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The interplay between massive volcanism and the local environment: Geochemistry of the Late Permian mass extinction across the Sydney Basin, Australia

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ABSTRACT

The isotopic, geochemical, and physical characteristics of the Late Permian mass extinction have been identified and assessed from terrestrial sections across the Sydney Basin, eastern Australia. These new data are used to both correlate the extinction event across the basin and elucidate its cause. Two stratigraphically well-constrained cores were examined, one each from the northern and southern regions of the Sydney Basin. Both sections show uninterrupted transitions from the last Permian coal to a carbonaceous shale, overlain by siltstones, mudstones, sandstones and shales whose mineralogical and physical characteristics are consistent with non-marine origins. These non-marine origins are also broadly supported by elemental data. Carbon isotopic data were the primary means for identifying the stratigraphic position of the Late Permian mass extinction across the basin; the data show that the mass extinction occurred as an interval with the form of a closely-spaced, double-negative $\delta^{13}C_{org}$ excursion within 1 m of the top of the last Permian coal, a feature previously unrecognised in the basin. This result is supported by coincident excursions in $\delta^{15}N$ and $\delta^{34}S_{pyrite}$, the first measurements of their kind for the Late Permian mass extinction in the Sydney Basin. The interrelationships between the C, N and S isotopic data, concentrations and elemental ratios, together with major, trace and rare earth element concentrations, ratios, and statistical analyses show severe environmental disruption occurred at the time of the extinction event with die-off of terrestrial vegetation and the injection of sulphate into the water column, consistent with massive volcanism. Geochemical evidence also shows, however, that local conditions have the potential to disrupt the Late Permian mass extinction signature and hence the data need to be interpreted carefully.

1. Introduction

Great advances in the understanding of the Late Permian mass extinction (LPME) and its relationship to paleontological and isotopic changes have been made in recent years, although much of the research still focuses on marine sections and the possible role played by anoxia (e.g. Korte et al., 2010; Payne and Kump, 2007). Links between the mass extinction and volcanism are also postulated because many continental flood basalts show close temporal relationships with mass extinction events, and are believed to have significantly affected global climatic conditions via the release of gases such as CO_2 and SO_2 (e.g. Bond and Wignall, 2014; Sobolev et al., 2011). The Siberian Traps in the Tunguska Basin is the largest of these flood basalts; the province is essentially contemporaneous with the LPME and is considered by many to be the trigger mechanism for it although some questions remain regarding the relative durations and timing of the eruptions and extinction event (Burgess et al., 2014). Recent studies show that the gas output from the Siberian Traps' emplacement had the potential to account for a large proportion of the $\delta^{13}C$ shift and environmental disruption associated with the mass extinction, and the sulphate aerosols released may explain the observed shifts in $\delta^{34}S$ in both marine and non-marine sequences (Black et al., 2012; Bond and Wignall, 2014; Brand et al., 2012; Cui and Kump, 2015; Payne and Kump, 2007; Saunders and Reichow, 2009; Tang et al., 2013; Williams et al., 2012b). Others postulate that the gases were released via the interaction of Siberian Traps phreatomagmatic eruptions with volatile-rich rocks rather than the direct release of magmatic gases (Black et al., 2014; Fristad et al., 2015; Jerram et al., 2016; Polozov et al., 2016; Svensen et al., 2009), or that eruptions occurred in closely-spaced multiple stages of varying intensity (Ivanov et al., 2013).

How the LPME manifests in non-marine sections and how this correlates with its appearance in marine sections are still debated, although recent dating strongly suggests no lag in the global massive die-off of organisms in both realms (Metcalfe et al., 2015). An added complication is the lack of a non-marine index fossil comparable to *Hindeodus parvus* in the marine sections. Recent information from China is proving beneficial for linking the mass extinction across transitional marine-terrestrial

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sections but is still reliant on marine fossils to do so, and possible terrestrial fossil markers are only regional (Chu et al., 2016; Peng et al., 2005; Shen et al., 2011; Yu et al., 2015; Zhang et al., 2016). Thus far the most information for non-marine sections comes from South Africa, specifically the Karoo Basin, but this has its own contradictions and limited geochemical data other than $\delta^{13}C$ are available (e.g. Coney et al., 2004; Coney et al., 2007; Cui and Kump, 2015; de Wit et al., 2002; Fildani et al., 2009; Gastaldo et al., 2015; Gastaldo and Neveling, 2016; Hancox et al., 2002; Retallack et al., 2006). Geochemical evidence for the LPME position in Australia, other than negative organic $\delta^{13}C$ ($\delta^{13}C_{org}$) excursions, is also limited and somewhat contradictory. Attempts to measure an Ir anomaly have met with mixed success and an initial report of shocked quartz grains was later retracted (Langenhorst et al., 2005; Retallack et al., 1998). Changes in major element ratios in paleosols indicate a shift to warmer and wetter conditions (e.g. Retallack, 1995; Retallack et al., 1998; Sheldon and Retallack, 2002) but information from trace elements is lacking. Similarly, investigations of mineralogical changes other than gross changes associated with altered fluvial regimes are few. The presence of a claystone breccia coincident with the negative $\delta^{13}C_{org}$ excursion and floral changes has been reported in some locations (e.g. Retallack, 1995; Retallack et al., 1998) but its basin-wide occurrence has not been confirmed. Additionally, much of the information from Australian non-marine basins is restricted to the Bowen Basin and, to a lesser extent, the northern Sydney Basin with fewer studies from the western and southern Sydney Basin (e.g. Retallack, 1999; Williams et al., 2012a; Williams et al., 2012b).

Placement of the LPME in the Sydney Basin relies, therefore, primarily on changes in $\delta^{13}C_{org}$ and palynofloral assemblages, complemented by lithological information. Those studies that examine sections from the southern part of the basin have invariably looked at the readily available coastal exposures, a number of which have evidence for an erosional surface and paleosol development (Retallack, 1999; Retallack et al., 1998). The most recent investigations of the southern Sydney Basin examined sections devoid of these features and used a higher sampling resolution than previous studies, finding both an apparent double negative excursion in $\delta^{13}C_{org}$ and indications of volcanism albeit with an influence from local conditions (Williams et al., 2012a, 2012b). There exists, therefore, a clear requirement to examine non-marine basin sections using a high resolution multidisciplinary approach to (i) unequivocally identify the LPME across the basin, (ii) establish a set of criteria for correlation with other non-marine areas, and (iii) establish a robust set of criteria for correlation with marine areas. To address these needs we present the first attempt at compiling a comprehensive geochemical data suite for the LPME across the Sydney Basin, including the first $\delta^{34}S_{pyrite}$ data and statistical analyses, whose changes and relationships are indicative of a link between severe environmental disruption and the injection of volcanic gases into the atmosphere and water column.

2. Regional setting

Fig. 1a shows the positions of the continents and the inferred palaeocoastline in the southernmost portion of Gondwana at the approximate time of the LPME. The paleogeography of Australia at this time was dominated by uplands with lowland areas along the western coastline and extending almost continuously east-west across central Australia (Veevers, 2006; Ziegler et al., 1997). The coastline of what is now Western Australia formed part of the southern Neo-Tethyan shoreline, extending north-eastwards into a broad shelf region. A narrow mountainous strip extended along the eastern margin of the continent, dropping sharply into lowlands, then into continental shelf, and finally into the deep Panthalassan ocean (Ziegler et al., 1997). The Sydney Basin forms the southern part of the Bowen-Gunnedah-Sydney Basin system, an asymmetric retro-arc foreland basin consisting of alternating shallow marine and fluvial sequences (Figs. 1b, c, 2).

In the southern Sydney Basin at the time of the LPME, the lithology changed significantly from the Late Permian Bulli Coal to the Triassic alluvial Wombarra Claystone with an intervening layer of either carbonaceous shale or the Coal Cliff Sandstone (Fig. 2). The carbonaceous shale immediately overlying the Bulli Coal has been, and still is, generally considered to be part of the Bulli Coal and, where the Coal Cliff Sandstone is absent, this shale has gradational contacts with both the Bulli Coal and Wombarra Claystone (Arditto, 1987, 1991; Bowman, 1974; Dehghani, 1994; Herbert, 1997). The alluvial Coal Cliff Sandstone is a localised unit and, where present, has an erosional contact with the underlying Bulli Coal or carbonaceous shale (Arditto, 1987, 1991; Bowman, 1974; Dehghani, 1994; Herbert, 1997).

The Newcastle Coal Measures show a more complex development than the coeval Bulli Coal (Fig. 2). The uppermost 10 m consists of the Great Northern, Wallarah and Vales Point Coals which split and coalesce across the area (Lindsay and Herbert, 2002). Towards the east the Great Northern Coal is separated from the overlying Wallarah Coal by the channel deposits of the Teralba Conglomerate, and towards the west the Wallarah and Vales Point Coals are separated by the Karignan Conglomerate (Lindsay and Herbert, 2002). Deposition of these coals and conglomerates is believed to have been controlled by cyclic changes in base level arising from sea-level fluctuations, and several erosion surfaces have been identified throughout the sequence (Lindsay and Herbert, 2002). Differential subsidence and uplift of the Newcastle Coal Measures preceded deposition of the overlying estuarine outwash sediments of the Dooralong Shale, the stratigraphic equivalent of the Wombarra Claystone (Dehghani, 1994 and references therein; Herbert, 1997).

Initial palynology studies led to the conclusion that the LPME occurred at the top of the Wombarra Claystone (Morante, 1995; Morante and Herbert, 1994; Morante et al., 1994). Subsequent investigations, however, place it either at the top of the Bulli Coal based on palynofloral data, $\delta^{13}C_{org}$ data and lithology (Hansen et al., 2000; Michaelsen, 2002; Retallack, 1995, 1999; Retallack et al., 1998; Sheldon and Retallack, 2002) or approximately 1 m above the last Permian coal on the basis of negative $\delta^{13}C_{org}$ shifts (Morante, 1996). Recent dating of tuffs, together with global correlation of CO_2 greenhouse spikes, place the LPME at the base of the Coal Cliff Sandstone in the southern Sydney Basin and the top of the Newcastle Coal Measures in the northern Sydney Basin (Metcalfe et al., 2015; Retallack, 2013), although it bears restating that the Coal Cliff Sandstone is a localised unit. Initial uncertainty regarding the suitability of the palynological and isotopic criteria used to identify the LPME in Australian sections based on the apparent differences in changes in $\delta^{13}C$ of bulk organic matter versus individual molecular species and the uncertainties in the ranges of floral and palynological markers (Foster et al., 1998; Foster et al., 1997b) has since been clarified by further correlation using U-Pb dating, $\delta^{13}C$, marine invertebrate data, and CO_2 greenhouse spikes (Metcalfe et al., 2015; Retallack, 2013). Additionally, recent work shows that some key palynological marker taxa occur diachronously in Australia and the Karoo Basin (Barbolini et al., 2016). Despite these developments, an abrupt negative shift in $\delta^{13}C_{org}$ remains currently the default marker for the LPME in non-marine basins in Australia, especially in the absence of a viable faunal marker.

3. Methods

Given that the majority of recent studies place the LPME at the top of the last Permian coal, the current study focuses on the detailed characterisation of the sequences immediately below and above this horizon. Samples were taken from two drill cores, one each from the northern and southern Sydney Basin. Both cores had been recently drilled and stored under cover, ensuring the material had not been subjected to degradation. The southern Sydney Basin drill core, Loddon C2-C3 (hereinafter referred to as L23; GDA94 34° 12′ 00.91″S, 150° 55′ 04.19″E), was supplied by BHP Billiton and includes the upper part of the Loddon