 2022).

Improved knowledge of past fire regimes and associated past climate will enable us to; [1] better understand how wildfires might change with future climate change, [2] better understand ecosystem resilience, which will inform land management practices, and [3] improve data-model comparisons. For example, long records of fire severity and frequency can provide baseline data for characterising long-term variability. This will enable us to determine the departure from this baseline, which will itself aid attribution studies on the impact of climate change. Current ecosystems have evolved over tens of thousands of years of Indigenous land management practices. Being able to better understand the impact of these land management practices on past fire regimes will enable better decision making about how ecosystems should be managed to optimise their resilience. For example, Mariani et al. (2022) showed that the disruption of cultural burning practices has changed ecosystems and led to recent unprecedented wildfires. Observational data-model comparisons have been used to quantify emissions and fire intensity, but satellite datasets are short, and do not capture the full range of climate variability (Hantson et al., 2016; van Marle et al., 2017). Using long-duration proxy data allows for better understanding of the full range of fire regime variability, and can be used to validate climate simulations under vastly different conditions to the present (Hantson et al., 2016; Harrison et al., 2014; Schmidt et al., 2014).

3 Palaeofires

Prior to the satellite era, fire documentation is poor. While historical records may document fire frequency and intensity, there is high uncertainty and variability around geographic and temporal extents. Fire records from archives which form with annual laminae, and which have extension rates high enough such that analytical requirements are met, may enable high-resolution reconstructions (Marlon, 2020). To date, such records have been sourced from archives including ice cores, fire-scarred trees, and charcoal preserved in sediment cores. Each of these archives have their own strengths, weaknesses, relevant temporal and spatial scales, and ideal applications (see Table 1 and Figure 1). While these traditional fire proxy archives have been extensively used to reconstruct past fire behaviour, speleothems are a novel fire archive with the potential to develop high resolution, absolutely dated coupled climate-fire records. This is especially exciting for regions such as southwest Australia where there are relatively few published tree ring and sediment palaeofire records, but a large network of caves which have already produced stalagmites suitable for palaeoclimate and palaeofire research (McDonough et al., 2022).

Table 1 Established sources of fire information, and their properties

Proxy Archive	Proxy/ies	Strengths	Weaknesses	Example references

Marine, lake, and peat cores	Charcoal (macro and micro)	Cost-effective collection, analyses and storage; Age measurements directly on charcoal; Widely preserved; global database allows for regional reconstructions; Potential for coupled fire-climate reconstructions using pollen from the same core.	May be biased towards large and intense fires; Usually decadal or lower resolution; May be discontinuous due to erosion or if peat burns; Charcoal quantity not related to fire extent or intensity limiting to qualitative interpretation; Reconstructions are unitless due to standardization.	Marlon, 2020; van Marle et al., 2017; Whitlock and Larsen, 2001
Ice cores	Biomarkers, aerosols, electrical resistivity, isotopes, and trace elements.	Potential for coupled climate-fire records; May be long-duration and resolvable at seasonal scales; Large-scale (regional to hemispheric) overview of fire activity.	Expensive to collect, store, and analyse; Cannot be resolved at sub-continental scales; Require understanding of large scale atmospheric transport processes for interpretation.	Bhattarai et al., 2019; Grieman et al., 2018; Legrand et al., 2016; Marlon, 2020; McConnell et al., 2007; Rubino et al., 2016
Trees	Fire scars and stand establishment dates.	Precisely dateable; Coupled climate-fire records; Cost-effective sample collection, storage, and analysis.	Survival and preservation bias; Highly local records; Cannot reconstruct fire intensity.	McBride, 1983; O'Donnell et al., 2010; Reifsnyder et al., 1967
Historical observations	Weather reports, journals, etc.	May be quantitative (e.g. fire extent); Digitisation has encouraged recovery of old records.	Relatively short duration; Highly local; May be discontinuous; Often qualitative.	(Gruell, 1985; Lucas, 2010; Stamou et al., 2016)

Marine, lake, and peat cores incorporate sedimentary charcoal as they accumulate. Sedimentary charcoal research has informed the bulk of palaeofire knowledge, largely underpinned by the development of the Global Charcoal Database (now Global Paleofire Database), a crowd-sourced public-access database of sedimentary fire proxies (Brücher et al., 2014; Marlon et al., 2016; Molinari et al., 2021, 2013; van Marle et al., 2017). Sediment cores can be retrieved from lakes, peat bogs, ocean floors, and alluvial fans, and both macro- and micro-charcoal can be used as fire proxies (Marlon, 2020; Whitlock and Larsen, 2001). Sedimentary charcoal records generally have approximately decadal temporal resolutions, although annual resolution may be achieved (Vachula et al., 2018). Sedimentary charcoal records can be biased towards larger and more intense fires as there is a bias in the transport and preservation of charcoal from small events, although this may be overcome by analysing only macro charcoal, or accounting for the source area by looking at the distribution of charcoal sizes (Mariani et al., 2016; Vachula et al., 2018). While peaks in charcoal concentrations are not empirically linked to fire intensity, other approaches such as Attenuated Total Reflectance

Fourier Transform Infrared spectroscopy have been used to characterise the structure and carbonization temperatures of charcoals (Constantine et al., 2021; Gosling et al., 2019), although burn temperature is just one aspect of fire intensity (Keeley, 2009).

Fire proxies found in ice cores include biomarkers (e.g. levoglucosan, vanillic acid), aerosols (e.g., black carbon), isotopes (e.g., δ13C-CH4), electrical resistivity, and trace elements and nutrients (e.g. potassium, nitrate and nitrite) (Rubino et al., 2016). Due to atmospheric processes, ice cores record an attenuated signal which cannot usually be linked to individual events, although their annual laminae do allow changes in fire emissions at a regional to continental scale to be precisely dated (Marlon, 2020; van Marle et al., 2017). Interpretation of ice core fire proxy data requires an understanding of atmospheric processes and transport, as they are remote proxies which give an overview of large scale changes in biomass burning (Battistel et al., 2018; Marlon, 2020). Nonetheless, ice core fire records have successfully been applied to investigate past fire activity (Battistel et al., 2018; Eichler et al., 2011; Nicewonger et al., 2020), and links to anthropogenic land clearing (Zennaro et al., 2015).

Trees record local fire events with fire scars, which can be precisely dated by counting tree rings. Annual growth rings mean that fire scar records have annual temporal resolutions, although their spatial resolution is highly localised. As scar size is not linked to fire intensity (and old scars may be enlarged by subsequent fires), tree scars only record fire frequency (McBride, 1983; Reifsnyder et al., 1967). Additionally, fire scar records are impacted by several biases, including survivorship bias which is related to tree age and fire intensity, and bark thickness bias as a result of thicker bark being less likely to scar, so as trees age they record fewer fire events (McBride, 1983; Reifsnyder et al., 1967). In environments where post-fire tree mortality is high, stand establishment (or replacement) dates may be used as a proxy for the last stand-replacing fire (Brown et al., 1999). Drawbacks of this approach are that creating a timeseries is difficult, lags in re-establishment are unknown, and chest-height samples may not include all growth rings (although this can be resolved by sampling at lower heights) (O'Donnell et al., 2010).

Figure 1 Proxy and observational sources of fire data and their spatial and temporal resolutions. Observational sources are maroon, proxies are black. Potential temporal and spatial resolution of speleothems is shown as a red box. Opacity for each archive except speleothems is 60%, so dark regions indicate where archives overlap. For example, historical records are mainly local, but cover periods of time from weeks to centuries. Adapted from Kehrwald et al. (2016).

4 Speleothems as palaeoenvironmental archives

Calcareous speleothems (stalagmites, stalactites, and flowstones) are naturally occurring formations which grow in caves due to the dissolution of limestone and subsequent precipitation of calcium carbonate. Stalagmites are excellent natural archives for palaeoenvironmental research as they are absolutely and precisely datable, can produce long, continuous records, include multiple proxies, and their links to surface hydroclimate and utility as palaeoclimate archives are well established.

Speleothems can be absolutely dated using radiometric techniques. Typically uranium-series techniques are preferred, with radiocarbon dating used where uranium-series dating is complicated by the inclusion of detrital thorium or low uranium concentrations (Hua et al., 2012; Zhao et al., 2009). In climates with high seasonality such as Mediterranean climates with distinct summer-winter seasonality speleothems form clear physical and chemical annual laminae (Baker et al., 2021). Where speleothems were sampled while actively growing, these annual laminae can be counted to develop highly accurate and precise annual chronologies with minimal error (Faraji et al., 2021; McDonough et al., 2022; Nagra et al., 2017).

Speleothems have been widely used to reconstruct regional temperature, precipitation and larger-scale atmospheric processes such as variability in the Asian Monsoon, and the El Niño-Southern Oscillation (Chen et al., 2016; Cheng et al., 2016). Speleothem proxy records which are both long and of very high resolution (seasonal or better) provide an almost-unique opportunity to reconstruct climate at human-relevant timescales, that is, seasonal to decadal fluctuations which have potential to influence human wellbeing and behaviour. Such speleothems have been found in the Levant, and have provided insight into the interplay between climate and early human migration through the Middle East during the Last Interglacial. Orland et al. (2019) undertook a data-model comparison of seasonal speleothem δ18O and simulated monthly precipitation δ18O from comparative atmospheric model runs of precession-high and precession-low northern hemisphere seasonality. Using Secondary Ion Mass Spectrometry, with replicates along each lamina, they were able to collect high-resolution (10 μm spots) in situ calcite δ18O (Orland et al., 2019). Their results tied periods of precession-high northern hemisphere seasonality with the appearance of early hominin fossils in the Levant (Hershkovitz et al., 2018; Orland et al., 2019). This demonstrates how high-resolution palaeoclimate records can provide insight into past human-environment interactions.

Datasets with multiple proxies allow for greater certainty in the interpretation of palaeoenvironmental records and for the use of multivariate statistical methods. Proxies derived from speleothems include oxygen and carbon stable isotopes, trace elements and metals, fluorescence, organic matter content, pollen, organic macromolecules, and growth rate. While stable isotopes are the most widely used speleothem proxy, in recent decades trace elements and physical properties such as growth rate and changes in speleothem fabric have become more commonly applied, (Frisia, 2014; McDonough et al., 2022; Orland et al., 2014; Treble et al., 2005). As a mature discipline, the links between speleothem geochemistry and regional hydroclimate are relatively well-constrained. Speleothem δ18O is controlled by precipitation δ18O and hydrological processes in the soil, epikarst, and cave system (Bradley et al., 2010; Lachniet, 2009). Karst flowpaths play an important role in often amplifying the drip δ18O response to climate and have been shown to be ubiquitous in a global analysis (Treble et al., 2022) and cave monitoring can assist with quantifying this.

Seasonal variations in trace elements (such as Sr/Ca), combined with the development of high-resolution, non- and minimally-destructive analytical techniques, mean that trace elements are becoming more commonly used in speleothem palaeoenvironmental research. Trace element ratios are controlled by atmospheric inputs, biological processes in vegetation and soil, hydrological processes in the karst and epikarst, crystal growth processes, and secondary alteration (Fairchild and Treble, 2009). Trace element variations have been used to investigate drought onset and duration, normally via the Mg/Ca ratio and its association with prior calcite precipitation, where precipitation of calcite within the flow path ‘upstream’ of the drip point during drier conditions results in higher ratios of magnesium to calcium (Fairchild and Treble, 2009; Griffiths et al., 2020). Subaqueous speleothem Mg/Ca has also been used as a palaeotemperature proxy (Drysdale et al., 2020). Sr/Ca is also affected by prior calcite precipitation and may be used as an aridity proxy, although analysis of strontium isotopes has shown that aeolian inputs can alter the signal (Goede et al., 1998). However, a correlation between Sr/Ca and Mg/Ca increases the confidence that variations are hydrological. Beyond palaeoenvironmental applications, seasonal changes in Sr/Ca may be used to develop precise annual speleothem chronologies (e.g. Nagra et al., 2017). It has been demonstrated that trace metals are transported in infiltrating karst waters as both particulates and colloids with organic matter, with dripwater-metal ratios closely associated with NICA-Donnan n1 humic binding affinity ratios (Hartland et al., 2012). Hartland et al. (2012) also showed that transport was partitioned by size, with all sizes more easily transported under high-flow conditions (when fractures are activated), while during low-flows particulates and small colloids decoupled.

Speleothem sulphur and sulphate concentrations and isotopes have been used to investigate industrial pollution and past volcanic activity, and sulphate isotopes enable pollution provenance as well as emissions quantification (Borsato et al., 2015; Wynn et al., 2010, 2008).

4.1 Previous attempts at using speleothems for palaeofire research

Black laminae and black cave deposits have been reported in stalagmites from Slovakia (Gradziński et al., 2007), the United States (Benington et al., 1962), Slovenia (Šebela et al., 2017, 2015), and Australia (Dredge, 2014; Spate and Ward, 1979; Webb et al., 2014). While black deposits are generally attributed to guano, fossil fuel combustion, cooking fires, and torches (Benington et al., 1962; Gradziński et al., 2003; Kaal et al., 2021; Šebela et al., 2015; Zupančič et al., 2011), in Australia and Slovakia it has been suggested that these black deposits are records of bushfires. Analyses conducted in the 1970s suggested that black layers at Yarrangobilly Caves, Australia, were comprised of silica and carbon, and that a bushfire origin was reasonable (Spate and Ward, 1979). However, subsequent research at Yarrangobilly found no evidence of charcoal in black cave residues, and comparisons of growth-rate-weighted polycyclic aromatic hydrocarbon concentrations in black and white calcite samples showed no difference (Dredge, 2014). A multi-proxy study of a flowstone form the same cave system concluded that the black layers were due to high concentrations of humic substances delivered during intense wet periods (Webb et al., 2014). These studies both suggest that speleothem colour at Yarrangobilly is unlikely to be a direct outcome of wildfire, with bacterial melanisation, bioaccumulation of iron and manganese oxides proposed as alternative mechanisms for calcite colouration (Dredge, 2014; Gázquez et al., 2011). Slovenian caves feature similar black deposits, which have been attributed to forest fires through comparison between calcite δ13C and δ13C of charcoal in soil, visualisation with scanning electron microscopy/energy dispersive spectroscopy, and quantification of organic carbon (Šebela et al., 2017). The authors acknowledged that transmission of particulates into the Postojna and Predjama Caves would be more likely to occur during winter when cool air is able to settle into the relatively warmer cave (Šebela et al., 2017). Following this, in regions where the wildfire season occurs during summer and outside temperatures are higher than cave temperatures, it is unlikely that smoke particulate would be able to enter and settle in caves due to the temperature gradient suppressing the entry of outside airmasses when external temperature exceeds cave temperature. This temperature gradient could be further enhanced by the fire locally influencing air temperature. While black residue in caves may record nearby bushfires, it is likely that this only occurs under specific circumstances (e.g., a cave with chimney ventilation in the side of a valley) likely explaining why black residue is so rarely reported. With polycyclic aromatic hydrocarbons just as common in black calcite as white calcite (Dredge, 2014), any palaeofire reconstruction built on calcite colouration alone is likely to be erroneous. Where black residues have been more strongly linked to fire activity, (that is, in Slovenia; Šebela et al., 2017), cave atmospheric processes may limit the recording of fire to cooler season fire activity, reducing its utility to investigate past fire regimes.

4.2 Developments in high-resolution fire proxies in speleothems

In recent years, publications have reported that fire and post-fire responses have been directly observed in cave monitoring studies highlighting the possibility of constructing fire records using speleothems (Bian et al., 2019; Coleborn et al., 2019, 2018; Nagra et al., 2016; Treble et al., 2016). Importantly, the results of these studies showed that speleothem-based palaeofire records could be achieved using a subset of typically measured variables such as speleothem stable isotopes, discharge rate, and trace elements and nutrients. This has subsequently been confirmed by McDonough et al. (2022) who showed in a young speleothem that: [1] the stalagmite recorded a response to all known fire events that had burnt over the cave in the four decades between 1966 and 2005; and [2] that this information could be applied to reconstruct palaeofires. Primarily, these studies have shown that fire events may be recorded by speleothems through the loss of stored shallow water and loss of vegetation, the infiltration and incorporation of ash- and soil-derived elements, changes in calcite fabric induced by the influx of foreign ions and particles and changes in speleothem extension rate owing to changes in carbonate chemistry resulting from heating of the limestone and impact on soil CO_2. Critically, these dripwater monitoring studies have shown that the proxy response is modulated by fire severity and cave depth (Figure 3). The proxy response is present in the largest number of proxies in shallow caves which experienced more severe fires (Bian et al., 2019; Nagra et al., 2016). Deeper caves which also experienced less severe fires showed a more muted (Treble et al., 2016) or entirely absent (Coleborn et al., 2019, 2018) proxy response. Here we have produced two new figures to summarise these studies. Figure 2 shows a conceptual illustration of the proxies and processes identified in these studies and Figure 3 shows which proxies showed a response to fire in each cave monitoring study, ordered by cave depth. In the remainder of Section 4, we expand on these proxies and the relevant processes from these and other studies.

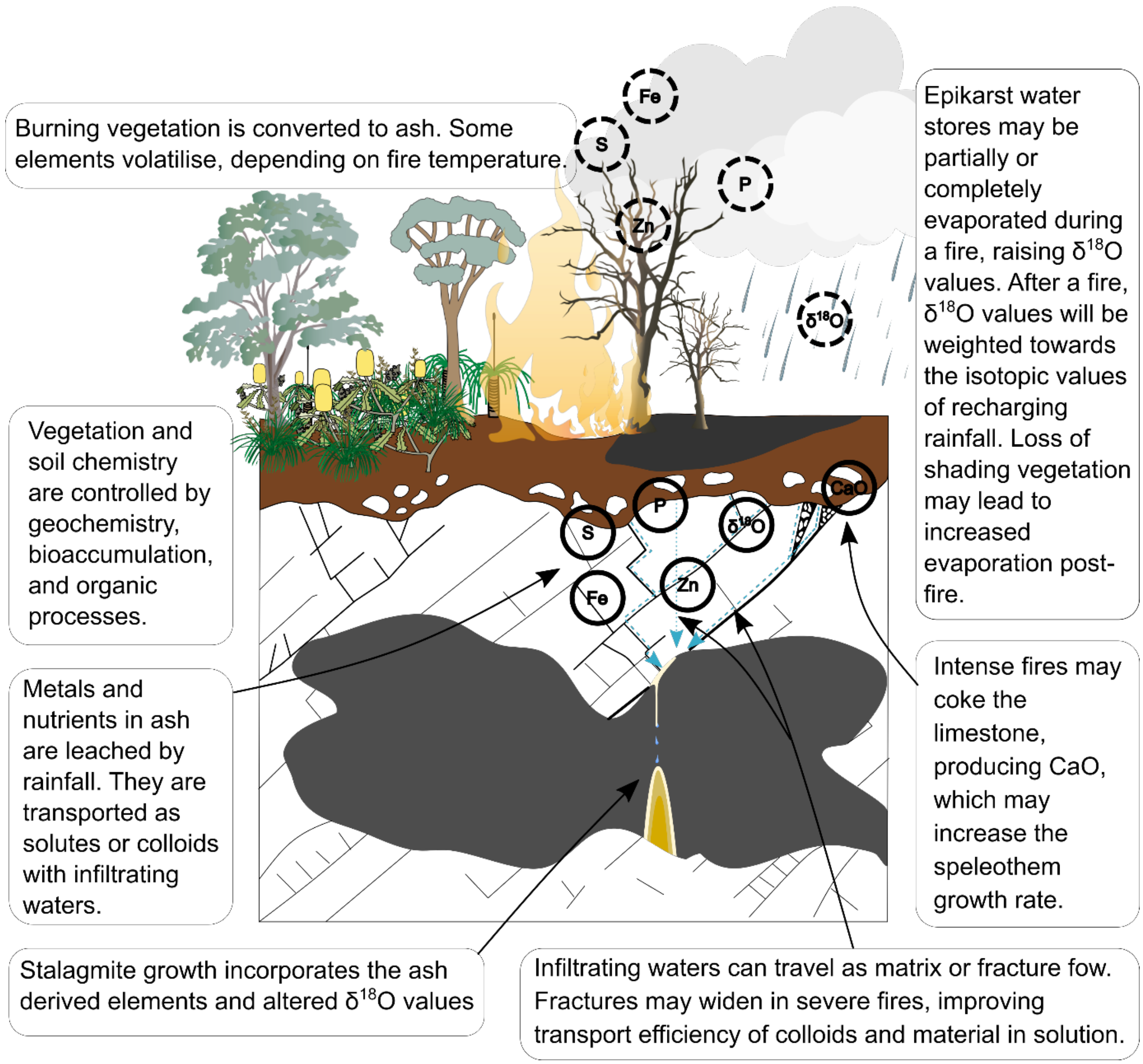

Figure 2 Conceptual model of processes underpinning the production, transport, and incorporation of known speleothem fire proxies.

Fire impacts have been well-documented in surface hydrology (predominantly in non-karst environments), with reported downstream increases in nitrate, phosphate, turbidity, and decreases in dissolved oxygen and pH (Dahm et al., 2015; Reale et al., 2015; Sherson et al., 2015). In surface waters, erosion (a primary driver of changes to hydrochemistry) may continue for many years following a fire event, particularly if vegetation recovery is slow and there is a delay in extreme precipitation events (Shakesby, 2011). Ash chemical composition is well-understood, and has been found to vary with underlying geology, vegetation composition, and fire intensity (Alriksson and Eriksson, 1998; Bodí et al., 2014; Cerrato et al., 2016; Khanna et al., 1994). Chemical concentrations in ash may be higher than in vegetation, suggesting bioaccumulation and concentration of elements (Cerrato et al., 2016).

In the highly porous karst landscape, dissolution and colloidal transport of a large proportion of ash-derived elements is likely to occur via infiltration to the epikarst and groundwater rather than via surface flow to rivers and streams. This is consistent with the colloidal and dissolved transport of common trace elements through karst (Borsato et al., 2007). Transport of ash-derived elements is a function of their solubility (or adsorption to colloidal particulates and minerals), and may be confounded by losses through mineralisation or biological uptake (Khanna et al., 1994; Treble et al., 2016). The geological and species controls on ash chemistry, as well as variable rates of dissolution, transport, mineralisation, and biological uptake suggest that it may not be possible to quantifiably compare changes in ash chemistry between regions.

The mechanisms by which a speleothem may incorporate the fire signal are broadly separated into physical and chemical processes. Physical processes include modifying the volume of stored water by evaporation, fracturing of host rock, increased soil hydrophobicity and preferential flow, conversion of limestone to lime, and changes to soil CO2 production. Chemical processes include the introduction and transport of ash-derived trace elements and metals and the impact of limestone coking on CaO production and speleothem extension rate.

4.2.1 Impact on hydrology

Increased evaporation can impact the δ18O signal depending on the relative loss of shallow stored water in the soil or epikarst zone and subsequent recharge events. Surface heating from fire may directly evaporate stored water during a fire event, and prolonged evaporation post-fire may occur due to reduced overstorey and ground cover (loss of shading) (Bian et al., 2019; Nagra et al., 2016). While transpiration can be elevated in post-fire regrowth (Buckley et al., 2012), transpiration does not result in fractionation of soil water. The post-fire δ18O response in cave dripwaters has been shown to vary, with both higher and lower values observed (Figure 3). Following a bushfire over a shallow forested cave in southwest Australia, Nagra et al. (2016) found an increase in dripwater δ18O values attributed to increased evaporation because of loss of canopy cover and reduced albedo (Nagra et al., 2016). Conversely, Bian et al., (2019) found that δ18O declined following an experimental fire over a shallow cave in southeast Australia. They attributed this to the complete evaporation of stored soil/epikarst water during the fire, followed by recharge by an isotopically low precipitation event (Bian et al., 2019). They also noted that reduced capillarity and increased preferential flow in the soil may have further assisted post-fire recharge (Bian et al., 2019). In the same cave monitored by Nagra et al. (2016), an increase in stalagmite δ18O in the year following a reconstructed fire event in 1897 CE was noted and this was attributed to increased evaporation as seen in Nagra et al. (2016) (McDonough et al., 2022). A subsequent shift to lower δ18O values in the stalagmite record was interpreted as a return to wetter conditions with the caveat that a change in hydrology due to fracturing and preferential flow may have amplified the shift in calcite δ18O values (McDonough et al., 2022).

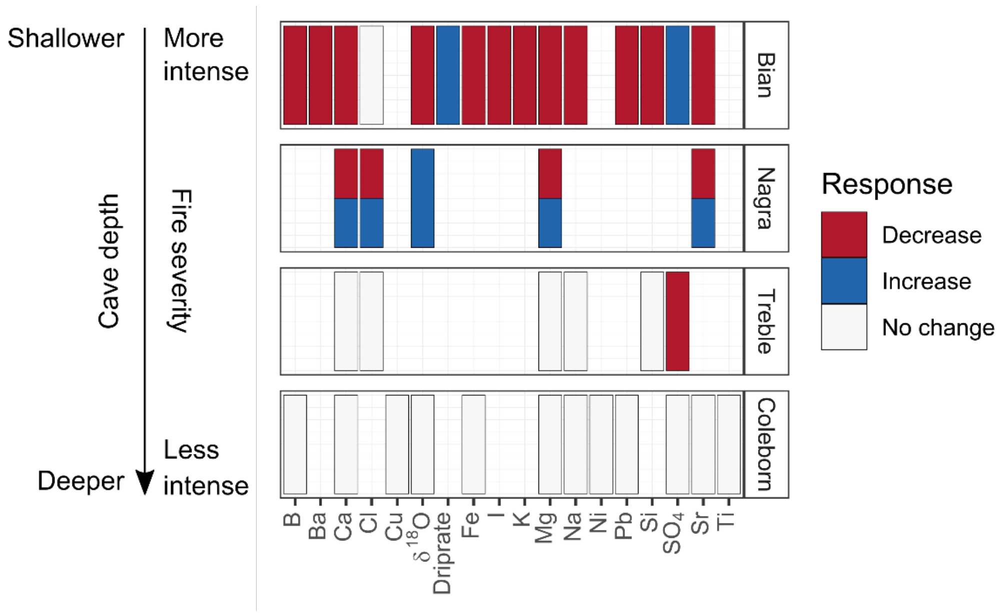

Figure 3 Published proxy responses to fire events in dripwater (Bian et al., 2019; Coleborn et al., 2018; Nagra et al., 2016; Treble et al., 2016). Red indicates a post-fire decrease in a proxy, blue indicates a post-fire increase in a proxy, and white shows that no change was recorded. Results are presented in order of cave depth and fire severity, with the shallowest cave and most severe fire at the top of the figure, and the deepest cave and least severe fire at the bottom of the figure.

Fracturing of host rock and increased soil hydrophobicity have been both observed and inferred in the δ18O, trace element and organic matter responses to fire (Bian et al., 2019; McDonough et al., 2022; Nagra et al., 2016). Limestone structure can be impacted by temperatures >500°C (base temperatures in a large fire can exceed 1000°C), with heating and cooling leading to fracturing or widening of fractures in the epikarst (Meng et al., 2020; Wu and Wang, 2012). Bushfires can also enhance soil hydrophobicity. In an experimental trial on eucalypt forest, Granged et al. (2011) found that post-fire water repellence was greatest after a low-intensity fire, and that soil water repellence persisted for some months. Medium and high-intensity fires completely destroyed soil water repellence, which was attributed to a large reduction in soil organic matter after peak temperatures of 317 and 525°C (Granged et al., 2011). Increased fracturing and soil water repellence can both result in increased preferential flow and so alter vadose zone hydrology, resulting in more direct connectivity between the surface and the cave. Bian et al. (2019) interpreted a post-fire negative excursion in δ18O to isotopically heavier precipitation being rapidly transported to the cave due to an increase in preferential flow. They noted that dripwater isotopic composition returned to an integrated mean after ~6 months as soil water stores were replaced (Bian et al., 2019). McDonough et al. (2022) attributed a rapid increase in organic matter concentration to enhanced meso- and macro-porosity of the bedrock as a result of limestone heating, and increased flushing of soil organic matter through the bedrock. This is consistent with field trials which have shown losses of organic matter from the soil surface associated with soil water repellence (Lowe et al., 2021). In places where soil water repellence is already high (such as in the sandy soils of Western Australia), exacerbation of soil water repellence by moderate fire and destruction of non-wetting soils by severe fire may be a key consideration in separating severe and moderate fire events in the proxy record. Beyond fracturing and hydrophobicity, heating of limestone can also result in localised lime formation. This leads to enhanced supersaturation as that lime is preferentially dissolved by infiltrating waters, resulting in a higher speleothem extension rate (Hartland et al., 2010; Kemperl and Maček, 2009; Moropoulou et al., 2001). This phenomenon was observed by McDonough et al. (2022), when extension rate increases followed a large inferred palaeo-fire event.

4.2.2 Impact on soil microbiology

Soil CO2 is a key driver of stalagmite formation, as it is a major control of dissolution in karst environments (Dreybrodt, 1999). Plant respiration and microbial activity produce soil CO2 with partial pressures 1—3 orders of magnitude greater than that of the atmosphere (Appelo et al., 2005). Fallen precipitation absorbs this CO2, becoming mildly acidic. This mildly acidic water then dissolves the parent rock as it infiltrates. Only when this infiltrating water encounters a region of lower partial pressure of CO2 will CO2 degas and calcite precipitate (Fairchild and Baker, 2012). When vegetation and microbes are destroyed by fire, soil CO2 concentrations are suppressed. The impact of fire on total soil respiration is a function of fire severity, vegetation, microbe age and species composition, fire regime, and soil moisture (Bárcenas-Moreno and Bååth, 2009; Certini, 2005; Gongalsky et al., 2012; Arturo J.P. Granged et al., 2011; Arturo J. P. Granged et al., 2011; Hart et al., 2005; Jenkins and Adams, 2010; Neary et al., 1999; Pharo et al., 2013; Uribe et al., 2013; Zedler, 2007). Coleborn et al. (2016) investigated the long-term response of karst soil CO2 in woodland and grassland, and subalpine forest environments. They found that soil CO2 concentrations take >5 years to return to pre-fire levels in a woodland and grassland landscape, and >10 years to recover in a subalpine forest, and that recovery was associated with the vegetation recovery rate (Coleborn et al., 2016b). It follows that disruption of soil microbiology and CO2 abundance due to fire may impact speleothem growth rate, δ13C, and 14C, although further research is required to quantify this phenomenon.

4.2.3 Impact on speleothem fabric

Speleothem fabric refers to the configuration of calcite or aragonite crystals forming the speleothem and is characterised by their size, orientation, arrangement, preservation, and intra-crystalline porosity. These are controlled by cave parameters such as dripwater flow type and variability, cave temperature, calcium saturation, solute chemistry, foreign particles and biological communities (Fairchild and Baker, 2012; Frisia and Borsato, 2010). Hence, speleothem fabric has been used to infer hydrology and post-depositional processes (Fairchild and Baker, 2012). Repeated fabric patterns have been observed in laminated speleothems from sites with high climatic seasonality, and likely reflects seasonal changes in dripwater composition (Frisia and Borsato, 2010). Speleothems dominated by low-porosity fabrics (e.g. columnar fabrics with low visible intercrystalline porosity; Frisia, 2014), are generally favoured for palaeofire reconstructions as these fabrics are more suitable for high resolution in situ techniques such as X-ray Fluorescence Microscopy XFM and Synchrotron micro X-ray fluorescence (S-μXRF), laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and secondary ionisation mass spectrometry (SIMS). See Frisia (2014) for further description of speleothem fabric types.

Analysis of speleothem fabric has been shown to be a useful tool for identifying palaeofires. McDonough et al. (2022) logged speleothem fabric following the schema of Frisia (2014) and found that a large palaeofire in the record (see also Section 6.3) coincided with a micro-hiatus in growth defined by optical continuity in crystal growth, no dissolution of crystal tips, and no evidence of renucleation. Following this micro-hiatus (after the fire event), crystal fabric became more porous with acute crystal tips (McDonough et al., 2022). They determined this was due to an influx of impurities, which initially occluded growth, and then temporarily poisoned growth sites at calcite surfaces over the next six years, resulting in higher porosity (McDonough et al., 2022).

4.2.4 Impact on inorganic proxies

Post-fire cave dripwater monitoring showed that dripwater geochemistry can be impacted by fires. Post-fire responses in dripwater δ18O values and sulphate concentrations are covered in Section 4.2.1 and 6.2, respectively. Here, we describe post-fire changes in inorganic proxies such as dripwater solutes that may be ultimately incorporated as trace metals in speleothems that are also summarised in Figure 3.

Dripwater monitoring following an intense fire in 2005 over Yonderup Cave (~4 m below ground level), southwest Australia, showed that the response of water soluble ions (chlorine, calcium, magnesium, strontium) differed between two monitored drip sites in the cave, with ions decreasing at Site 1a, and increasing at Site 2a (Figure 3; Nagra et al., 2016). Solute concentration through increased evaporation was suggested as the reason for increased post-fire concentrations at Site 2a, with declining solutes at Site 1a attributed to reduced transpiration and a gradual return to base concentrations following a pulse of ash-derived solutes (Nagra et al., 2016).

To further test the hypothesis that dripwater geochemistry is influenced by fires, experimental burns were carried out over two caves in southeast Australia (Bian et al., 2019; Coleborn et al., 2018). Following a low intensity controlled burn over South Glory Cave, a deep (~40 m) cave in southeast Australia, no significant change in dripwater chemistry was noted (Coleborn et al., 2019, 2018). Conversely, a high intensity prescribed burn over Wildman's Cave in southeast Australia (~1 m below ground surface) led to declines in a suite of elements (boron, barium, calcium, iron. iodine, potassium, magnesium, sodium, silicon, and strontium) and an increase in dripwater sulphate (Bian et al., 2019). Flow to the shallow Wildman's Cave is entirely dominated by fractures, and the karst has no remaining matrix porosity (Bian et al., 2019; Osborne, 1993). This may explain the clear and significant post-fire change in dripwater chemistry as the signal is transported rapidly with minimal opportunity for mixing. Conversely, South Glory Cave karst (Yarrangobilly Karst) is also highly fractured with little matrix porosity, but the much deeper cave may have allowed for mixing and attenuation of the chemical signal, which itself may have been minimised as the fire was of low intensity (Coleborn et al., 2019, 2018, 2016a). Dripwater monitoring results highlight that site and sample selection is a key step in speleothem palaeofire research, with sample selection further discussed in Section 5.1. An understanding of cave hydrogeology (through cave monitoring) will facilitate appropriate sample selection.

4.2.5 Impact on organic biomarkers

Organic biomarkers have been extensively used to investigate past fires in ice and sediment cores (Battistel et al., 2018; Brittingham et al., 2019; Thomas et al., 2022; Vachula et al., 2019). In speleothems, organic biomarkers have been applied to investigate climate-terrestrial carbon feedbacks (Wang et al., 2019) and past temperature (Baker et al., 2019; Blyth et al., 2016; Huguet et al., 2018). The use of organic biomarkers in speleothem research has been limited by the low concentrations of organic matter in speleothems, with analyses generally requiring large sample sizes (up to 20 g), resulting in coarse resolutions (Blyth et al., 2016) and the loss of source signature due to the biodegradation and sorption of organic biomarkers between the source and the speleothem (Blyth et al., 2016; Jex et al., 2014). Additionally, organic biomarker analyses are susceptible to contamination, and require care in sample preparation and laboratory protocols (Blyth et al., 2016; Wynn and Brocks, 2014). However, recent analytical advances have enabled high resolution analysis of polycyclic aromatic carbons in calcite (Argiriadis et al., 2019). This could be significant, as polycyclic aromatic carbons have been extensively used in sediment core fire research (Denis et al., 2012; Vachula et al., 2022). Noting that their low water solubility might limit their concentrations in speleothems, polycyclic aromatic hydrocarbons offer an exciting new application for speleothem palaeoenvironmental research. In speleothems, recent research has shown feasibility, with high-resolution analyses finding detectable concentrations of these hydrocarbons in a stalagmite coinciding with a known fire event over a shallow cave in northwest Australia (Argiriadis et al., 2019).

4.2.6 Impact on mineral magnetism

When sedimentary minerals are heated (e.g. in a hearth or in a wildfire), they undergo magnetic enhancement (Gedye et al., 2000; McClean and Kean, 1993). Mineral magnetism has been used to determine dominant fuel type in Iron Age and Medieval hearths (Peters et al., 2001), to detect Holocene hearths in North America (Urban et al., 2019), and to reconstruct palaeofire from sediment cores (Gedye et al., 2000). Recent advances in microscopy have allowed for speleothems, which typically do not have sufficient concentrations of magnetic minerals for high-resolution palaeomagnetic analyses (Lascu et al., 2016), to be analysed at spatial resolutions of 200 µm or better (Feinberg et al., 2020; Fu et al., 2021; Naoto et al., 2021). Recently, Quantum Diamond Microscopy achieved a mineral magnetism spatial resolution of 4.7 µm on analysis of an annually laminated speleothem from Brazil, finding that changes in magnetism reflected changes in hydroclimate (Fu et al., 2021). These high-resolution techniques have enabled stalagmite hydroclimate reconstructions at temporal resolutions comparable with or exceeding that of conventional methods such as Isotope Ratio Mass Spectrometry (Feinberg et al., 2020; Fu et al., 2021). It has been demonstrated that magnetic enhancement can occur in ash (McClean and Kean, 1993). Following this, there is potential for speleothem palaeomagnetism to record past fire events or past fire regimes, and changes in the magnetic properties of a Tongan speleothem have been tentatively linked to anthropogenic fire use (Naoto et al., 2021).

5 Methods and techniques

5.1 Speleothem sample selection

Honey to brown coloured calcite generally has higher organic content, with the colour indicating that a speleothem was fed by dripwater that underwent both high soil-water contact and efficient surface-to-stalagmite transport of organics (Pearson et al., 2020; Treble et al., 2017; van Beynen et al., 2001). Inclusion of organic matter is critical for the transport and inclusion of insoluble trace metals which are non-exchangeable in short thin-film residence times, but which may be bound and incorporated in speleothems with organic matter (Hartland et al., 2014, 2011; Pearson et al., 2020). Following this, calcite colour may be used as a simple diagnostic for sample selection. Climates with high seasonality produce stalagmites with annual chemical and physical laminae (e.g. Orland et al., 2014), which aids in the development of an accurate annual-resolution chronology such as that used by McDonough et al. (2022). McDonough et al. (2022) were able to constrain fire events with a maximum age error of ±13 years over a period of ~250 years. Faster-growing stalagmites allow for higher temporal resolutions as common analytical approaches require a growth rate of >20 μm yr-1 to capture annual data, and even higher to capture seasonal data (see Section 5.2 for instrumental spatial resolutions). As stalagmites have been shown to record discrete fire events (McDonough et al., 2022) rather than mean fire behaviour, higher growth rates allow for better confidence around the timing of those events. Globally, stalagmite growth rate has been shown to positively correlate with mean annual temperature (Baker et al., 2021), which suggests that warmer fire-prone regions may be more likely to produce faster growing stalagmites.

High sample porosity, and cracks or poor sample polishing can confound micro-analytical results. For LA-ICP-MS, calcium is used as an internal standard to acccount for variations in the volume of material ablated but relatively large variations in calcium over porous regions and cracks may introduce an analytical artefact to this correction (Sinclair et al., 1998). For SIMS, these features can interupt the integrity of sample coating and thus create potential for analytical artefacts. For S-μXRF, porous samples, including fluid inclusion-rich samples produce scattering of the fluorescence signal which can significantly affect the clarity of the elemental map. This can be overcome by careful sample selection, petrographical examination of thin sections and comparison with the S-μXRF calcite and elastic scattering maps (Borsato et al., 2021).

5.2 Lab methods

Here, we provide an overview of methods with applications to the detection of inorganic palaeofire proxies in speleothems, including laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and solution ICP-MS, Synchrotron micro-XFM (S-μXRF) and benchtop micro-XFM, U-series dating, carbon dating, and lamina counting, isotope ratio mass spectrometry (IRMS), and secondary ion mass spectrometry (SIMS). As multi-proxy archives, analysis of speleothems for palaeoenvironmental applications generally requires a combination of laboratory methods.

5.2.1 Inductively coupled plasma mass spectrometry

Both laser-ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and solution inductively coupled mass spectrometry (solution ICP-MS) can measure most elements with high analytical precision and low limits of detection. LA-ICP-MS element detection may be hindered by non-carbonate inclusions which cannot be excluded, while solution ICP-MS is mainly limited by elemental interferences (Fairchild et al., 2006; Fairchild and Treble, 2009). LA-ICP-MS has typical detection limits of 0.1-10 ppm (s) and typical spatial resolution of 20-1000 μm, but sometimes as low as 3 μm (Müller and Fietzke, 2016), while solution ICP-MS detection limits can reach ppb levels, with a sample size of 100-5000 μg (100 μg of calcite is ~0.34 mm3; Fairchild et al., 2006). Advantages of LA-ICP-MS are its rapid and precise measurement, it is minimally destructive, and generally affordable and accessible. Solution ICP-MS is also precise, accurate, affordable and accessible, but sample preparation and analysis are more time consuming and destructive than LA-ICP-MS. A disadvantage of LA-ICP-MS is that false positives can be introduced by cracks, porosity, and imperfections in the sample, as trace elements are generally presented as a ratio of calcium, and these regions will have lower calcium counts. McDonough et al. (2022) presented five parallel LA-ICP-MS tracks and showed that a decrease in calcium associated with a crack produced a false peak in phosphorous. This can be overcome through careful sample preparation and choice of laser track, and multiple tracks or operating in raster mode may be used to overcome this limitation (Sliwinski and Stoll, 2021; Treble et al., 2005). There is currently no widely-available matrix-matched calcite standard for LA-ICP-MS, and while glass standards are commonly used, they are imperfect (Baldini et al., 2021).

5.2.2 Synchrotron micro-XFM and benchtop micro-XFM

Trace element concentrations can vary laterally along growth layers (Treble et al., 2003, 2005), and elemental maps allow lateral heterogeneity to be resolved. While LA-ICP-MS can be used to analyse a wide range of elements with very low detection limits (Treble et al., 2005; Woodhead et al., 2007), resolution is limited to ~20 µm (Borsato et al., 2021; Sliwinski and Stoll, 2021). X-ray fluorescence (XRF) or X-ray fluorescence microscopy or mapping (XFM) allows for the quantification of elements through the bombardment of a sample (e.g. speleothem calcite) with high energy primary X-rays (Ramsey et al., 1995). This bombardment removes inner shell electrons, and as outer orbit shell electrons fall to lower energy orbitals, they fluoresce characteristic secondary X-rays which may be measured to quantify elemental concentrations (Ramsey et al., 1995; Scroxton et al., 2018). Both S-µXRF and benchtop micro-XFM have been used to analyse speleothems.

S-µXRF can produce elemental maps with resolutions as high as 1 µm per pixel (Borsato et al., 2021). As mean annual growth rate for laminated speleothems is ~160 µm yr-1 (Baker et al., 2021), the very high resolution provided by S-µXRF allows for sub-seasonal data to be collected (Baldini et al., 2021). As well as changes in chemical concentration, S-µXRF can visualise changes in porosity and large-scale variation in speleothem fabric (Borsato et al., 2021, 2007; Frisia et al., 2005; McDonough et al., 2022). Accompanying X-Ray Absorption Near Edge structure can be used to determine chemical speciation (Baldini et al., 2021; Frisia et al., 2008). S-µXRF limits of detection depend on the excitation energy, dwell time, porosity, pixel size, and detector type, and tend to be higher than for LA-ICP-MS (approximately 10-100 ppm for S-uXRF). While S-µXRF is non-destructive it does require that samples be sectioned to fit the mount, polished or double-polished, and sample preparation can impact results (Borsato et al., 2021). In calcite, high excitation of Ca, and escape and sum peaks of the same, can interfere with nearby elements (Borsato et al., 2021). A significant disadvantage of S-µXRF is the expense, although merit-based free access can be achieved for many of the world's research synchrotrons. Borsato et al. (2021) and Baldini et al. (2021) present comprehensive guides to the application of S-µXRF to speleothems.

Micro-XFM is a more commonly available alternative technique but with a lower-energy compared with S-µXRF that produces a compromise on resolution and detection limits. Some non-vacuum micro-XFM have the advantage of being able to analyse full sample lengths. Non-vacuum 'benchtop' and core-scanner micro-XFM has been used to measure heavier elements such as strontium, iron, silicon, copper, potassium, nickel and barium (Buckles and Rowe, 2016; Guo et al., 2021; Scroxton et al., 2018; Tan et al., 2015; Wu et al., 2012), but lighter elements (e.g. magnesium) are generally confounded by the attenuation of secondary X-rays in the air-gap (Scroxton et al., 2018). Vacuum or near-vacuum micro-XFM may enable the analysis of lighter elements such as sulphur or magnesium. However, recently sulphur was successfully measured using benchtop non-vacuum micro-XFM, with artefacts due to the diffraction of the incident beam overcome by the use of multi point statistics (Wang et al., 2022). The ability to measure strontium by micro-XFM is a key advantage, as it allows for the rapid and economic development of Sr-based chronologies in annually laminated samples.

5.2.3 Chronology building

Uranium-series techniques (e.g. U-Th disequilibrium, U-Pb, (U-Th)/He) are used to absolutely date speleothems at scales from the modern to millions of years old (Fairchild and Baker, 2012; Makhubela and Kramers, 2022; Richards et al., 1998). They are based on the radiogenic decay of uranium isotopes (234U, 235U, and 238U), whose half-lives are well-constrained (Cheng et al., 2000; Jaffey et al., 1971; Rasbury and Cole, 2009), to various daughter isotopes . U-Th disequilibrium dating generally has high precision (~1%) but may be complicated by the inclusion of 'detrital' thorium (Fairchild and Baker, 2012; Zhao et al., 2009). Detrital thorium is transported with organic matter, colloids, and sediments and may result in overestimation of the U-Th age without correction (Fairchild and Baker, 2012). U-Th dating is challenging in young carbonates where the daughter 230Th is very low, and may be confounded by the presence of non-radiogenic 230Th (Zhao et al., 2009). Non-radiogenic 230Th may form a greater proportion of total 230Th in young carbonates, and so have a greater impact in young carbonates than in old carbonates (Zhao et al., 2009). Precision of the U-Th geochronometer declines after ~400 ka (Fairchild and Baker, 2012). U-Pb dating has slightly lower precision than U-Th dating (1-5%), but can be applied to much older carbonates (>400 Ma) (Fairchild and Baker, 2012). As with the U-Th geochronometer, U-Pb dating may be complicated by detrital lead as well as variable initial Pb (Fairchild and Baker, 2012; Rasbury and Cole, 2009). The problem of common Pb may be overcome by screening for detrital Th, as they are likely to have the same source (Fairchild and Baker, 2012; Woodhead et al., 2006). Recently, (U-Th)/He dating has been applied to South African speleothems (Makhubela and Kramers, 2022). (U-Th)/He is an alternative to U-Pb for samples older than 500 ka, and has some advantages in that more He atoms are produced per decay than Pb, and He is not expected to be included in speleothems other than by radiogenic decay (Makhubela and Kramers, 2022). As such, (U-Th)/He dating may be a suitable method for dirty samples and samples low in uranium (Makhubela and Kramers, 2022), although apatite and zircon He ages may be reset by wildfire (Mitchell and Reiners, 2003), which could complicate (U-Th)/He dating of speleothems.

Carbon dating of speleothems is complicated by the processes which transport atmospheric 14C to calcite. Bedrock, soil, and occasionally cave atmosphere all contribute carbon to speleothems. The potentially large and variable proportion of bedrock-derived carbon, which is termed 'dead carbon' as all 14C has generally decayed (except in very young parent rocks) must be accounted for to accurately use 14C as a geochronometer in speleothems (Fairchild and Baker, 2012; Hua et al., 2012). However, in modern samples, the 'bomb-pulse' may be used as a chronological anchor to constrain 20th Century speleothem growth (Genty and Massault, 1999; Markowska et al., 2019). Hua et al., (2012) demonstrated that when the dead carbon fraction can be determined and corrected for, reliable 14C-derived chronologies can be achieved, while Lechleitner et al. (2016) have developed an algorithm to date speleothems independent of the dead carbon fraction (although it does require that the dead carbon fraction has no long-term trend. Nonetheless, radiocarbon dating is probably best-reserved for young speleothems, where U-series techniques are not applicable.

Speleothems may form both physical and chemical annual laminae, and stalagmites which form annual laminae are most common where precipitation is highly seasonal (Baker et al., 2021). In a global synthesis of annually-laminated stalagmites, Baker et al. (2021) observed centennial-scale stability in stalagmite extension rates, with climate forcing of growth rate variations observed only where the multi-year climate signal was large enough to dominate the calcite extension rate. This suggests that annual lamination is robust enough to persist through climate fluctuations, and therefore be a reliable addition to chronology-building (Baker et al., 2021). Annual laminae for improving speleothem chronologies are especially useful where radiometric dating uncertainties are high due to (for example) low environmental uranium/high initial 230Th, as seen in the Tropical Pacific, or insufficient ingrowth of 230Th, as seen in modern speleothems. Smith et al. (2009) used chemical variations obtained by ion microprobe to date non-laminated Alpine speleothems. More cently, Faraji et al. (2021) used S-µXRF mapping of strontium concentrations and optical imaging of stalagmite laminae to generate an annual chronology with a maximum of ±15 years of uncertainty over the 336-year record. In modern speleothems from southwest Australia (a region with a Mediterranean climate with strong seasonality and seasonal controls on prior calcite precipitation), annual fluctuations in trace element concentrations have been used to construct chronologies for modern stalagmites with low uncertainties (McDonough et al., 2022; Nagra et al., 2017).

5.2.4 Isotope ratio mass spectrometry

Stable carbon and oxygen isotopes may be measured with isotope ratio mass spectrometry, typically by milling discrete samples, although laser-ablation techniques exist (Spötl and Mattey, 2006). While laser ablation is much more time-efficient, the use of the laser adds additional fractionation to not just the ablated sample but also to the ablation pit and the thermal halo, which can be 2-4 times the size of the laser spot (Fairchild et al., 2006; Spötl and Mattey, 2006). Milled IRMS has better external precision than LA-IRMS, and can achieve better spatial resolution (as low as 0.05 mm) (Fairchild et al., 2006), although disadvantages are that milled IRMS is more destructive and resolution can be variable depending on the density of the material (with sample weights of 50-120 µg typically required).

5.2.5 Secondary ionisation mass spectrometry

Secondary Ion Mass Spectrometry (SIMS) can measure both trace elements and stable isotope ratios in carbonates. SIMS is minimally destructive, requiring only a very small amount (<1 ng) of material. However, sample preparation requires sectioning, polishing and mounting, leading to some loss of material. SIMS has excellent lateral resolution for both trace elements (1—2 µm spot size) and stable isotope ratios (~10 µm), meaning it is capable of producing seasonal-resolution data (Baldini et al., 2021; Orland et al., 2019). However, sample size is restricted to <15 mm, which along with the comparatively long analysis duration (e.g., 3—4 min per δ18O spot analysis, complicates the construction of long seasonal records. A clear advantage over LA-ICP-MS is that SIMS can overcome polyatomic interferences from 48Ca and 16O and measure sulphur (Wynn et al., 2010), which is valuable in palaeofire research as sulphur has been shown to be a key indicator of past fire (McDonough et al. 2022).

5.3 Statistical approaches

Statistical methods can be used to identify the timing of fire events. McDonough et al. (2022) used timeseries Principal Component Analyses (PCA) and k-means clustering of variables to identify key processes affecting stalagmite geochemistry. Both PCA and clustering approaches are widely used in speleothem science to analyse multivariate datasets (e.g. (Markowska et al., 2015; Nagra et al., 2017; Orland et al., 2014). McDonough et al. (2022) identified dry and wet periods, the contributions of bedrock- vs aerosol-derived parameters, and short-term increases in phosphorus and trace metals including zinc, lead, copper and aluminium which aligned with the timing of known fire events occurring over the cave. They concluded that increases in phosphorous and trace metals were the likely result of soluble and colloidal ash-derived elements entering the dripwater and being incorporated into the speleothem. Identification of changes in dry and wet conditions allowed for an observed change in hydrology after a particularly intense fire event resulted in a decrease in water-rock interaction and dilution of bedrock and aerosol sourced components (McDonough et al., 2022). McDonough et al. (2022) found that peaks in their 'fire' principal component were not always driven by peaks in the same elements, and that no single chemical tracer could identify each fire event, highlighting that a multivariate statistical approach was required. McDonough et al. (2022) also used changepoint analysis to identify which parameters were most affected by these longer-term changes in hydrology, although they found that changepoints were not suitable for identifying short term changes in trace metals and phosphorus. Hope et al. (2010) previously used changepoint analysis to identify dry periods in rainfall timeseries data, while Tibby et al. (2018) used the same approach to analyse proxy rainfall data. Their results suggest this technique could be useful for detecting changes in climate and hydrology leading up to, or following, fire events, but less useful for identifying individual fire events.

6 Southwest Australian case studies

Here, we present four case studies which illustrate [1] that ash geochemistry is related to fire severity, [2] how sulphur cycling is impacted by fire events [3] how a catastrophic palaeofire in southwest Australia was related to changed land management and climate, and [4] that fires may be recorded in deep cave stalagmites, if hydrological processes allow the transport of the fire signal. These case studies are drawn from published and unpublished research, and analytical methods for each case study except the third (published in full in McDonough et al., 2022) are presented in the supplemental material.

6.1 Geochemistry of bushfire ash leachates

Ash from fires can alter soil and cave dripwater chemistry. This ash can form directly on soils above a cave after a fire, or be transported into the region via surface runoff and winds. Cave dripwater may be impacted through leaching of the ash and transportation of elements as either soluble ions or colloids (both bound to organic matter and as particulates) (Hartland et al., 2012). The composition of wildfire ash derived from the burning of biomass is a function of the plant species burned and the extent of their bioaccumulation of elements, burn temperature and combustion completeness (Bodí et al., 2014). Ash colour is related to the combustion completeness (Roy et al., 2010; Stronach and McNaughton, 1989). Black char is the primary by-product of biomass pyrolysis and occurs at low temperatures (≤350°C; Bodí et al., 2014), while white ash occurs when vegetation is at or near complete combustion (500-1400°C; Bodí et al., 2014). Elements with high volatilisation temperatures, such as potassium, zinc, cadmium, copper, sodium, magnesium, calcium, and manganese (all >700 °C) increase in relative proportion to other elements at higher burn temperatures, due to the removal of other elements such as nitrogen and sulphur at lower temperatures (<600 °C; Figure 4).

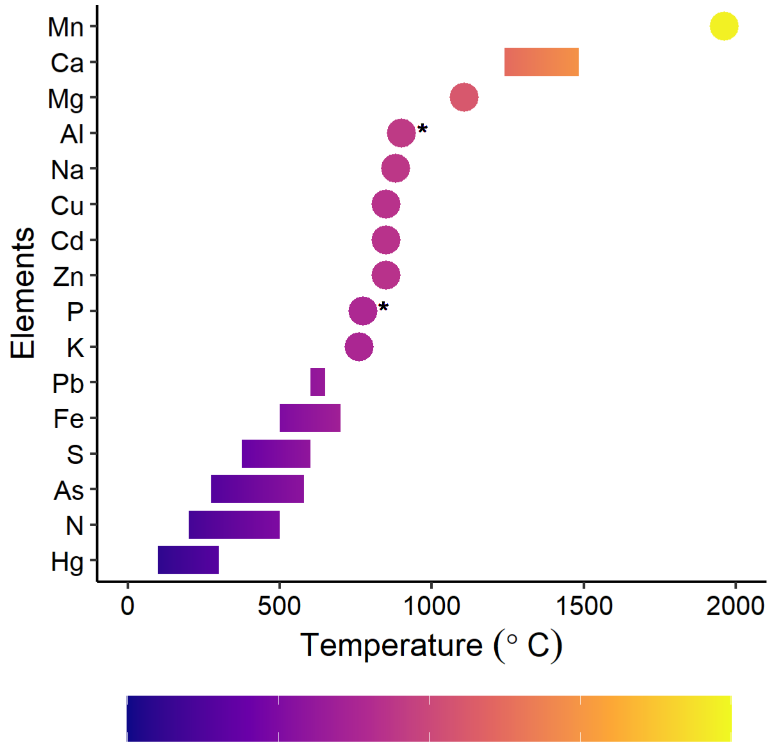

Figure 4 Volatilisation temperatures for select elements. Bars show the range of temperatures reported, while circles show singular values. The asterisk (*) indicates that this is a minimum volatilisation temperature, with the actual temperature likely to be higher. Colour indicates temperature in °C, the colour bar is to the same scale as the x-axis. Mn, Ca, Mg, Na, K, S, N and Hg volatilisation temperatures reported in Bodí et al. (2014) and references therein. Zn volatilisation temperature from Clifford et al. (1993), Pb, As, Cd and Cu volatisation temperatures from Tuhý et al. (2021), Fe, and Al volatilisation temperatures from Balfour and Woods (2013). P volatilisation temperature as reported in Bodí et al. (2014) and Balfour and Woods (2013). Note that different terminologies and experimental designs were used. Adapted from Bodí et al. (2014).

While few studies have investigated the concentrations of heavy metals in ash, or how these vary with plant species composition and burn temperature, Pereira and Úbeda (2010) reported that concentrations of aluminium are higher than other metals leached from ash after the burning of oak and pine trees. They also identified high variability in iron and zinc concentrations, with lower concentrations associated with upslope locations which was suggested to be the result of greater burn temperatures. Since trace metals are usually present in very low concentrations in uncontaminated soils, increases in concentrations due to the leaching of ash could be a useful indicator of past fire events in speleothems. In addition, nutrients such as phosphorous and sulphur can be present in high concentrations in plant ash (Etiegni et al., 1991; Sander and Andrén, 1997) and may also be a useful proxy for past fire events. The addition of plant ash to soils has been observed to result in the leaching of 3—10 times more phosphorus from soils compared to soils that do not contain ash (Escudey et al., 2010). McDonough et al., (2022) identified that trace metals and nutrients such as phosphorous from ash were useful fire proxies in a speleothem, however the combination of phosphorous and trace metals that increased during known fire events above the cave was found to be inconsistent. The authors hypothesised this to be the result of differences in fire intensities.

Ash leachate analyses on white and black ash collected after a wildfire in Yanchep National Park, Western Australia, in December 2019 are presented below (Figure 5). Boxplots show clear and statistically significant differences in concentrations of phosphorous, sulphur, sulphate, zinc, aluminium, iron, copper, and magnesium. Strontium concentrations are not significantly different, although white ash results are more variable. This is a positive outcome as it suggests that strontium in speleothems is unlikely to be impacted by fire events, and so strontium-based chronologies are robust to fire impacts, at least for this karst region where strontium has been shown to be bedrock derived (Treble et al., 2016). Generally, ash leachate results are consistent with volatilisation temperatures from the literature (Figure 4). That is, elements with very high volatilisation temperatures have higher relative abundances in white ash (e.g. magnesium and copper), while elements with lower volatilisation temperatures have higher relative abundances in black ash (e.g. phosphorous and zinc). Our data also show this same pattern in Al and Fe, but our literature review did not locate soil or vegetation volatilisation temps for those elements. Sulphur and sulphate are the exception, having high concentrations in white ash, despite S volatilising at a relatively low temperature. Similar results have been reported for sulphate in an analysis of global ash leachates, although analysing ash chemistry as a function of fire intensity was not the primary aim of that research (Harper et al., 2019). Differences in ash-derived metals measured in speleothem archives are hypothesised to differentiate between the intensity of palaeofires, and is an area of future research.

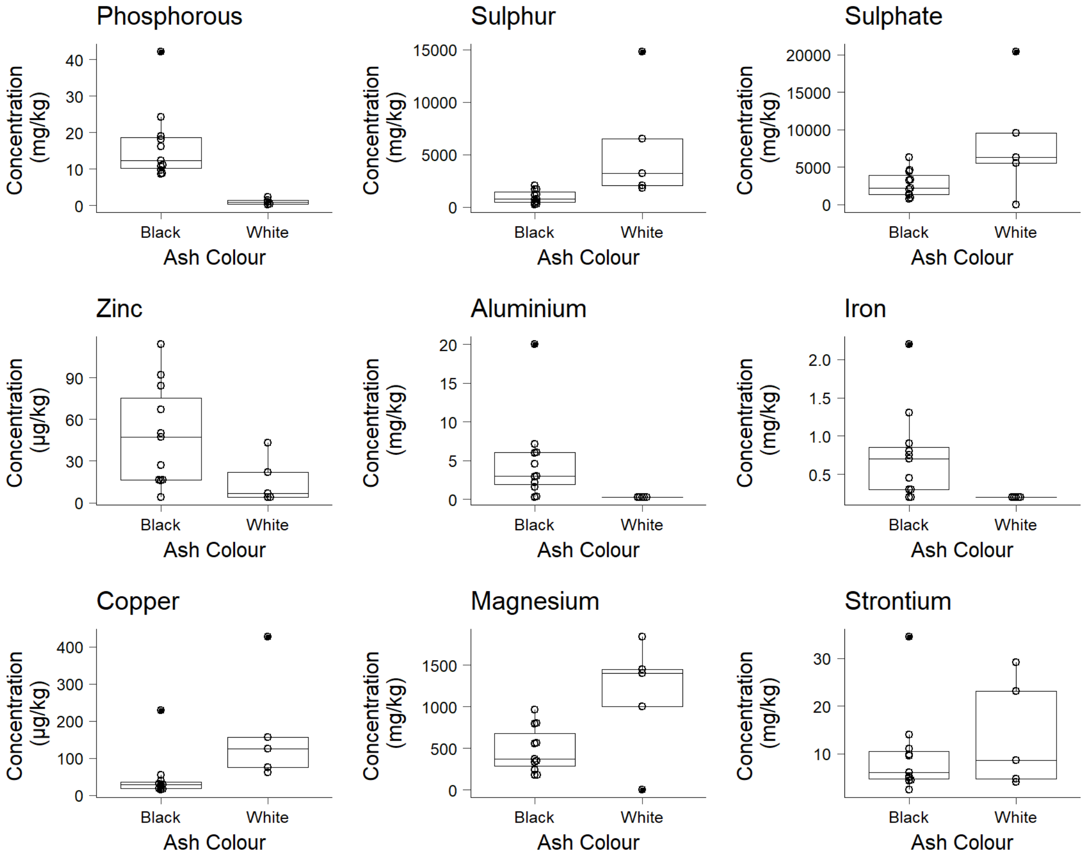

Figure 5 Boxplots of ash leachate concentrations by ash colour. Individual data points are overlayed and slightly offset from one another to reduce overlap.

6.2 Sulphur as a proxy for post-fire recovery

Treble et al. (2016) observed a declining trend in dripwater sulphate over the duration of a dataset between 2005—2015 CE. This was demonstrated by mass balance to represent a net loss (sink) of sulphate over the studied interval in the Golgotha Cave system, southwest Australia (Treble et al., 2016). Mass balance also identified that the source of sulphate in dripwaters at this site is ≥62% marine aerosol, consistent with the coastal location (Treble et al., 2016). Analysis of dual sulphate isotopes ($\delta^{34}S$-SO_4 $\delta^{18}O$-SO_4) in the rainfall at this site confirmed the main source of sulphate to be of marine origin. The dual sulphate isotopes in the dripwaters (n=4) suggested that the sulphate sink identified through element mass balance, was due to sulphur sequestration into biomass, and attributed to the post-fire recovery of the forest understorey following fires that impacted the site in 1992 and 2006 CE (Treble et al.; 2016). The post-fire recovery interpretation was also supported by rising dripwater chlorine trends interpreted to represent increasing transpiration as the shrubby understorey recovered (Treble et al.; 2016).

SIMS measurements of stalagmite sulphur and chlorine concentrations from a stalagmite (GL-S4) sampled from one of the monitored dripwater locations in Golgotha Cave are shown in Figure 6 together with dripwater chlorine and sulphate (Coleborn, 2020). The stalagmite data (1926—2005 CE) enabled a longer-term examination of the trends detected in the dripwater. It revealed that the observed decline in dripwater sulphate was a continuation of a trend which began at least five decades earlier, commensurate with the largest known wildfire to have impacted the forest above and surrounding the cave area which occurred in 1961, and not only after less severe wildfires in 1992 or 2006, as previously thought (Treble et al., 2016). The stalagmite chlorine concentration trend also switched at around this time, providing strong evidence that these observed trends in sulphur and chlorine are due to the 1961 fire (Figure 6). Figure 6 also shows the dripwater chemistry data extended to 2021. Recent reversal of the downward trend in dripwater sulphate may be attributed to reduced sulphur uptake by overlying vegetation, which has now reached maturity, or the domination of the transpiration signal (indicated by the increase in the chlorine rise around the same time) in a region experiencing prolonged drying.

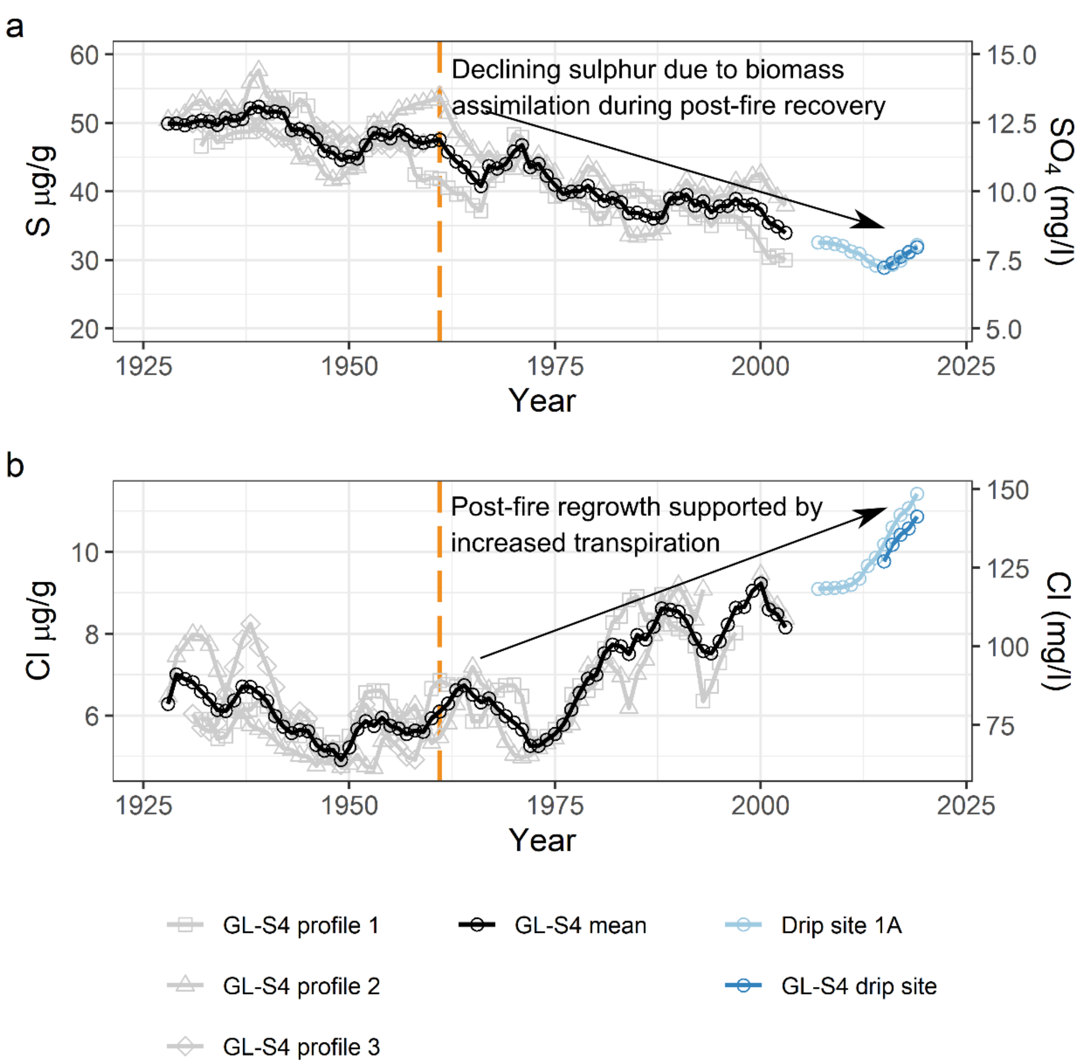

Figure 6 Time series of stalagmite and dripwater S and SO_4 (a) and Cl (b) concentrations from Golgotha Cave, southwest Australia. Data are aggregated annually and presented as a running 5-year mean. Drip site 1A is close to the sampling site of GL-S4 (~1 m). The orange dashed line indicates the 1961 fire, while black arrows indicate the trend in sulphur and sulphate (a) and

chlorine (b). The right-hand axis is scaled to visualise the continuation of the GL-S4 sulphur and chlorine trends.

Subsequent and more comprehensive analyses of dual sulphate isotopes of dripwater, bedrock, and rainfall is summarised in Table 2, together with $\delta^{34}S$ analyses of vegetation and soil. The expanded $\delta^{18}O$-SO_4 and $\delta^{34}S$-SO_4 isotopic data for rainfall confirmed that the sulphate was from a marine source (Table 2). Sulphate reduction was ruled out as a potential cause of the sulphate sink as this would result in higher dripwater $\delta^{18}O$-SO_4 values compared with rainfall, whereas the opposite was observed (Table 2). Mean dripwater $\delta^{18}O$-SO_4 values were lower than rainfall by 4.1‰, strongly supporting biogeochemical cycling of the input rainfall signal before reaching the cave under oxidising conditions. Mean $\delta^{34}S$-SO_4 of dripwaters were ~1‰ higher than rainfall (Table 2). This is theoretically consistent with biomass assimilation, which results in ~1—2‰ fractionation due to preferential assimilation of ^{32}S (Marty et al., 2011; Wynn et al., 2013). Vegetation appeared to support similar $\delta^{34}S$ values to those observed in the cave drip waters (Table 2; Coleborn, 2020).No observable counterpart fractionation to lighter isotopic values in the vegetation due to assimilation is likely due to a pool size effect, with vegetation representing the biggest sink of sulphur in the system. Bedrock was found to contribute <5% of SO_4 to dripwaters.

Table 2 Dual SO_4 isotope values for rainfall, cave dripwater, and bedrock from Golgotha Cave, southwest Australia. $\delta^{34}S$ results for vegetation and soil samples from the Golgotha Cave region. Mean values presented with minimum and maximum values reported in brackets, n shows the number of replicates. Vienna Standard Mean Ocean Water (VSMOW) was the $\delta^{18}O$ standard, and Vienna-Canyon Diablo Troilite (VCDT) was the $\delta^{34}S$ standard. Data from (Coleborn, 2020).

	$\delta^{18}O$-SO_4 (‰ VSMOW)		$\delta^{34}S$-SO_4(‰ VCDT)		$\delta^{34}S$ (‰ VCDT)	
	n		n		n	
Rainfall	6	+8.1 (+6.9 to +9.7)	7	+18.8 (+17.8 to +19.8)	0	-
Cave dripwater					0	-
1A	8	+4.0 (+1.4 to +6.1)	9	+20.1 (+18.5 to +21.7) 8	0	-
1IV	0	-	1	19.6	0	-
Bedrock	1	+7.8	1	+18.7	0	
Vegetation	0	-	0	-	31	+20.5 (+17.9 to +22.1)
Soil	0	-	0	-	20	+19.1 (+17.8 to +20.3)

Results presented here suggest that speleothem sulphur may be useful as a proxy for fire due to the observed multi-decadal duration of reduced sulphur concentrations, attributed to increased biomass assimilation as a forest recovers after fire. This approach would likely be limited to sites where the supply of sulphur becomes source limited for a prolonged period after fire and where sulphur supply is not complicated by multiple sources. Dual sulphate isotopes may assist in characterising the latter, and theoretically could be applied to speleothems (as could $\delta^{34}S$ measured in situ) to detect disruptions in biomass cycling due to fire. It is also recognised that sulphur incorporation into speleothems may be dominated by pH control (Wynn et al., 2018, 2014). For example, sulphur was examined in stalagmite YD-S2, also from southwest Australia (McDonough et al, 2022). In that study, only a short-term depletion in sulphur was observed, directly coinciding with an inferred intense fire in 1897 (±5 years). This was attributed to either volatilisation of sulphur and/or an increase in dripwater pH caused by calcination of the limestone above the cave (McDonough et al, 2022). That speleothem-based paleo-fire record is further examined in the third case study (Section 6.3). Further development work on sulphur as a fire proxy in speleothems is required.

6.3 Catastrophic palaeofire and links to climate and land management

McDonough et al., (2022) used LA-ICP-MS, S-µXRF, and stable isotopes ($\delta^{18}O$ and $\delta^{13}C$) to compare the speleothem proxy response to recent known fires and to apply this to reconstruct past fire frequency in a stalagmite from a shallow (< 6 m depth) cave in Yanchep, Western Australia. A particularly intense paleo-fire was identified to have occurred in 1897 ±5 CE identified by changes in fabric and both short and long-term changes in the isotopic and elemental composition. They identified a short-term peak in $\delta^{18}O$ just after the 1897 CE fire, understood to have resulted from evaporation of soil and karst stores from the fire. This evaporation also resulted in short-term peaks in other bedrock derived parameters including strontium and magnesium (Figure 7). Of note was a large short-lived peak in phosphorous (Figure 7) which exceeded 6 times the concentrations of phosphorous anywhere else in the 245-year record, and a smaller spike in zinc. These were taken to have been derived from ash which was leached into dripwater and incorporated into the stalagmite post-fire. An increase in porosity of the sample for approximately 5 years after the fire was interpreted to have occurred due to the occlusion of growth sites by impurities from ash. The authors also identified an increase in organic matter content post-fire, and a decline in bedrock-derived parameters, suggesting an increase in fracturing and porosity caused by intense heating and cooling of the limestone. This appears to have allowed for reduced physical filtering of OM, and reduced water-rock interaction resulting in higher concentrations of OM and lower concentrations of bedrock-derived elements in the decades following the fire event.

The 1897±5 years fire came at a critical point in Australia's colonial history. Prior to establishment of the Swan River Colony in 1829, the Noongar people had practiced land management through the use of frequent low-intensity burns (Hallam, 2014). By the late 1800s, they had been prevented from practicing cultural burning for 30-60 years (Abbott, 2002; Hallam, 2014). McDonough et al. (2022) suggested that a subsequent build-up of fuel, combined with antecedent dry conditions in the late 19th Century may have resulted in this large fire in 1897 CE. This adds to a growing body of work that has linked the cessation of Indigenous land practices to broad-scale landscape change and subsequent higher risk of catastrophic wildfires (Fletcher et al., 2021b; Mariani et al., 2022)

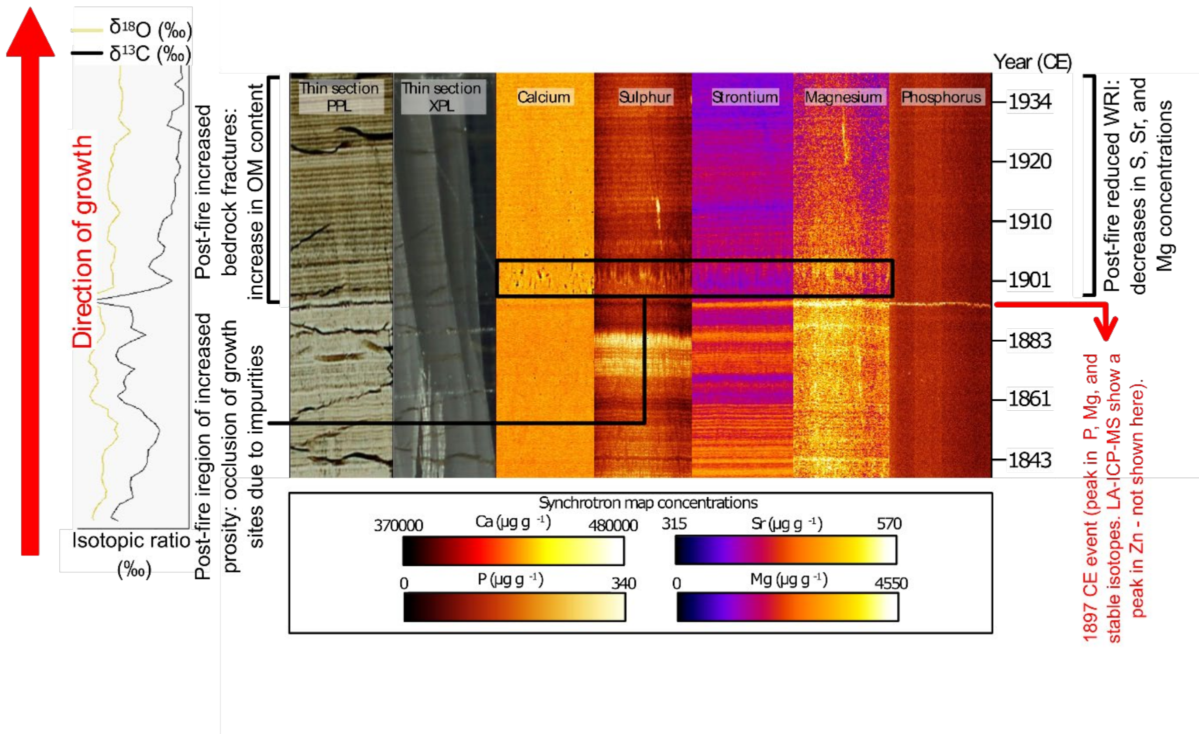

Figure 7 Plane polar light (PPL) and cross polar light (XPL) thin section scans and S-µXRF maps from a sub-section of stalagmite YDS2. An inferred fire event in 1897 CE is identified in McDonough et al. (2022), coinciding with a short-lived peak in phosphorus, strontium and magnesium. A post-fire increase in porosity is evident in the Ca, S and Sr maps, likely due to occlusion of growth sites by impurities. Post-fire impacts such as increases in organic matter (OM) incorporation and decreases in bedrock-derived parameters such as Mg, Sr and S due to increased or widening of fractures after heating and cooling of the bedrock, and subsequent reduced water-rock interaction (WRI), are visible through the darkening of the S, Sr and Mg maps after 1897 CE. Figure adapted from McDonough et al. (2022).

6.4 Fires recorded in deep caves

Dripwater monitoring (Figure 3) and McDonough et al. (2022) showed that infiltration to shallow caves could transport a fire signal which could then be recorded in speleothem calcite. Evidence from dripwater monitoring appeared to indicate that deep caves would not record fires (see Section 4.2). Coleborn et al. (2018; 2019) found no significant change in post-fire dripwater chemistry in a 40 m deep cave in southeast Australia. However, recent (unpublished) data from a deep (~40 m) cave from southwest Australia has demonstrated that deep cave stalagmites (stalagmite CRY-S1) may be able to record fires. Following methods outlined in McDonough et al. (2022) S-µXRF analyses of a speleothem collected from Crystal Cave in southwest Australia showed increases in zinc and iron (Figure 8), and distortion of the speleothem fabric following large forest fires over the site in 1961, the same fire that impacted Golgotha Cave in our second case study. Zinc and iron concentrations at the 1961 event were >600 ppm and >1000 ppm, respectively. Outside of the 1961 fire layer, zinc concentrations were ~50 ppm and iron concentrations were ~200 ppm. The 1961 fire was a large and intense fire which occurred during the catastrophic 1960-61 Western Australian fire season, and which burned >40 000 ha. The fire season was preceded by an anomalously wet winter. -The calcium and strontium maps show the fabric is impacted around the 1961 event (Figure 8), with increased porosity and new crystal growth impacted by renucleation and competitive growth after foreign particle poisoning of the calcite. The high strontium is likely an artefact from scattering of the differently orientated crystals during this competitive growth phase. Other known fires burned over Crystal Cave in 1972, 1975, and 1991, although only the 1972 prescribed fire event is evident in the S-μXRF trace element maps, with spikes in iron observed (Figure 8). The 1972 fire was also preceded by an anomalously wet winter, although as a prescribed burn the climatic precursors may have been less relevant. The CRY-S1 chronology is well-constrained and based on annual S-μXRF strontium bands.

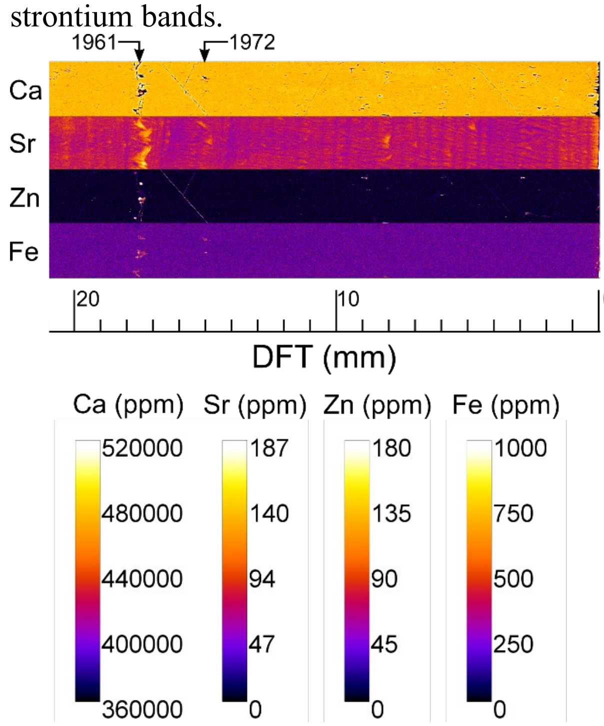

Figure 8 S-μXRF map of modern calcite from Crystal Cave (CRY-S1), in the Margaret River Region of southwest Australia.

The Tamala Limestone of southwest Western Australia has high primary porosity but fracture flow is also an important contribution to dripwaters (Treble et al., 2022). Focussing of flow along fractures may explain how a stalagmite from such a deep cave could have recorded a fire event. This suggests that hydrogeology is just as important as cave depth for the transport and incorporation of a fire proxy signal. That the 1961 wildfire event is so clear in the S-μXRF while later prescribed burns are either missing (1975, 1991) or less clear (1972) suggests that this deep cave may act as a fire severity filter, with the CRY-S1 stalagmite recording only severe bushfires. Additionally, since the fire signal is predominantly due to the dissolution and transport of ash-derived elements (see Section 4.2) transport of that signal requires soil hydrological connectivity. This reinforces the necessity of choosing speleothem samples that have efficient surface-cave transport with minimal mixing to minimise the attenuation of the fire proxy signal.

Detecting a fire signal at depth in a highly porous young limestone shows promise for fire signal detection in older limestones where fracture flow is more likely.

Unlike the previous case study and dripwater observations, where an anomaly in $\delta^{18}O$ was associated with fires, CRY-S1 shows no change in $\delta^{18}O$ after the large bushfire in 1961, or after subsequent prescribed burns in 1972, 1975, or 1991 (Figure 9). This absence of a $\delta^{18}O$ response may be associated with local karst processes, cave depth, past land use, and long-term climate and precipitation patterns. This is an important find for the community as it suggests that $\delta^{18}O$ hydroclimate records from deep caves are less likely to be impacted by wildfires.

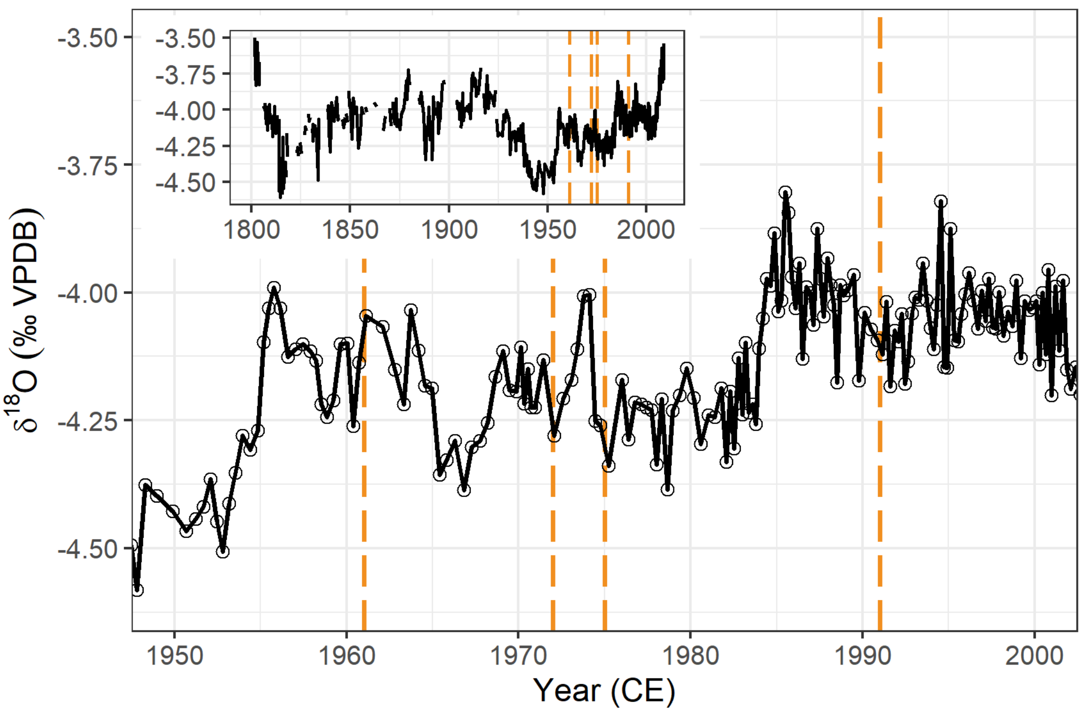

Figure 9 $\delta^{18}O$ record for speleothem CRY-S1, with bushfires in 1691, 1972,1975, and 1991 indicated by orange dashed lines. The inset shows the full $\delta^{18}O$ record for this sample.

7 Summary and future research directions

Speleothems offer an exciting new field of research for investigating past fire regimes. Modern analytical and computational advances have allowed for the high-resolution analyses of speleothem trace elements, stable isotopes, and fabric. Robust palaeofire reconstructions are necessary to better understand future wildfire regimes in relation to climate change, to better appreciate ecosystem resilience and the interplay between climate and land management, and to improve data-model comparisons. Below, we discuss where speleothems fit in the palaeofire archive landscape, highlight that speleothem palaeofire research is only possible because of analytical and computational advances, discuss how new knowledge about fire proxies may impact δ18O-derived climate reconstructions, detail how the SISAL V2 database may be used to identify suitable samples for palaeofire research, and discuss future research questions.

While many proxy archives already exist to investigate past fire, speleothems offer a complimentary new archive. The benefits of speleothems are clear: they are absolutely dateable, recoverable from most continents, and include a range of proxies. Collectively, this makes them ideal candidates for high resolution, precisely dated, palaeofire reconstructions. Additionally, ash is the source of the majority of inorganic fire proxies in speleothems. Ash is a fire end-member that is typically not preserved in existing fire proxy archives and so speleothems offer a unique opportunity to preserve chemical signals from this fire end-member, and speleothem-derived fire reconstructions will compliment sedimentary fire proxy reconstructions, which are typically based on charcoal preservation.

Analytical and computational advances have been critical for the development of speleothems as fire proxy archives. McDonough et al. (2022) clearly demonstrated that S-μXRF is a key analytical tool for the detection and precise dating of fire events in speleothems. New results presented here for stalagmite CRY-S1 which demonstrate that speleothems from a deep cave may record past fires also highlight the necessity of S-μXRF analyses by showing that some key trace metals (e.g., Fe) are inconsistently deposited along the growth layer. 2-D Elemental mapping identified these inconsistent peaks in trace metals which may have been missed by LA-ICP-MS line scans (see Section 6.4). Computational advances and the generosity of open-source developers mean that complicated multivariate statistical analyses, such as principal component analysis, can now be performed quickly and easily (and often freely). McDonough et al. (2022) showed that no single speleothem proxy could reliably identify a past fire, and it was only through principal component analyses that past fire frequency could be reconstructed. Recent advances in analytical methods for mineral magnetism has potential to enable the development of a novel fire proxy at comparable or greater resolution to those presented in this review. Similarly, refinements to the analyses of biomarkers in speleothems may allow for better quantification of polycyclic aromatic hydrocarbons in speleothems.

δ18O in both dripwater and calcite can be impacted by fire events, although the sign of that impact varies. δ18O values have been shown to shift higher in some instances while lower in others, depending on the extent of evaporation of soil stores, the isotopic value of recharging rainfall, whether hydrological pathways were altered to allow for more efficient infiltration, and whether post-fire evaporation rates were enhanced by loss of shade cover (Bian et al., 2019; McDonough et al., 2022; Nagra et al., 2016). This has implications for the interpretation of speleothem δ18O records. The SISAL V2 database is the largest database of speleothem δ18O and δ13C data, with 691 speleothem records from 294 cave sites (Comas-Bru et al., 2020). Between November 2000 and May 2021, ~50% of the SISAL V2 sites experienced at least one fire (when comparing overlap of sites with aggregated MODIS Burned Area data; Figure 10). This represents a significant proportion of the publicly available stalagmite δ18O datasets, and researchers should consider potential fire impacts when interpreting the speleothem δ18O record for both existing and new stalagmite proxy data. The extent of potential fire impacts on calcite δ18O may be quantified through comparison with other hydroclimate proxies that are unaffected by fire (e.g., Sr), or by comparing with δ18O records from nearby deeper caves.

The SISAL V2 database also offers an opportunity for researchers interested in speleothem palaeofire reconstructions. The full suite of data and metadata in the database (including δ18O and δ13C data, dates, age models, location, cave depth, whether there are annual laminae, etc.) may allow for suitable samples to be identified, i.e., shallow caves in fire susceptible regions and for recently formed stalagmites, because using sites known to have recorded at least one fire in the satellite era as a site-specific calibration is likely to be important. By way of inclusion in the SISAL V2 database, datasets are readily available that could be built upon by use of elemental mapping and petrographic analyses on targeted areas of the records where shifts in stable isotopes might suggest a fire was involved.

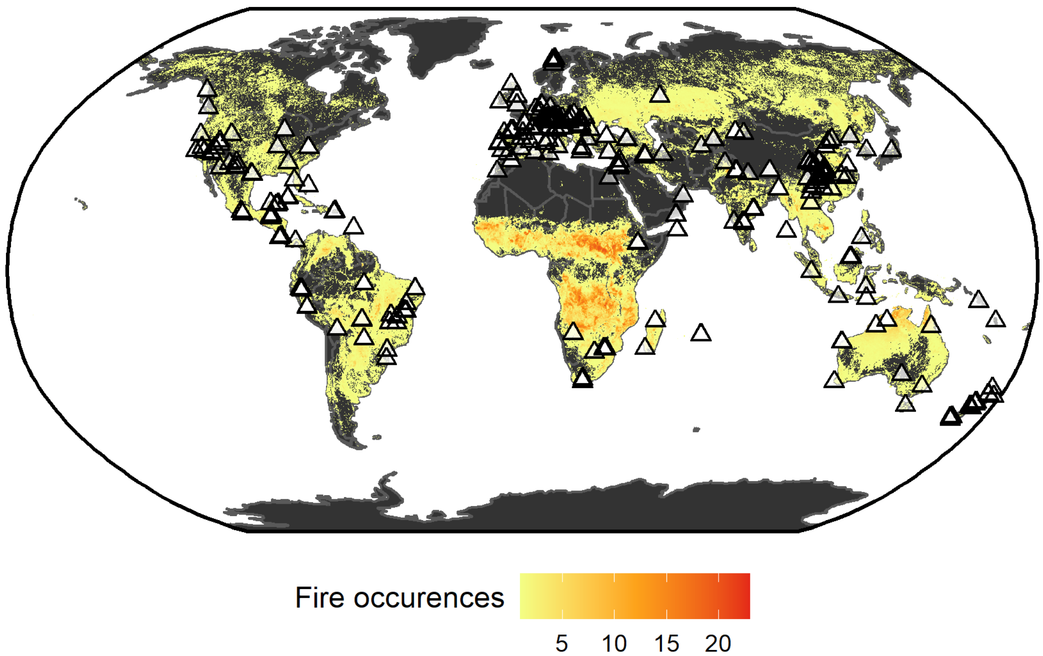

Figure 10 Samples from the SISAL V2 database (Comas-Bru et al., 2020) plotted against aggregated monthly MODIS Burned Area data (Giglio et al., 2015) for the period November 2000 to May 2021. MODIS data were compiled using Google Earth Engine.

McDonough et al. (2022) showed that not all trace metals contributed similarly to their ‘fire’ principal component during each fire event. They proposed that high peaks could be found where multiple metals loaded on the principal component. This could be achieved during, for example, a ‘moderate’ fire where a lot of material was mobilised, but temperatures were not high enough for those metals to be volatilised (Bodí et al., 2014; McDonough et al., 2022; Figure 4). Conversely, a very intense fire event might produce a smaller peak, as metals volatilised and therefore did not load on the principal component. To investigate this, future work should aim to test this hypothesis by analysing coeval stalagmites which experienced different fires of different fire severities. Being able to reconstruct past fire severity would be a significant outcome for both speleothem palaeoclimatologists and the broader palaeoclimate community, as reconstructing past fire severity is challenging and generally inferred from charcoal abundance and pollen assemblages (Minckley and Long, 2016).

This review has demonstrated that discrete horizons of highly enriched metals (such as iron and zinc) are the ‘smoking gun’ for fire events. Case studies presenting S-µXRF maps have demonstrated that these event horizons are clearly visible, and have shown that ash is a likely source. These metals are insoluble and will only be transported through the soil and epikarst when chelated (likely organically bound). While the evidence is strong that these layers are caused by wildfires (i.e. they have been chronologically tied to known fire events) major precipitation events could produce a similar effect by washing in soil organic matter. This effect has been demonstrated in dripwaters (Hartland et al., 2012) and in speleothem calcite (Borsato et al., 2007; Fairchild et al., 2010; Wynn et al., 2014). More research is needed to separate the soil organic matter metal signal from the wildfire ash metal signal. Further proxy development and validation is needed to determine whether and how δ13C and 14C are impacted by wildfires. It has been demonstrated that soil microbial communities are affected by wildfires, and that soil CO2 can take >5 years post-wildfire to recover (Coleborn et al., 2016b). It follows that speleothem δ13C and 14C may also be impacted by wildfire, but this effect has yet to be shown. Similarly, high-resolution mineral magnetism is a promising new speleothem proxy, although the applications for palaeofire reconstruction have yet to be fully explored.

As fire regimes are a function of human activity, climate, and vegetation composition, and since speleothems can produce very long, high-resolution, precisely-dated palaeoclimate datasets, they have perhaps unmatched potential to investigate the transition from ‘unmanaged’ fire regimes to ‘managed’ fire regimes when both early and modern humans migrated and started managing landscapes. Speleothems have already been used to investigate the climatic conditions governing early hominin migration (El-Shenawy et al., 2018; Orland et al., 2019), and adding palaeofire would be a natural extension of that research. This research would be of significant importance to our understanding of those early peoples, their use of fire, and how ecosystems changed with their arrival. Resulting research would be of global interest and significance as it could help to pinpoint the arrival time of early hominins (and their successors), and further elucidate the relationship between climate, human activity, and vegetation which comprises fire regimes. This research would also allow the transition from Indigenous to colonial land management practices to be better understood, and could provide important lessons about best practice land management. This research would be truly multi-disciplinary, and appeal to archaeologists, hydrologists, climatologists, and ecologists.

Acknowledgments

This review was funded by the Australian Research Council (DP200100203 and LP130100177). NK was supported by an Honours Scholarship from the Australian Institute of Nuclear Science and Engineering (ALNSTU21014). We thank WA Parks and Wildlife staff for enthusiastic assistance in the collection of ash. S-µXRF analyses were undertaken on the XFM beamline at the Australian Synchrotron, part of ANSTO, with thanks to David Patterson. Thanks to Henri Wong and Chris Vardanega at ANSTO ITNS for analyses of ash leachates. Mass spectrometric results were obtained at the Bioanalytical Mass Spectrometry Facility within the Mark Wainwright Analytical Centre of the University of New South Wales, with thanks to Lewis Adler. The authors respectfully acknowledge both the Whadjuk Noongar and Wadandi Noongar peoples as the traditional and spiritual custodians of the Yanchep (on Whadjuk Noongar boodja) and Margaret River (on Wadandi boodja) regions of Western Australia, which are the sites for all case studies presented in Section 6.

Open Research

Data for case studies 6.1, 6.2, and 6.4 are available at 10.6084/m9.figshare.20289540 (Campbell et al. 2022) (temporary link until data are published https://figshare.com/s/04ac226c54e8b93ff98e). Data for case study 6.3 is available with the original publication (McDonough et al., 2022). R and Google Earth Engine scripts to produce Figures 5, 6, 9 and 10 are also included in the data archive at the above DOI.

References

Abatzoglou, J.T., Williams, A.P., 2016. Impact of anthropogenic climate change on wildfire across western US forests. Proc. Natl. Acad. Sci. 113, 11770–11775. https://doi.org/10.1073/pnas.1607171113

Abatzoglou, J.T., Williams, A.P., Barbero, R., 2019. Global Emergence of Anthropogenic Climate Change in Fire Weather Indices. Geophys. Res. Lett. 46, 326–336. https://doi.org/10.1029/2018GL080959

Abbott, I., 2002. Historical records of Noongar fires, 1658-1888: a compendium. Department of Conservation & Land Management, Kensignton, WA.

Abram, N.J., Henley, B.J., Sen Gupta, A., Lippmann, T.J.R., Clarke, H., Dowdy, A.J., Sharples, J.J., Nolan, R.H., Zhang, T., Wooster, M.J., Wurtzel, J.B., Meissner, K.J., Pitman, A.J., Ukkola, A.M., Murphy, B.P., Tapper, N.J., Boer, M.M., 2021. Connections of climate change and variability to large and extreme forest fires in southeast Australia. Commun. Earth Environ. 2, 8. https://doi.org/10.1038/s43247-020-00065-8

Alriksson, A., Eriksson, H.M., 1998. Variations in mineral nutrient and C distribution in the soil and vegetation compartments of five temperate tree species in NE Sweden. For. Ecol. Manag. 108, 261–273. https://doi.org/10.1016/S0378-1127(98)00230-8

Appelo, C.A.J., Postma, D., Appelo, C.A.J., Postma, D., 2005. Geochemistry, Groundwater and Pollution, 2nd ed. CRC Press, London. https://doi.org/10.1201/9781439833544

Argiriadis, E., Denniston, R.F., Barbante, C., 2019. Improved Polycyclic Aromatic Hydrocarbon and n-Alkane Determination in Speleothems through Cleanroom Sample Processing. Anal. Chem. 91, 7007–7011. https://doi.org/10.1021/acs.analchem.9b00767

Ashe, B., McAneney, K.J., Pitman, A.J., 2009. Total cost of fire in Australia. J. Risk Res. 12, 121–136. https://doi.org/10.1080/13669870802648528

Baker, A., Blyth, A.J., Jex, C.N., Mcdonald, J.A., Woltering, M., Khan, S.J., 2019. Glycerol dialkyl glycerol tetraethers (GDGT) distributions from soil to cave: Refining the speleothem paleothermometer. Org. Geochem. 136, 103890. https://doi.org/10.1016/j.orggeochem.2019.06.011

Baker, A., Mariethoz, G., Comas-Bru, L., Hartmann, A., Frisia, S., Borsato, A., Treble, P.C., Asrat, A., 2021. The Properties of Annually Laminated Stalagmites-A Global Synthesis. Rev. Geophys. 59. https://doi.org/10.1029/2020RG000722

Baldini, J.U.L., Lechleitner, F.A., Breitenbach, S.F.M., van Hunen, J., Baldini, L.M., Wynn, P.M., Jamieson, R.A., Ridley, H.E., Baker, A.J., Walczak, I.W., Fohlmeister, J., 2021. Detecting and quantifying palaeoseasonality in stalagmites using geochemical and modelling approaches. Quat. Sci. Rev. 254, 106784. https://doi.org/10.1016/j.quascirev.2020.106784

Balfour, V.N., Woods, S.W., 2013. The hydrological properties and the effects of hydration on vegetative ash from the Northern Rockies, USA. CATENA 111, 9–24. https://doi.org/10.1016/j.catena.2013.06.014

Bárcenas-Moreno, G., Bååth, E., 2009. Bacterial and fungal growth in soil heated at different temperatures to simulate a range of fire intensities. Soil Biol. Biochem. 41, 2517–2526. https://doi.org/10.1016/j.soilbio.2009.09.010

Battistel, D., Kehrwald, N.M., Zennaro, P., Pellegrino, G., Barbaro, E., Zangrando, R., Pedeli, X.X., Varin, C., Spolaor, A., Vallelonga, P.T., Gambaro, A., Barbante, C., 2018. High-latitude Southern Hemisphere fire history during the mid- to late Holocene (6000–750 BP). Clim. Past 14, 871–886. https://doi.org/10.5194/cp-14-871-2018

Benington, F., Melton, C., Watson, P.J., 1962. Carbon Dating Prehistoric Soot from Salts Cave, Kentucky. Am. Antiq. 28, 238–241. https://doi.org/10.2307/278384

Bhattarai, H., Saikawa, E., Wan, X., Zhu, H., Ram, K., Gao, S., Kang, S., Zhang, Q., Zhang, Y., Wu, G., Wang, X., Kawamura, K., Fu, P., Cong, Z., 2019. Levoglucosan as a tracer of biomass burning: Recent progress and perspectives. Atmospheric Res. 220, 20–33. https://doi.org/10.1016/j.atmosres.2019.01.004

Bian, F., Coleborn, K., Flemons, I., Baker, Andy, Treble, P.C., Hughes, C.E., Baker, Andrew, Andersen, M.S., Tozer, M.G., Duan, W., Fogwill, C.J., Fairchild, I.J., 2019. Hydrological and geochemical responses of fire in a shallow cave system. Sci. Total Environ. 662, 180–191. https://doi.org/10.1016/j.scitotenv.2019.01.102

Blyth, A.J., Hartland, A., Baker, A., 2016. Organic proxies in speleothems – New developments, advantages and limitations. Quat. Sci. Rev. 149, 1–17. https://doi.org/10.1016/j.quascirev.2016.07.001

Bodí, M.B., Doerr, S.H., Cerdà, A., Mataix-Solera, J., 2012. Hydrological effects of a layer of vegetation ash on underlying wettable and water repellent soil. Geoderma, Fire effects on soil properties 191, 14–23. https://doi.org/10.1016/j.geoderma.2012.01.006

Bodí, M.B., Martin, D.A., Balfour, V.N., Santín, C., Doerr, S.H., Pereira, P., Cerdà, A., Mataix-Solera, J., 2014. Wildland fire ash: Production, composition and eco-hydro-geomorphic effects. Earth-Sci. Rev. 130, 103–127. https://doi.org/10.1016/j.earscirev.2013.12.007

BOM, CSIRO, 2020. State of the Climate 2020. corporateName=Bureau of Meteorology.

Borsato, A., Frisia, S., Fairchild, I.J., Somogyi, A., Susini, J., 2007. Trace element distribution in annual stalagmite laminae mapped by micrometer-resolution X-ray fluorescence: Implications for incorporation of environmentally significant species. Geochim. Cosmochim. Acta 71, 1494–1512. https://doi.org/10.1016/j.gca.2006.12.016

Borsato, A., Frisia, S., Howard, D., Greig, A., 2021. A guide to synchrotron hard X-ray fluorescence mapping of annually laminated stalagmites: Sample preparation, analysis and evaluation. Spectrochim. Acta Part B At. Spectrosc. 185, 106308. https://doi.org/10.1016/j.sab.2021.106308

Borsato, A., Frisia, S., Wynn, P.M., Fairchild, I.J., Miorandi, R., 2015. Sulphate concentration in cave dripwater and speleothems: long-term trends and overview of its significance as proxy for environmental processes and climate changes. Quat. Sci. Rev., Novel approaches to and new insights from speleothem-based climate reconstructions 127, 48–60. https://doi.org/10.1016/j.quascirev.2015.05.016

Bowman, D.M.J.S., Balch, J.K., Artaxo, P., Bond, W.J., Carlson, J.M., Cochrane, M.A., D’Antonio, C.M., DeFries, R.S., Doyle, J.C., Harrison, S.P., Johnston, F.H., Keeley, J.E., Krawchuk, M.A., Kull, C.A., Marston, J.B., Moritz, M.A., Prentice, I.C., Roos, C.I., Scott, A.C., Swetnam, T.W., van der Werf, G.R., Pyne, S.J., 2009. Fire in the Earth System. Science 324, 481–484. https://doi.org/10.1126/science.1163886

Bradley, C., Baker, A., Jex, C.N., Leng, M.J., 2010. Hydrological uncertainties in the modelling of cave drip-water δ18O and the implications for stalagmite palaeoclimate reconstructions. Quat. Sci. Rev. 29, 2201–2214. https://doi.org/10.1016/j.quascirev.2010.05.017

Brittingham, A., Hren, M.T., Hartman, G., Wilkinson, K.N., Mallol, C., Gasparyan, B., Adler, D.S., 2019. Geochemical Evidence for the Control of Fire by Middle Palaeolithic Hominins. Sci. Rep. 9, 15368. https://doi.org/10.1038/s41598-019-51433-0

Brown, P.M., Kaufmann, M.R., Shepperd, W.D., 1999. Long-term, landscape patterns of past fire events in a montane ponderosa pine forest of central Colorado. Landsc. Ecol. 14, 513–532. https://doi.org/10.1023/A:1008137005355

Brücher, T., Brovkin, V., Kloster, S., Marlon, J.R., Power, M.J., 2014. Comparing modelled fire dynamics with charcoal records for the Holocene. Clim. Past 10, 811–824. https://doi.org/10.5194/cp-10-811-2014

Bryant, R.A., Waters, E., Gibbs, L., Gallagher, H.C., Pattison, P., Lusher, D., MacDougall, C., Harms, L., Block, K., Snowdon, E., Sinnott, V., Ireton, G., Richardson, J., Forbes, D., 2014. Psychological outcomes following the Victorian Black Saturday bushfires. Aust. N. Z. J. Psychiatry 48, 634–643. https://doi.org/10.1177/0004867414534476

Buckles, J., Rowe, H.D., 2016. Development and optimization of microbeam X-ray fluorescence analysis of Sr in speleothems. Chem. Geol. 426, 28–32. https://doi.org/10.1016/j.chemgeo.2016.02.003

Buckley, T.N., Turnbull, T.L., Pfautsch, S., Gharun, M., Adams, M.A., 2012. Differences in water use between mature and post-fire regrowth stands of subalpine Eucalyptus delegatensis R. Baker. For. Ecol. Manag. 270, 1–10. https://doi.org/10.1016/j.foreco.2012.01.008

Campbell, M. et al. (2022) 'Speleothems as archives for palaeofire proxies'. Figshare. Available at: https://figshare.com/s/04ac226c54e8b93ff98e.

Canadell, J.G., Meyer, C.P. (Mick), Cook, G.D., Dowdy, A., Briggs, P.R., Knauer, J., Pepler, A., Haverd, V., 2021. Multi-decadal increase of forest burned area in Australia is linked to climate change. Nat. Commun. 12, 6921. https://doi.org/10.1038/s41467-021-27225-4

Cerrato, J.M., Blake, J.M., Hirani, C., Clark, A.L., Ali, A.-M.S., Artyushkova, K., Peterson, E., Bixby, R.J., 2016. Wildfires and water chemistry: effect of metals associated with wood ash. Environ. Sci. Process. Impacts 18, 1078–1089. https://doi.org/10.1039/C6EM00123H

Certini, G., 2005. Effects of fire on properties of forest soils: a review. Oecologia 143, 1–10. https://doi.org/10.1007/s00442-004-1788-8

Chapin, F.S., Matson, P.A., Vitousek, P.M., 2011. Principles of Terrestrial Ecosystem Ecology. Springer New York, New York, NY. https://doi.org/10.1007/978-1-4419-9504-9

Chen, S., Hoffmann, S.S., Lund, D.C., Cobb, K.M., Emile-Geay, J., Adkins, J.F., 2016. A high-resolution speleothem record of western equatorial Pacific rainfall: Implications for Holocene ENSO evolution. Earth Planet. Sci. Lett. 442, 61–71. https://doi.org/10.1016/j.epsl.2016.02.050

Cheng, H., Edwards, R.L., Hoff, J., Gallup, C.D., Richards, D.A., Asmerom, Y., 2000. The half-lives of uranium-234 and thorium-230. Chem. Geol. 169, 17–33. https://doi.org/10.1016/S0009-2541(99)00157-6

Cheng, H., Edwards, R.L., Sinha, A., Spötl, C., Yi, L., Chen, S., Kelly, M., Kathayat, G., Wang, X., Li, X., Kong, X., Wang, Y., Ning, Y., Zhang, H., 2016. The Asian monsoon over the past 640,000 years and ice age terminations. Nature 534, 640–646. https://doi.org/10.1038/nature18591

Clifford, D.A., Chen, S.-S., Reznik, C., 1993. Volatilizing toxic metals from soil. Waste Manag., 1993 Symposium on emerging technologies 13, 467–479. https://doi.org/10.1016/0956-053X(93)90078-B

Coleborn, K., 2020. Developing a new proxy for speleothem paleofire records (PhD Thesis). University of New South Wales, Australia.

Coleborn, K., Baker, Andy, Treble, P.C., Andersen, M.S., Baker, Andrew, Tadros, C.V., Tozer, M., Fairchild, I.J., Spate, A., Meehan, S., 2019. Corrigendum to "The impact of fire on the geochemistry of speleothem-forming drip water in a sub-alpine cave" [Sci. Total Environ. (2018) 408–420]. Sci. Total Environ. 668, 1339–1340. https://doi.org/10.1016/j.scitotenv.2019.02.350

Coleborn, K., Baker, Andy, Treble, P.C., Andersen, M.S., Baker, Andrew, Tadros, C.V., Tozer, M., Fairchild, I.J., Spate, A., Meehan, S., 2018. The impact of fire on the geochemistry of speleothem-forming drip water in a sub-alpine cave. Sci. Total Environ. 642, 408–420. https://doi.org/10.1016/j.scitotenv.2018.05.310

Coleborn, K., Rau, G.C., Cuthbert, M.O., Baker, A., Navarre, O., 2016a. Solar-forced diurnal regulation of cave drip rates via phreatophyte evapotranspiration. Hydrol. Earth Syst. Sci. 20, 4439–4455. https://doi.org/10.5194/hess-20-4439-2016

Coleborn, K., Spate, A., Tozer, M., Andersen, M.S., Fairchild, I.J., MacKenzie, B., Treble, P.C., Meehan, S., Baker, Andrew, Baker, Andy, 2016b. Effects of wildfire on long-term soil CO2 concentration: implications for karst processes. Environ. Earth Sci. 75, 330. https://doi.org/10.1007/s12665-015-4874-9

Comas-Bru, L., Rehfeld, K., Roesch, C., Amirnezhad-Mozhdehi, S., Harrison, S.P., Atsawawaranunt, K., Ahmad, S.M., Brahim, Y.A., Baker, A., Bosomworth, M., Breitenbach, S.F.M., Burstyn, Y., Columbu, A., Deininger, M., Demény, A., Dixon, B., Fohlmeister, J., Hatvani, I.G., Hu, J., Kaushal, N., Kern, Z., Labuhn, I., Lechleitner, F.A., Lorrey, A., Martrat, B., Novello, V.F., Oster, J., Pérez-Mejías, C., Scholz, D., Scroxton, N., Sinha, N., Ward, B.M., Warken, S., Zhang, H., SISAL Working Group members, 2020. SISALv2: a comprehensive speleothem isotope database with multiple age–depth models. Earth Syst. Sci. Data 12, 2579–2606. https://doi.org/10.5194/essd-12-2579-2020

Constantine, M., Mooney, S., Hibbert, B., Marjo, C., Bird, M., Cohen, T., Forbes, M., McBeath, A., Rich, A., Stride, J., 2021. Using charcoal, ATR FTIR and chemometrics to model the intensity of pyrolysis: Exploratory steps towards characterising fire events. Sci. Total Environ. 783, 147052. https://doi.org/10.1016/j.scitotenv.2021.147052

Dahm, C.N., Candelaria-Ley, R.I., Reale, C.S., Reale, J.K., Van Horn, D.J., 2015. Extreme water quality degradation following a catastrophic forest fire. Freshw. Biol. 60, 2584–2599. https://doi.org/10.1111/fwb.12548

Denis, E.H., Toney, J.L., Tarozo, R., Scott Anderson, R., Roach, L.D., Huang, Y., 2012. Polycyclic aromatic hydrocarbons (PAHs) in lake sediments record historic fire events: Validation using HPLC-fluorescence detection. Org. Geochem. 45, 7–17. https://doi.org/10.1016/j.orggeochem.2012.01.005

Di Virgilio, G., Evans, J.P., Blake, S.A.P., Armstrong, M., Dowdy, A.J., Sharples, J., McRae, R., 2019. Climate Change Increases the Potential for Extreme Wildfires. Geophys. Res. Lett. 46, 8517–8526. https://doi.org/10.1029/2019GL083699

Dredge, J., 2014. Aerosol contributions to speleothem geochemistry (d_ph). University of Birmingham.

Dreybrodt, W., 1999. Chemical kinetics, speleothem growth and climate. Boreas 28, 347–356. https://doi.org/10.1111/j.1502-3885.1999.tb00224.x

Drysdale, R., Couchoud, I., Zanchetta, G., Isola, I., Regattieri, E., Hellstrom, J., Govin, A., Tzedakis, P.C., Ireland, T., Corrick, E., Greig, A., Wong, H., Piccini, L., Holden, P., Woodhead, J., 2020. Magnesium in subaqueous speleothems as a potential palaeotemperature proxy. Nat. Commun. 11, 5027. https://doi.org/10.1038/s41467-020-18083-7

Dutta, R., Das, A., Aryal, J., 2016. Big data integration shows Australian bush-fire frequency is increasing significantly. R. Soc. Open Sci. 3, 150241. https://doi.org/10.1098/rsos.150241

Eichler, A., Tinner, W., Brütsch, S., Olivier, S., Papina, T., Schwikowski, M., 2011. An ice-core based history of Siberian forest fires since AD 1250. Quat. Sci. Rev. 30, 1027–1034. https://doi.org/10.1016/j.quascirev.2011.02.007

El-Shenawy, M.I., Kim, S.-T., Schwarcz, H.P., Asmerom, Y., Polyak, V.J., 2018. Speleothem evidence for the greening of the Sahara and its implications for the early human dispersal out of sub-Saharan Africa. Quat. Sci. Rev. 188, 67–76. https://doi.org/10.1016/j.quascirev.2018.03.016

Escudey, M., Fuente, P. de la, Antilén, M., Molina, M., Escudey, M., Fuente, P. de la, Antilén, M., Molina, M., 2010. Effect of ash from forest fires on phosphorus availability, transport, chemical forms, and content in volcanic soils. Environ. Chem. 7, 103–110. https://doi.org/10.1071/EN09067

Etiegni, L., Campbell, A.G., Mahler, R.L., 1991. Evaluation of wood ash disposal on agricultural land. I. Potential as a soil additive and liming agent. Commun. Soil Sci. Plant Anal. 22, 243–256. https://doi.org/10.1080/00103629109368412

Fairchild, I., Spötl, C., Frisia, S., Borsato, A., Susini, J., Wynn, P., Cauzid, J., 2010. Petrology and geochemistry of annually laminated stalagmites from an Alpine cave (Obir, Austria): Seasonal cave physiology. Geol. Soc. Lond. Spec. Publ. 336, 295–321. https://doi.org/10.1144/SP336.16

Fairchild, I.J., Baker, A., 2012. Speleothem science: from process to past environments. John Wiley & Sons.

Fairchild, I.J., Smith, C.L., Baker, A., Fuller, L., Spötl, C., Mattey, D., McDermott, F., E.I.M.F., 2006. Modification and preservation of environmental signals in speleothems. Earth-Sci. Rev. 75, 105–153. https://doi.org/10.1016/j.earscirev.2005.08.003

Fairchild, I.J., Treble, P.C., 2009. Trace elements in speleothems as recorders of environmental change. Quat. Sci. Rev. 28, 449–468. https://doi.org/10.1016/j.quascirev.2008.11.007

Faraji, M., Borsato, A., Frisia, S., Hellstrom, J.C., Lorrey, A., Hartland, A., Greig, A., Mattey, D.P., 2021. Accurate dating of stalagmites from low seasonal contrast tropical Pacific climate using Sr 2D maps, fabrics and annual hydrological cycles. Sci. Rep. 11, 2178. https://doi.org/10.1038/s41598-021-81941-x

Feinberg, J.M., Lascu, I., Lima, E.A., Weiss, B.P., Dorale, J.A., Alexander, E.C., Edwards, R.L., 2020. Magnetic detection of paleoflood layers in stalagmites and implications for historical land use changes. Earth Planet. Sci. Lett. 530, 115946. https://doi.org/10.1016/j.epsl.2019.115946

Filkov, A.I., Ngo, T., Matthews, S., Telfer, S., Penman, T.D., 2020. Impact of Australia's catastrophic 2019/20 bushfire season on communities and environment. Retrospective analysis and current trends. J. Saf. Sci. Resil. 1, 44–56. https://doi.org/10.1016/j.jnlssr.2020.06.009

Fletcher, M.-S., Hall, T., Alexandra, A.N., 2021a. The loss of an indigenous constructed landscape following British invasion of Australia: An insight into the deep human imprint on the Australian landscape. Ambio 50, 138–149. https://doi.org/10.1007/s13280-020-01339-3

Fletcher, M.-S., Romano, A., Connor, S., Mariani, M., Maezumi, S.Y., 2021b. Catastrophic Bushfires, Indigenous Fire Knowledge and Reframing Science in Southeast Australia. Fire 4, 61. https://doi.org/10.3390/fire4030061

Fohlmeister, J., 2012. A statistical approach to construct composite climate records of dated archives. Quat. Geochronol. 14, 48–56. https://doi.org/10.1016/j.quageo.2012.06.007

Frisia, S., 2014. Microstratigraphic logging of calcite fabrics in speleothems as tool for palaeoclimate studies. Int. J. Speleol. 44. https://doi.org/<p>http://dx.doi.org/10.5038/1827-806X.44.1.1</p>

Frisia, S., Borsato, A., 2010. Chapter 6 Karst, in: Alonso-Zarza, A.M., Tanner, L.H. (Eds.), Developments in Sedimentology, Carbonates in Continental Settings: Facies, Environments, and Processes. Elsevier, pp. 269–318. https://doi.org/10.1016/S0070-4571(09)06106-8

Frisia, S., Borsato, A., Fairchild, I.J., Susini, J., 2005. Variations in atmospheric sulphate recorded in stalagmites by synchrotron micro-XRF and XANES analyses. Earth Planet. Sci. Lett. 235, 729–740. https://doi.org/10.1016/j.epsl.2005.03.026

Frisia, S., Borsato, A., Susini, J., 2008. Synchrotron radiation applications to past volcanism archived in speleothems: An overview. J. Volcanol. Geotherm. Res., Explosive volcanism in the central Mediterranean area during the late Quaternary - linking sources and distal archives 177, 96–100. https://doi.org/10.1016/j.jvolgeores.2007.11.010

Fu, R.R., Hess, K., Jaqueto, P., Novello, V.F., Kukla, T., Trindade, R.I.F., Stríkis, N.M., Cruz, F.W., Ben Dor, O., 2021. High-Resolution Environmental Magnetism Using the Quantum Diamond Microscope (QDM): Application to a Tropical Speleothem. Front. Earth Sci. 8.

Gázquez, F., Calaforra, J.M., Forti, P., 2011. Black Mn-Fe Crusts as Markers of Abrupt Palaeoenvironmental Changes in El Soplao Cave (Cantabria, Spain). Int. J. Speleol. 40, 163–169. https://doi.org/10.5038/1827-806X.40.2.8

Gedalof, Z., Peterson, D.L., Mantua, N.J., 2005. Atmospheric, Climatic, and Ecological Controls on Extreme Wildfire Years in the Northwestern United States. Ecol. Appl. 15, 154–174. https://doi.org/10.1890/03-5116

Gedye, S.J., Jones, R.T., Tinner, W., Ammann, B., Oldfield, F., 2000. The use of mineral magnetism in the reconstruction of fire history: a case study from Lago di Origlio, Swiss Alps. Palaeogeogr. Palaeoclimatol. Palaeoecol., Fire and the Palaeoenvironment 164, 101–110. https://doi.org/10.1016/S0031-0182(00)00178-4

Genty, D., Massault, M., 1999. Carbon transfer dynamics from bomb-14C and d13C time series of a laminated stalagmite from SW France—Modelling and comparison with other stalagmite records. Geochim. Cosmochim. Acta 63, 1537–1548.

Giglio, L., Justice, C., Boschetti, L., Roy, D., 2015. MCD64A1 MODIS/Terra+Aqua Burned Area Monthly L3 Global 500m SIN Grid V006.

Giglio, L., Randerson, J.T., van der Werf, G.R., Kasibhatla, P.S., Collatz, G.J., Morton, D.C., DeFries, R.S., 2010. Assessing variability and long-term trends in burned area by merging multiple satellite fire products. Biogeosciences 7, 1171–1186. https://doi.org/10.5194/bg-7-1171-2010

Goede, A., McCulloch, M., McDermott, F., Hawkesworth, C., 1998. Aeolian contribution to strontium and strontium isotope variations in a Tasmanian speleothem. Chem. Geol. 149, 37–50. https://doi.org/10.1016/S0009-2541(98)00035-7

Gongalsky, K.B., Malmström, A., Zaitsev, A.S., Shakhab, S.V., Bengtsson, J., Persson, T., 2012. Do burned areas recover from inside? An experiment with soil fauna in a heterogeneous landscape. Appl. Soil Ecol. 59, 73–86. https://doi.org/10.1016/j.apsoil.2012.03.017

Gosling, W.D., Cornelissen, H.L., McMichael, C.N.H., 2019. Reconstructing past fire temperatures from ancient charcoal material. Palaeogeogr. Palaeoclimatol. Palaeoecol. 520, 128–137. https://doi.org/10.1016/j.palaeo.2019.01.029

Gradziński, M., Górny, A., Pazdur, A., Pazdur, M.F., 2003. Origin of black coloured laminae in speleothems from the Kraków-Wieluń; Upland, Poland. Boreas 32, 532–542. https://doi.org/10.1111/j.1502-3885.2003.tb01233.x

Gradziński, M., Hercman, H., Nowak, M., Bella, P., 2007. Age of Black Coloured Laminae Within Speleothems from Domica Cave and Its Significance for Dating of Prehistoric Human Settlement. GEOCHR 28, 39–45. https://doi.org/10.2478/v10003-007-0029-7

Granged, Arturo J.P., Jordán, A., Zavala, L.M., Muñoz-Rojas, M., Mataix-Solera, J., 2011. Short-term effects of experimental fire for a soil under eucalyptus forest (SE Australia). Geoderma 167–168, 125–134. https://doi.org/10.1016/j.geoderma.2011.09.011

Granged, Arturo J. P., Zavala, L.M., Jordán, A., Bárcenas-Moreno, G., 2011. Post-fire evolution of soil properties and vegetation cover in a Mediterranean heathland after experimental burning: A 3-year study. Geoderma 164, 85–94. https://doi.org/10.1016/j.geoderma.2011.05.017

Grieman, M.M., Aydin, M., Isaksson, E., Schwikowski, M., Saltzman, E.S., 2018. Aromatic acids in an Arctic ice core from Svalbard: a proxy record of biomass burning. Clim. Past 14, 637–651. https://doi.org/10.5194/cp-14-637-2018

Griffiths, M.L., Johnson, K.R., Pausata, F.S.R., White, J.C., Henderson, G.M., Wood, C.T., Yang, H., Ersek, V., Conrad, C., Sekhon, N., 2020. End of Green Sahara amplified mid- to late Holocene megadroughts in mainland Southeast Asia. Nat. Commun. 11, 4204. https://doi.org/10.1038/s41467-020-17927-6

Gruell, G.E., 1985. Fire on the early western landscape: An annotated record of wildland fires 1776-1900. Northwest Sci. 592 97-107 59, 97–107.

Guillong, M., Latkoczy, C., Seo, J.H., Günther, D., Heinrich, C.A., 2008. Determination of sulfur in fluid inclusions by laser ablation ICP-MS. J. Anal. At. Spectrom. 23, 1581–1589. https://doi.org/10.1039/B807383J

Guo, F., Clemens, S., Liu, X., Long, Y., Li, D., Tan, L., Liu, C., Yan, H., Sun, Y., 2021. Application of XRF Scanning to Different Geological Archives. Earth Space Sci. 8, e2020EA001589. https://doi.org/10.1029/2020EA001589

Haberle, S.G., David, B., 2004. Climates of change: human dimensions of Holocene environmental change in low latitudes of the PEPII transect. Quat. Int., Climates, human, and natural system of the PEPII transect 118–119, 165–179. https://doi.org/10.1016/S1040-6182(03)00136-8

Hageman, P.L., 2007. U.S. Geological Survey Field Leach Test for Assessing Water Reactivity and Leaching Potential of Mine Wastes, Soils, and Other Geologic and Environmental Materials (USGS Numbered Series No. 5-D3), U.S. Geological Survey Field Leach Test for Assessing Water Reactivity and Leaching Potential of Mine Wastes, Soils, and Other Geologic and Environmental Materials, Techniques and Methods. https://doi.org/10.3133/tm5D3

Halas, S., Szaran, J., 2001. Improved thermal decomposition of sulfates to SO2 and mass spectrometric determination of δ34S of IAEA SO-5, IAEA SO-6 and NBS-127 sulfate standards. Rapid Commun. Mass Spectrom. 15, 1618–1620. https://doi.org/10.1002/rcm.416

Hallam, S., 2014. Fire and Hearth: A study of Aboriginal usage and European usurpation in south-western Australia. UWA Publishing, Perth.

Hanan, E.J., Ren, J., Tague, C.L., Kolden, C.A., Abatzoglou, J.T., Bart, R.R., Kennedy, M.C., Liu, M., Adam, J.C., 2021. How climate change and fire exclusion drive wildfire regimes at actionable scales. Environ. Res. Lett. 16, 024051. https://doi.org/10.1088/1748-9326/abd78e

Hantson, S., Arneth, A., Harrison, S.P., Kelley, D.I., Prentice, I.C., Rabin, S.S., Archibald, S., Mouillot, F., Arnold, S.R., Artaxo, P., Bachelet, D., Ciais, P., Forrest, M., Friedlingstein, P., Hickler, T., Kaplan, J.O., Kloster, S., Knorr, W., Lasslop, G., Li, F., Mangeon, S., Melton, J.R., Meyn, A., Sitch, S., Spessa, A., van der Werf, G.R., Voulgarakis, A., Yue, C., 2016. The status and challenge of global fire modelling. Biogeosciences 13, 3359–3375. https://doi.org/10.5194/bg-13-3359-2016

Harper, A.R., Santin, C., Doerr, S.H., Froyd, C.A., Albini, D., Otero, X.L., Viñas, L., Pérez-Fernández, B., 2019. Chemical composition of wildfire ash produced in contrasting ecosystems and its toxicity to Daphnia magna. Int. J. Wildland Fire 28, 726. https://doi.org/10.1071/WF18200

Harrison, S.P., Bartlein, P.J., Brewer, S., Prentice, I.C., Boyd, M., Hessler, I., Holmgren, K., Izumi, K., Willis, K., 2014. Climate model benchmarking with glacial and mid-Holocene climates. Clim. Dyn. 43, 671–688. https://doi.org/10.1007/s00382-013-1922-6

Hart, S.C., DeLuca, T.H., Newman, G.S., MacKenzie, M.D., Boyle, S.I., 2005. Post-fire vegetative dynamics as drivers of microbial community structure and function in forest soils. For. Ecol. Manag., Forest Soils Research: Theory, Reality and its Role in TechnologY 220, 166–184. https://doi.org/10.1016/j.foreco.2005.08.012

Hartland, A., Adam, Fairchild, I., Lead, J., Dominguezvillar, D., Baker, A., Gunn, J., Baalousha, M., 2010. The dripwaters and speleothems of Poole's Cavern: A review of recent and ongoing research. Cave Karst Sci. 36, 37–46.

Hartland, A., Fairchild, I.J., Lead, J.R., Borsato, A., Baker, A., Frisia, S., Baalousha, M., 2012. From soil to cave: Transport of trace metals by natural organic matter in karst dripwaters. Chem. Geol. 304–305, 68–82. https://doi.org/10.1016/j.chemgeo.2012.01.032

Hartland, A., Fairchild, I.J., Lead, J.R., Zhang, H., Baalousha, M., 2011. Size, speciation and lability of NOM–metal complexes in hyperalkaline cave dripwater. Geochim. Cosmochim. Acta 75, 7533–7551. https://doi.org/10.1016/j.gca.2011.09.030

Hartland, A., Fairchild, I.J., Müller, W., Dominguez-Villar, D., 2014. Preservation of NOM-metal complexes in a modern hyperalkaline stalagmite: Implications for speleothem trace element geochemistry. Geochim. Cosmochim. Acta 128, 29–43. https://doi.org/10.1016/j.gca.2013.12.005

Hawkins, L.R., Abatzoglou, J.T., Li, S., Rupp, D.E., 2022. Anthropogenic Influence on Recent Severe Autumn Fire Weather in the West Coast of the United States. Geophys. Res. Lett. 49, e2021GL095496. https://doi.org/10.1029/2021GL095496

Hershkovitz, I., Weber, G.W., Quam, R., Duval, M., Grün, R., Kinsley, L., Ayalon, A., Bar-Matthews, M., Valladas, H., Mercier, N., Arsuaga, J.L., Martinón-Torres, M., Castro, J.M.B. de, Fornai, C., Martín-Francés, L., Sarig, R., May, H., Krenn, V.A., Slon, V., Rodríguez, L., García, R., Lorenzo, C., Carretero, J.M., Frumkin, A., Shahack-Gross, R., Mayer, D.E.B.-Y., Cui, Y., Wu, X., Peled, N., Groman-Yaroslavski, I., Weissbrod, L., Yeshurun, R., Tsatskin, A., Zaidner, Y., Weinstein-Evron, M., 2018. The earliest modern humans outside Africa. Science. https://doi.org/10.1126/science.aap8369

Hope, P., Timbal, B., Fawcett, R., 2010. Associations between rainfall variability in the southwest and southeast of Australia and their evolution through time. Int. J. Climatol. 30, 1360–1371. https://doi.org/10.1002/joc.1964

Hua, Q., McDonald, J., Redwood, D., Drysdale, R., Lee, S., Fallon, S., Hellstrom, J., 2012. Robust chronological reconstruction for young speleothems using radiocarbon. Quat. Geochronol. 14, 67–80. https://doi.org/10.1016/j.quageo.2012.04.017

Huguet, C., Routh, J., Fietz, S., Lone, M.A., Kalpana, M.S., Ghosh, P., Mangini, A., Kumar, V., Rangarajan, R., 2018. Temperature and Monsoon Tango in a Tropical Stalagmite: Last Glacial-Interglacial Climate Dynamics. Sci. Rep. 8, 5386. https://doi.org/10.1038/s41598-018-23606-w

Iglesias, V., Balch, J.K., Travis, W.R., 2022. U.S. fires became larger, more frequent, and more widespread in the 2000s. Sci. Adv. 8, eabc0020. https://doi.org/10.1126/sciadv.abc0020

Iglesias, V., Yospin, G.I., Whitlock, C., 2015. Reconstruction of fire regimes through integrated paleoecological proxy data and ecological modeling. Front. Plant Sci. 5. https://doi.org/10.3389/fpls.2014.00785

Jaffey, A.H., Flynn, K.F., Glendenin, L.E., Bentley, W.C., Essling, A.M., 1971. Precision Measurement of Half-Lives and Specific Activities of ^{235}U and ^{238}U Phys. Rev. C 4, 1889–1906. https://doi.org/10.1103/PhysRevC.4.1889

Jenkins, M., Adams, M.A., 2010. Vegetation type determines heterotrophic respiration in subalpine Australian ecosystems. Glob. Change Biol. 16, 209–219. https://doi.org/10.1111/j.1365-2486.2009.01954.x

Jex, C.N., Pate, G.H., Blyth, A.J., Spencer, R.G., Hernes, P.J., Khan, S.J., Baker, A., 2014. Lignin biogeochemistry: from modern processes to Quaternary archives. Quat. Sci. Rev. 87, 46–59.

Jones, M.W., Abatzoglou, J.T., Veraverbeke, S., Andela, N., Lasslop, G., Forkel, M., Smith, A.J.P., Burton, C., Betts, R.A., van der Werf, G.R., Sitch, S., Canadell, J.G., Santín, C., Kolden, C., Doerr, S.H., Le Quéré, C., 2022. Global and regional trends and drivers of fire under climate change. Rev. Geophys. n/a, e2020RG000726. https://doi.org/10.1029/2020RG000726

Kaal, J., Martínez-Pillado, V., Cortizas, A.M., Sánchez, J.S., Aranburu, A., Arsuaga, J.-L., Iriarte, E., 2021. Bacteria, guano and soot: Source assessment of organic matter preserved in black laminae in stalagmites from caves of the Sierra de Atapuerca (N Spain). Int. J. Speleol. 50. https://doi.org/<p>https://doi.org/10.5038/1827-806X.50.2.2382</p>

Keeley, J.E., 2009. Fire intensity, fire severity and burn severity: a brief review and suggested usage. Int. J. Wildland Fire 18, 116–126. https://doi.org/10.1071/WF07049

Kehrwald, N.M., Aleman, J., Coughlan, M., Courtney-Mustaphi, C., Githumbi, E., Magi, B., Marlon, J., Power, M.J., 2016. One thousand years of fires: Integrating proxy and model data. Front. Biogeogr. 8. https://doi.org/10.21425/F5FBG29606

Kemperl, J., Maček, J., 2009. Precipitation of calcium carbonate from hydrated lime of variable reactivity, granulation and optical properties. Int. J. Miner. Process. 93, 84–88. https://doi.org/10.1016/j.minpro.2009.05.006

Khanna, P.K., Raison, R.J., Falkiner, R.A., 1994. Chemical properties of ash derived from Eucalyptus litter and its effects on forest soils. For. Ecol. Manag., Ameliorative practices for restoring and maintaining 66, 107–125. https://doi.org/10.1016/0378-1127(94)90151-1

Lachniet, M.S., 2009. Climatic and environmental controls on speleothem oxygen-isotope values. Quat. Sci. Rev. 28, 412–432. https://doi.org/10.1016/j.quascirev.2008.10.021

Lascu, I., Feinberg, J.M., Dorale, J.A., Cheng, H., Edwards, R.L., 2016. Age of the Laschamp excursion determined by U-Th dating of a speleothem geomagnetic record from North America. Geology 44, 139–142. https://doi.org/10.1130/G37490.1

Lechleitner, F.A., Fohlmeister, J., McIntyre, C., Baldini, L.M., Jamieson, R.A., Hercman, H., Gąsiorowski, M., Pawlak, J., Stefaniak, K., Socha, P., Eglinton, T.I., Baldini, J.U.L., 2016. A novel approach for construction of radiocarbon-based chronologies for speleothems. Quat. Geochronol. 35, 54–66. https://doi.org/10.1016/j.quageo.2016.05.006

Legrand, M., McConnell, J., Fischer, H., Wolff, E.W., Preunkert, S., Arienzo, M., Chellman, N., Leuenberger, D., Maselli, O., Place, P., Sigl, M., Schüpbach, S., Flannigan, M., 2016. Boreal fire records in Northern Hemisphere ice cores: a review. Clim. Past 12, 2033–2059. https://doi.org/10.5194/cp-12-2033-2016

Li, F., Levis, S., Ward, D.S., 2013. Quantifying the role of fire in the Earth system – Part 1: Improved global fire modeling in the Community Earth System Model (CESM1). Biogeosciences 10, 2293–2314. https://doi.org/10.5194/bg-10-2293-2013

Liu, Y., 2018. New development and application needs for Earth system modeling of fire–climate–ecosystem interactions. Environ. Res. Lett. 13, 011001. https://doi.org/10.1088/1748-9326/aaa347

Lowe, M.-A., McGrath, G., Leopold, M., 2021. The Impact of Soil Water Repellency and Slope upon Runoff and Erosion. Soil Tillage Res. 205, 104756. https://doi.org/10.1016/j.still.2020.104756

Lucas, C., 2010. On developing a historical fire weather data-set for Australia. Aust. Meteorol. Oceanogr. J. 60, 1–14.

Makhubela, T.V., Kramers, J.D., 2022. Testing a new combined (U,Th)–He and U/Th dating approach on Plio-Pleistocene calcite speleothems. Quat. Geochronol. 67, 101234. https://doi.org/10.1016/j.quageo.2021.101234

Mariani, M., Connor, S.E., Theuerkauf, M., Herbert, A., Kuneš, P., Bowman, D., Fletcher, M.-S., Head, L., Kershaw, A.P., Haberle, S.G., Stevenson, J., Adeleye, M., Cadd, H., Hopf, F., Briles, C., 2022. Disruption of cultural burning promotes shrub encroachment and unprecedented wildfires. Front. Ecol. Environ. n/a. https://doi.org/10.1002/fee.2395

Mariani, M., Fletcher, M.-S., Holz, A., Nyman, P., 2016. ENSO controls interannual fire activity in southeast Australia. Geophys. Res. Lett. 43, 10,891-10,900. https://doi.org/10.1002/2016GL070572

Markowska, M., Baker, A., Treble, P.C., Andersen, M.S., Hankin, S., Jex, C.N., Tadros, C.V., Roach, R., 2015. Unsaturated zone hydrology and cave drip discharge water response: Implications for speleothem paleoclimate record variability. J. Hydrol., Advances in Paleohydrology Research and Applications 529, 662–675. https://doi.org/10.1016/j.jhydrol.2014.12.044

Markowska, M., Fohlmeister, J., Treble, P.C., Baker, A., Andersen, M.S., Hua, Q., 2019. Modelling the 14C bomb-pulse in young speleothems using a soil carbon continuum model. Geochim. Cosmochim. Acta 261, 342–367. https://doi.org/10.1016/j.gca.2019.04.029

Marlon, J.R., 2020. What the past can say about the present and future of fire. Quat. Res. 96, 66–87. https://doi.org/10.1017/qua.2020.48

Marlon, J.R., Bartlein, P.J., Gavin, D.G., Long, C.J., Anderson, R.S., Briles, C.E., Colombaroli, D., Hallett, D.J., Power, M.J., Scharf, E.A., Walsh, M.K., 2012. Long-term perspective on wildfires in the western USA. Proc. Natl. Acad. Sci. 109, E535–E543. https://doi.org/10.1073/pnas.1112839109

Marlon, J.R., Kelly, R., Daniau, A.-L., Vannière, B., Power, M.J., Bartlein, P., Higuera, P., Blarquez, O., Brewer, S., Brücher, T., Feurdean, A., Romera, G.G., Iglesias, V., Maezumi, S.Y., Magi, B., Courtney Mustaphi, C.J., Zhihai, T., 2016. Reconstructions of biomass burning from sediment-charcoal records to improve data–model comparisons. Biogeosciences 13, 3225–3244. https://doi.org/10.5194/bg-13-3225-2016

Marty, C., Houle, D., Gagnon, C., Duchesne, L., 2011. Isotopic compositions of S, N and C in soils and vegetation of three forest types in Québec, Canada. Appl. Geochem. 26, 2181–2190. https://doi.org/10.1016/j.apgeochem.2011.08.002

May, N., 2022. 'Disaster's in the recovery': bushfire survivors still waiting for homes. The Guardian.

McBride, J.R., 1983. Analysis of Tree Rings and Fire Scars to Establish Fire History.

McClean, R.G., Kean, W.F., 1993. Contributions of wood ash magnetism to archaeomagnetic properties of fire pits and hearths. Earth Planet. Sci. Lett. 119, 387–394. https://doi.org/10.1016/0012-821X(93)90146-Z

McConnell, J.R., Edwards, R., Kok, G.L., Flanner, M.G., Zender, C.S., Saltzman, E.S., Banta, J.R., Pasteris, D.R., Carter, M.M., Kahl, J.D.W., 2007. 20th-Century Industrial Black Carbon Emissions Altered Arctic Climate Forcing. Science 317, 1381–1384. https://doi.org/10.1126/science.1144856

McDonough, L.K., Treble, P.C., Baker, A., Borsato, A., Frisia, S., Nagra, G., Coleborn, K., Gagan, M.K., Zhao, J., Paterson, D., 2022. Past fires and post-fire impacts reconstructed from a southwest Australian stalagmite. Geochim. Cosmochim. Acta. https://doi.org/10.1016/j.gca.2022.03.020

McWethy, D.B., Whitlock, C., Wilmshurst, J.M., McGlone, M.S., Fromont, M., Li, X., Dieffenbacher-Krall, A., Hobbs, W.O., Fritz, S.C., Cook, E.R., 2010. Rapid landscape transformation in South Island, New Zealand, following initial Polynesian settlement. Proc. Natl. Acad. Sci. 107, 21343–21348. https://doi.org/10.1073/pnas.1011801107

Meng, Q.-B., Wang, C.-K., Liu, J.-F., Zhang, M.-W., Lu, M.-M., Wu, Y., 2020. Physical and micro-structural characteristics of limestone after high temperature exposure. Bull. Eng. Geol. Environ. 79, 1259–1274. https://doi.org/10.1007/s10064-019-01620-0

Minckley, T.A., Long, C.J., 2016. Paleofire severity and vegetation change in the Cascade Range, Oregon, USA. Quat. Res. 85, 211–217. https://doi.org/10.1016/j.yqres.2015.12.010

Mitchell, S.G., Reiners, P.W., 2003. Influence of wildfires on apatite and zircon (U-Th)/He ages. Geology 31, 1025–1028. https://doi.org/10.1130/G19758.1

Molinari, C., Hantson, S., Nieradzik, L.P., 2021. Fire Dynamics in Boreal Forests Over the 20th Century: A Data-Model Comparison. Front. Ecol. Evol. 9, 598. https://doi.org/10.3389/fevo.2021.728958

Molinari, C., Lehsten, V., Bradshaw, R.H.W., Power, M.J., Harmand, P., Arneth, A., Kaplan, J.O., Vannière, B., Sykes, M.T., 2013. Exploring potential drivers of European biomass burning over the Holocene: a data-model analysis. Glob. Ecol. Biogeogr. 22, 1248–1260. https://doi.org/10.1111/geb.12090

Mooney, S.D., Harrison, S.P., Bartlein, P.J., Daniau, A.-L., Stevenson, J., Brownlie, K.C., Buckman, S., Cupper, M., Luly, J., Black, M., Colhoun, E., D'Costa, D., Dodson, J., Haberle, S., Hope, G.S., Kershaw, P., Kenyon, C., McKenzie, M., Williams, N., 2011. Late Quaternary fire regimes of Australasia. Quat. Sci. Rev. 30, 28–46. https://doi.org/10.1016/j.quascirev.2010.10.010

Moropoulou, A., Bakolas, A., Aggelakopoulou, E., 2001. The effects of limestone characteristics and calcination temperature to the reactivity of the quicklime. Cem. Concr. Res. 31, 633–639. https://doi.org/10.1016/S0008-8846(00)00490-7

Müller, W., Fietzke, J., 2016. The Role of LA–ICP–MS in Palaeoclimate Research. Elements 12, 329–334. https://doi.org/10.2113/gselements.12.5.329

Nagra, G., Treble, P.C., Andersen, M.S., Bajo, P., Hellstrom, J., Baker, A., 2017. Dating stalagmites in mediterranean climates using annual trace element cycles. Sci. Rep. 7, 621. https://doi.org/10.1038/s41598-017-00474-4

Nagra, G., Treble, P.C., Andersen, M.S., Fairchild, I.J., Coleborn, K., Baker, A., 2016. A post-wildfire response in cave dripwater chemistry. Hydrol. Earth Syst. Sci. 20, 2745–2758. https://doi.org/10.5194/hess-20-2745-2016

Naoto, F., Link to external site, this link will open in a new window, Hirokuni, O., Yusuke, Y., Clark, G., Yuhji, Y., 2021. High spatial resolution magnetic mapping using ultra-high sensitivity scanning SQUID microscopy on a speleothem from the Kingdom of Tonga, southern Pacific. Earth Planets Space Online 73. http://dx.doi.org/10.1186/s40623-021-01401-8

Neary, D.G., Klopatek, C.C., DeBano, L.F., Ffolliott, P.F., 1999. Fire effects on belowground sustainability: a review and synthesis. For. Ecol. Manag. 122, 51–71. https://doi.org/10.1016/S0378-1127(99)00032-8

Nicewonger, M.R., Aydin, M., Prather, M.J., Saltzman, E.S., 2020. Reconstruction of Paleofire Emissions Over the Past Millennium From Measurements of Ice Core Acetylene. Geophys. Res. Lett. 47, e2019GL085101. https://doi.org/10.1029/2019GL085101

O'Donnell, A.J., Cullen, L.E., Lachlan McCaw, W., Boer, M.M., Grierson, P.F., 2010. Dendroecological potential of Callitris preissii for dating historical fires in semi-arid shrublands of southern Western Australia. Dendrochronologia 28, 37–48. https://doi.org/10.1016/j.dendro.2009.01.002

Orland, I.J., Burstyn, Y., Bar-Matthews, M., Kozdon, R., Ayalon, A., Matthews, A., Valley, J.W., 2014. Seasonal climate signals (1990–2008) in a modern Soreq Cave stalagmite as revealed by high-resolution geochemical analysis. Chem. Geol. 363, 322–333. https://doi.org/10.1016/j.chemgeo.2013.11.011

Orland, I.J., He, F., Bar-Matthews, M., Chen, G., Ayalon, A., Kutzbach, J.E., 2019. Resolving seasonal rainfall changes in the Middle East during the last interglacial period. Proc. Natl. Acad. Sci. 116, 24985–24990. https://doi.org/10.1073/pnas.1903139116

Osborne, R.A.L., 1993. The History of Karstification at Wombeyan Caves, New South Wales, Australia, as revealed by Palaeokarst Deposits. Cave Sci. 20, 1–8.

Pearce, N.J.G., Perkins, W.T., Westgate, J.A., Gorton, M.P., Jackson, S.E., Neal, C.R., Chenery, S.P., 1997. A Compilation of New and Published Major and Trace Element Data for NIST SRM 610 and NIST SRM 612 Glass Reference Materials. Geostand. Newsl. 21, 115–144. https://doi.org/10.1111/j.1751-908X.1997.tb00538.x

Pearson, A.R., Hartland, A., Frisia, S., Fox, B.R.S., 2020. Formation of calcite in the presence of dissolved organic matter: Partitioning, fabrics and fluorescence. Chem. Geol. 539, 119492. https://doi.org/10.1016/j.chemgeo.2020.119492

Pechony, O., Shindell, D.T., 2010. Driving forces of global wildfires over the past millennium and the forthcoming century. Proc. Natl. Acad. Sci. 107, 19167–19170. https://doi.org/10.1073/pnas.1003669107

Pereira, P., Úbeda, X., 2010. Spatial distribution of heavy metals released from ashes after a wildfire. J. Environ. Eng. Landsc. Manag. 18, 13–22. https://doi.org/10.3846/jeelm.2010.02

Peters, C., Church, M.J., Mitchell, C., 2001. Investigation of fire ash residues using mineral magnetism. Archaeol. Prospect. 8, 227–237. https://doi.org/10.1002/arp.171

Pharo, E.J., Meagher, D.A., Lindenmayer, D.B., 2013. Bryophyte persistence following major fire in eucalypt forest of southern Australia. For. Ecol. Manag. 296, 24–32. https://doi.org/10.1016/j.foreco.2013.01.018

Power, M.J., Marlon, J., Ortiz, N., Bartlein, P.J., Harrison, S.P., Mayle, F.E., Ballouche, A., Bradshaw, R.H.W., Carcaillet, C., Cordova, C., Mooney, S., Moreno, P.I., Prentice, I.C., Thonicke, K., Tinner, W., Whitlock, C., Zhang, Y., Zhao, Y., Ali, A.A., Anderson, R.S., Beer, R., Behling, H., Briles, C., Brown, K.J., Brunelle, A., Bush, M., Camill, P., Chu, G.Q., Clark, J., Colombaroli, D., Connor, S., Daniau, A.-L., Daniels, M., Dodson, J., Doughty, E., Edwards, M.E., Finsinger, W., Foster, D., Frechette, J., Gaillard, M.-J., Gavin, D.G., Gobet, E., Haberle, S., Hallett, D.J., Higuera, P., Hope, G., Horn, S., Inoue, J., Kaltenrieder, P., Kennedy, L., Kong, Z.C., Larsen, C., Long, C.J., Lynch, J., Lynch, E.A., McGlone, M., Meeks, S., Mensing, S., Meyer, G., Minckley, T., Mohr, J., Nelson, D.M., New, J., Newnham, R., Noti, R., Oswald, W., Pierce, J., Richard, P.J.H., Rowe, C., Sanchez Goñi, M.F., Shuman, B.N., Takahara, H., Toney, J., Turney, C., Urrego-Sanchez, D.H., Umbanhowar, C., Vandergoes, M., Vanniere, B., Vescovi, E., Walsh, M., Wang, X., Williams, N., Wilmshurst, J., Zhang, J.H., 2008. Changes in fire regimes since the Last Glacial Maximum: an assessment based on a global synthesis and analysis of charcoal data. Clim. Dyn. 30, 887–907. https://doi.org/10.1007/s00382-007-0334-x

Power, M.J., Marlon, J.R., Bartlein, P.J., Harrison, S.P., 2010. Fire history and the Global Charcoal Database: A new tool for hypothesis testing and data exploration. Palaeogeogr. Palaeoclimatol. Palaeoecol. 291, 52–59. https://doi.org/10.1016/j.palaeo.2009.09.014

Ramsey, M.H., Potts, P.J., Webb, P.C., Watkins, P., Watson, J.S., Coles, B.J., 1995. An objective assessment of analytical method precision: comparison of ICP-AES and XRF for the analysis of silicate rocks. Chem. Geol., Analytical Spectroscopy in the Earth Sciences 124, 1–19. https://doi.org/10.1016/0009-2541(95)00020-M

Rasbury, E.T., Cole, J.M., 2009. Directly dating geologic events: U-Pb dating of carbonates. Rev. Geophys. 47. https://doi.org/10.1029/2007RG000246

Read, P., Denniss, R., 2020. With costs approaching $100 billion, the fires are Australia's costliest natural disaster [WWW Document]. The Conversation. URL http://theconversation.com/with-costs-approaching-100-billion-the-fires-are-australias-costliest-natural-disaster-129433 (accessed 6.29.21).

Reale, J.K., Van Horn, D.J., Condon, K.E., Dahm, C.N., 2015. The effects of catastrophic wildfire on water quality along a river continuum. Freshw. Sci. 34, 1426–1442. https://doi.org/10.1086/684001

Rehn, E., Rowe, C., Ulm, S., Woodward, C., Bird, M., 2021. A late-Holocene multiproxy fire record from a tropical savanna, eastern Arnhem Land, Northern Territory, Australia. The Holocene 31, 870–883. https://doi.org/10.1177/0959683620988030

Reifsnyder, W.E., Herrington, L.P., Splat, K.W., 1967. Thermophysical Properties of Bark of Shortleaf, Longleaf, and Red Pine. Yale Sch. For. Environ. Stud. Bull. Ser. 80.

Richards, D.A., Bottrell, S.H., Cliff, R.A., Ströhle, K., Rowe, P.J., 1998. U-Pb dating of a speleothem of Quaternary age. Geochim. Cosmochim. Acta 62, 3683–3688. https://doi.org/10.1016/S0016-7037(98)00256-7

Richardson, D., Black, A.S., Irving, D., Matear, R.J., Monselesan, D.P., Risbey, J.S., Squire, D.T., Tozer, C.R., 2022. Global increase in wildfire potential from compound fire weather and drought. Npj Clim. Atmospheric Sci. 5, 23. https://doi.org/10.1038/s41612-022-00248-4

Roy, D.P., Boschetti, L., Maier, S.W., Smith, A.M.S., 2010. Field estimation of ash and char colour-lightness using a standard grey scale. Int. J. Wildland Fire 19, 698. https://doi.org/10.1071/WF09133

Rubino, M., D'Onofrio, A., Seki, O., Bendle, J.A., 2016. Ice-core records of biomass burning. Anthr. Rev. 3, 140–162. https://doi.org/10.1177/2053019615605117

Sander, M.-L., Andrén, O., 1997. Ash from Cereal and Rape Straw Used for Heat Production: Liming Effect and Contents of Plant Nutrients and Heavy Metals. Water. Air. Soil Pollut. 93, 93–108. https://doi.org/10.1023/A:1022179708289

Santín, C., Doerr, S.H., Shakesby, R.A., Bryant, R., Sheridan, G.J., Lane, P.N.J., Smith, H.G., Bell, T.L., 2012. Carbon loads, forms and sequestration potential within ash deposits produced by wildfire: new insights from the 2009 'Black Saturday' fires, Australia. Eur. J. For. Res. 131, 1245–1253. https://doi.org/10.1007/s10342-012-0595-8

Schmidt, G.A., Annan, J.D., Bartlein, P.J., Cook, B.I., Guilyardi, E., Hargreaves, J.C., Harrison, S.P., Kageyama, M., LeGrande, A.N., Konecky, B., Lovejoy, S., Mann, M.E., Masson-Delmotte, V., Risi, C., Thompson, D., Timmermann, A., Tremblay, L.-B., Yiou, P., 2014. Using palaeo-climate comparisons to constrain future projections in CMIP5. Clim. Past 10, 221–250. https://doi.org/10.5194/cp-10-221-2014

Scroxton, N., Burns, S., Dawson, P., Rhodes, J.M., Brent, K., McGee, D., Heijnis, H., Gadd, P., Hantoro, W., Gagan, M., 2018. Rapid measurement of strontium in speleothems using core-scanning micro X-ray fluorescence. Chem. Geol. 487, 12–22. https://doi.org/10.1016/j.chemgeo.2018.04.008

Šebela, S., Miler, M., Skobe, S., Torkar, S., Zupančič, N., 2015. Characterization of black deposits in karst caves, examples from Slovenia. Facies 61, 6. https://doi.org/10.1007/s10347-015-0430-z

Šebela, S., Zupančič, N., Miler, M., Grčman, H., Jarc, S., 2017. Evidence of Holocene surface and near-surface palaeofires in karst caves and soils. Palaeogeogr. Palaeoclimatol. Palaeoecol. 485, 224–235. https://doi.org/10.1016/j.palaeo.2017.06.015

Shakesby, R.A., 2011. Post-wildfire soil erosion in the Mediterranean: Review and future research directions. Earth-Sci. Rev. 105, 71–100. https://doi.org/10.1016/j.earscirev.2011.01.001

Sherson, L.R., Van Horn, D.J., Gomez-Velez, J.D., Crossey, L.J., Dahm, C.N., 2015. Nutrient dynamics in an alpine headwater stream: use of continuous water quality sensors to examine responses to wildfire and precipitation events. Hydrol. Process. 29, 3193–3207. https://doi.org/10.1002/hyp.10426

Sinclair, D.J., Kinsley, L.P.J., McCulloch, M.T., 1998. High resolution analysis of trace elements in corals by laser ablation ICP-MS. Geochim. Cosmochim. Acta 62, 1889–1901. https://doi.org/10.1016/S0016-7037(98)00112-4

Sliwinski, J.T., Stoll, H.M., 2021. Combined fluorescence imaging and LA-ICP-MS trace element mapping of stalagmites: Microfabric identification and interpretation. Chem. Geol. 581, 120397. https://doi.org/10.1016/j.chemgeo.2021.120397

Smith, C.L., Fairchild, I.J., Spötl, C., Frisia, S., Borsato, A., Moreton, S.G., Wynn, P.M., 2009. Chronology building using objective identification of annual signals in trace element profiles of stalagmites. Quat. Geochronol. 4, 11–21. https://doi.org/10.1016/j.quageo.2008.06.005

Spate, A., Ward, J.K., 1979. A preliminary note on the black speleothems at Jersey Cave, Yarrangobilly, NSW, in: Proceedings of the 12th Conference of the Australian Speleological Federation. Presented at the 12th Conference of the Australian Speleological Federation, The Australian Speleological Federation, Perth.

Spötl, C., Mattey, D., 2006. Stable isotope microsampling of speleothems for palaeoenvironmental studies: A comparison of microdrill, micromill and laser ablation techniques. Chem. Geol. 235, 48–58. https://doi.org/10.1016/j.chemgeo.2006.06.003

Stamou, Z., Xystrakis, F., Koutsias, N., 2016. The role of fire as a long-term landscape modifier: Evidence from long-term fire observations (1922–2000) in Greece. Appl. Geogr. 74, 47–55. https://doi.org/10.1016/j.apgeog.2016.07.005

Stronach, N.R.H., McNaughton, S.J., 1989. Grassland Fire Dynamics in the Serengeti Ecosystem, and a Potential Method of Retrospectively Estimating Fire Energy. J. Appl. Ecol. 26, 1025–1033. https://doi.org/10.2307/2403709

Swetnam, T.W., Baisan, C.H., Caprio, A.C., Brown, P.M., Touchan, R., Anderson, R.S., Hallett, D.J., 2009. Multi-Millennial Fire History of the Giant Forest, Sequoia National Park, California, USA. Fire Ecol. 5, 120–150. https://doi.org/10.4996/fireecology.0503120

Tan, L., Cai, Y., An, Z., Cheng, H., Shen, C.-C., Breitenbach, S.F.M., Gao, Y., Edwards, R.L., Zhang, H., Du, Y., 2015. A Chinese cave links climate change, social impacts and human adaptation over the last 500 years. Sci. Rep. 5, 12284. https://doi.org/10.1038/srep12284

Teixeira, J.C., Folberth, G.A., O'Connor, F.M., Unger, N., Voulgarakis, A., 2021. Coupling interactive fire with atmospheric composition and climate in the UK Earth System Model. Geosci. Model Dev. 14, 6515–6539. https://doi.org/10.5194/gmd-14-6515-2021

Thomas, Z.A., Mooney, S., Cadd, H., Baker, A., Turney, C., Schneider, L., Hogg, A., Haberle, S., Green, K., Weyrich, L.S., Pérez, V., Moore, N.E., Zawadzki, A., Kelloway, S.J., Khan, S.J., 2022. Late Holocene climate anomaly concurrent with fire activity and ecosystem shifts in the eastern Australian Highlands. Sci. Total Environ. 802, 149542. https://doi.org/10.1016/j.scitotenv.2021.149542

Tibby, J., Tyler, J.J., Barr, C., 2018. Post little ice age drying of eastern Australia conflates understanding of early settlement impacts. Quat. Sci. Rev. 202, 45–52. https://doi.org/10.1016/j.quascirev.2018.10.033

Treble, P., Shelley, J.M.G., Chappell, J., 2003. Comparison of high resolution sub-annual records of trace elements in a modern (1911–1992) speleothem with instrumental climate data from southwest Australia. Earth Planet. Sci. Lett. 216, 141–153. https://doi.org/10.1016/S0012-821X(03)00504-1

Treble, P.C., Baker, A., Abram, N.J., Hellstrom, J.C., Crawford, J., Gagan, M.K., Borsato, A., Griffiths, A.D., Bajo, P., Markowska, M., Priestley, S.C., Hankin, S., Paterson, D., 2022. Ubiquitous karst hydrological control on speleothem oxygen isotope variability in a global study. Commun. Earth Environ. 3, 1–10. https://doi.org/10.1038/s43247-022-00347-3

Treble, P.C., Baker, A., Ayliffe, L.K., Cohen, T.J., Hellstrom, J.C., Gagan, M.K., Frisia, S., Drysdale, R.N., Griffiths, A.D., Borsato, A., 2017. Hydroclimate of the Last Glacial Maximum and deglaciation in southern Australia's arid margin interpreted from speleothem records (23–15 ka). Clim. Past 13, 667–687. https://doi.org/10.5194/cp-13-667-2017

Treble, P.C., Chappell, J., Shelley, J.M.G., 2005. Complex speleothem growth processes revealed by trace element mapping and scanning electron microscopy of annual layers. Geochim. Cosmochim. Acta 69, 4855–4863. https://doi.org/10.1016/j.gca.2005.06.008

Treble, P.C., Fairchild, I.J., Baker, A., Meredith, K.T., Andersen, M.S., Salmon, S.U., Bradley, C., Wynn, P.M., Hankin, S.I., Wood, A., McGuire, E., 2016. Roles of forest bioproductivity, transpiration and fire in a nine-year record of cave dripwater chemistry from southwest Australia. Geochim. Cosmochim. Acta 184, 132–150. https://doi.org/10.1016/j.gca.2016.04.017

Tuhý, M., Ettler, V., Rohovec, J., Matoušková, Š., Mihaljevič, M., Kříbek, B., Mapani, B., 2021. Metal(loid)s remobilization and mineralogical transformations in smelter-polluted savanna soils under simulated wildfire conditions. J. Environ. Manage. 293, 112899. https://doi.org/10.1016/j.jenvman.2021.112899

Urban, T.M., Rasic, J.T., Alix, C., Anderson, D.D., Chisholm, L., Jacob, R.W., Manning, S.W., Mason, O.K., Tremayne, A.H., Vinson, D., 2019. Magnetic detection of archaeological hearths in Alaska: A tool for investigating the full span of human presence at the gateway to North America. Quat. Sci. Rev. 211, 73–92. https://doi.org/10.1016/j.quascirev.2019.03.018

Uribe, C., Inclán, R., Sánchez, D.M., Clavero, M.A., Fernández, A.M., Morante, R., Cardeña, A., Blanco, A., Van Miegroet, H., 2013. Effect of wildfires on soil respiration in three typical Mediterranean forest ecosystems in Madrid, Spain. Plant Soil 369, 403–420. https://doi.org/10.1007/s11104-012-1576-x

Vachula, R.S., Huang, Y., Longo, W.M., Dee, S.G., Daniels, W.C., Russell, J.M., 2019. Evidence of Ice Age humans in eastern Beringia suggests early migration to North America. Quat. Sci. Rev. 205, 35–44. https://doi.org/10.1016/j.quascirev.2018.12.003

Vachula, R.S., Karp, A.T., Denis, E.H., Balascio, N.L., Canuel, E.A., Huang, Y., 2022. Spatially calibrating polycyclic aromatic hydrocarbons (PAHs) as proxies of area burned by vegetation fires: Insights from comparisons of historical data and sedimentary PAH fluxes. Palaeogeogr. Palaeoclimatol. Palaeoecol. 596, 110995. https://doi.org/10.1016/j.palaeo.2022.110995

Vachula, R.S., Russell, J.M., Huang, Y., Richter, N., 2018. Assessing the spatial fidelity of sedimentary charcoal size fractions as fire history proxies with a high-resolution sediment record and historical data. Palaeogeogr. Palaeoclimatol. Palaeoecol. 508, 166–175. https://doi.org/10.1016/j.palaeo.2018.07.032

van Beynen, P., Bourbonniere, R., Ford, D., Schwarcz, H., 2001. Causes of colour and fluorescence in speleothems. Chem. Geol. 175, 319–341. https://doi.org/10.1016/S0009-2541(00)00343-0

van Etten, E.J.B., Davis, R.A., Doherty, T.S., 2021. Fire in Semi-Arid Shrublands and Woodlands: Spatial and Temporal Patterns in an Australian Landscape. Front. Ecol. Evol. 9, 382. https://doi.org/10.3389/fevo.2021.653870

van Marle, M.J.E., Kloster, S., Magi, B.I., Marlon, J.R., Daniau, A.-L., Field, R.D., Arneth, A., Forrest, M., Hantson, S., Kehrwald, N.M., Knorr, W., Lasslop, G., Li, F., Mangeon, S., Yue, C., Kaiser, J.W., van der Werf, G.R., 2017. Historic global biomass burning emissions for CMIP6 (BB4CMIP) based on merging satellite observations with proxies and fire models (1750–2015). Geosci. Model Dev. 10, 3329–3357. https://doi.org/10.5194/gmd-10-3329-2017

Wang, C., Bendle, J.A., Greene, S.E., Griffiths, M.L., Huang, J., Moossen, H., Zhang, H., Ashley, K., Xie, S., 2019. Speleothem biomarker evidence for a negative terrestrial feedback on climate during Holocene warm periods. Earth Planet. Sci. Lett. 525, 115754. https://doi.org/10.1016/j.epsl.2019.115754

Wang, D., Guan, D., Zhu, S., Kinnon, M.M., Geng, G., Zhang, Q., Zheng, H., Lei, T., Shao, S., Gong, P., Davis, S.J., 2021. Economic footprint of California wildfires in 2018. Nat. Sustain. 4, 252–260. https://doi.org/10.1038/s41893-020-00646-7

Wang, H., Treble, P., Baker, A., Rich, A.M., Bhattacharyya, S., Oriani, F., Akter, R., Chinu, K., Wainwright, I., Marjo, C.E., 2022. Sulphur variations in annually layered stalagmites using benchtop micro-XRF. Spectrochim. Acta Part B At. Spectrosc. 189, 106366. https://doi.org/10.1016/j.sab.2022.106366

Wang, X., Xiao, J., Cui, L., Ding, Z., 2013. Holocene changes in fire frequency in the Daihai Lake region (north-central China): indications and implications for an important role of human activity. Quat. Sci. Rev. 59, 18–29. https://doi.org/10.1016/j.quascirev.2012.10.033

Ward, M., Tulloch, A.I.T., Radford, J.Q., Williams, B.A., Reside, A.E., Macdonald, S.L., Mayfield, H.J., Maron, M., Possingham, H.P., Vine, S.J., O'Connor, J.L., Massingham, E.J., Greenville, A.C., Woinarski, J.C.Z., Garnett, S.T., Lintermans, M., Scheele, B.C., Carwardine, J., Nimmo, D.G., Lindenmayer, D.B., Kooyman, R.M., Simmonds, J.S., Sonter, L.J., Watson, J.E.M., 2020. Impact of 2019–2020 mega-fires on Australian fauna habitat. Nat. Ecol. Evol. 4, 1321–1326. https://doi.org/10.1038/s41559-020-1251-1

Webb, M., Dredge, J., Barker, P.A., Müller, W., Jex, C., Desmarchelier, J., Hellstrom, J., Wynn, P.M., 2014. Quaternary climatic instability in south-east Australia from a multi-proxy speleothem record. J. Quat. Sci. 29, 589–596. https://doi.org/10.1002/jqs.2734

Whitlock, C., Larsen, C., 2001. Charcoal as a Fire Proxy, in: Smol, J.P., Birks, H.J.B., Last, W.M., Bradley, R.S., Alverson, K. (Eds.), Tracking Environmental Change Using Lake Sediments: Terrestrial, Algal, and Siliceous Indicators, Developments in Paleoenvironmental Research. Springer Netherlands, Dordrecht, pp. 75–97. https://doi.org/10.1007/0-306-47668-1_5

Woodhead, J., Hellstrom, J., Maas, R., Drysdale, R., Zanchetta, G., Devine, P., Taylor, E., 2006. U–Pb geochronology of speleothems by MC-ICPMS. Quat. Geochronol. 1, 208–221. https://doi.org/10.1016/j.quageo.2006.08.002

Woodhead, J.D., Hellstrom, J., Hergt, J.M., Greig, A., Maas, R., 2007. Isotopic and Elemental Imaging of Geological Materials by Laser Ablation Inductively Coupled Plasma-Mass Spectrometry. Geostand. Geoanalytical Res. 31, 331–343. https://doi.org/10.1111/j.1751-908X.2007.00104.x

Woods, S.W., Balfour, V.N., 2010. The effects of soil texture and ash thickness on the post-fire hydrological response from ash-covered soils. J. Hydrol. 393, 274–286. https://doi.org/10.1016/j.jhydrol.2010.08.025

Wu, G., Wang, D.Y., 2012. Mechanical and Acoustic Emission Characteristics of Limestone after High Temperature. Adv. Mater. Res. 446–449, 23–28. https://doi.org/10.4028/www.scientific.net/AMR.446-449.23

Wu, J.Y., Wang, Y.J., Cheng, H., Kong, X.G., Liu, D.B., 2012. Stable isotope and trace element investigation of two contemporaneous annually-laminated stalagmites from northeastern China surrounding the "8.2 ka event" Clim. Past 8, 1497–1507. https://doi.org/10.5194/cp-8-1497-2012

Wynn, P.M., Borsato, A., Baker, A., Frisia, S., Miorandi, R., Fairchild, I.J., 2013. Biogeochemical cycling of sulphur in karst and transfer into speleothem archives at Grotta di Ernesto, Italy. Biogeochemistry 114, 255–267. https://doi.org/10.1007/s10533-012-9807-z

Wynn, P.M., Brocks, J.J., 2014. A framework for the extraction and interpretation of organic molecules in speleothem carbonate. Rapid Commun. Mass Spectrom. 28, 845–854. https://doi.org/10.1002/rcm.6843

Wynn, P.M., Fairchild, I.J., Baker, A., Baldini, J.U.L., McDermott, F., 2008. Isotopic archives of sulphate in speleothems. Geochim. Cosmochim. Acta 72, 2465–2477. https://doi.org/10.1016/j.gca.2008.03.002

Wynn, P.M., Fairchild, I.J., Borsato, A., Spötl, C., Hartland, A., Baker, A., Frisia, S., Baldini, J.U.L., 2018. Sulphate partitioning into calcite: Experimental verification of pH control and application to seasonality in speleothems. Geochim. Cosmochim. Acta 226, 69–83. https://doi.org/10.1016/j.gca.2018.01.020

Wynn, P.M., Fairchild, I.J., Frisia, S., Spötl, C., Baker, A., Borsato, A., 2010. High-resolution sulphur isotope analysis of speleothem carbonate by secondary ionisation mass spectrometry. Chem. Geol. 271, 101–107. https://doi.org/10.1016/j.chemgeo.2010.01.001

Wynn, P.M., Fairchild, I.J., Spötl, C., Hartland, A., Mattey, D., Fayard, B., Cotte, M., 2014. Synchrotron X-ray distinction of seasonal hydrological and temperature patterns in speleothem carbonate. Environ. Chem. 11, 28. https://doi.org/10.1071/EN13082

Wynn, P.M., Morrell, D.J., Tuffen, H., Barker, P., Tweed, F.S., Burns, R., 2015. Seasonal release of anoxic geothermal meltwater from the Katla volcanic system at Sólheimajökull, Iceland. Chem. Geol. 396, 228–238. https://doi.org/10.1016/j.chemgeo.2014.12.026

Zedler, P.H., 2007. Fire Effects on Grasslands, in: Johnson, E.A., Miyanishi, K. (Eds.), Plant Disturbance Ecology. Academic Press, Burlington, pp. 397–439. https://doi.org/10.1016/B978-012088778-1/50015-7

Zennaro, P., Kehrwald, N., Marlon, J., Ruddiman, W.F., Brücher, T., Agostinelli, C., Dahl-Jensen, D., Zangrando, R., Gambaro, A., Barbante, C., 2015. Europe on fire three thousand years ago: Arson or climate? Geophys. Res. Lett. 42, 5023–2033. https://doi.org/10.1002/2015GL064259

Zhao, J., Yu, K., Feng, Y., 2009. High-precision 238U–234U–230Th disequilibrium dating of the recent past: a review. Quat. Geochronol. 4, 423–433. https://doi.org/10.1016/j.quageo.2009.01.012

Zupančič, N., Šebela, S., Miler, M., 2011. Mineralogical and chemical characteristics of black coatings in Postojna cave system. Acta Carsologica 40. https://doi.org/10.3986/ac.v40i2.15