



## Stable nitrogen isotope analysis of the Upper Devonian palynomorph, *Tasmanites*



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### ABSTRACT

Bulk samples are commonly used in stable (N) isotope studies to infer climate changes. However, due to uncertainties in the composition of bulk samples, the inconsistency of diagenetic alteration and the variation of dominant oceanic features, such as N-fixation and denitrification, the isolation of specific sedimentary N fractions has become a crucial step to understanding the nitrogen cycle. This paper describes the extraction techniques and the stable nitrogen isotope analysis (on a nano-EA-IRMS) of the palynomorph, *Tasmanites* spp. (80–200 μm) found in Upper Devonian (Famennian) black shales from Kentucky, USA. *Tasmanites* is a widely occurring and long-ranging prasinophyte (unicellular green algae) genus. Palynomorphs, such as *Tasmanites*, are highly resistant to most forms of decay. It is therefore suggested that the  $\delta^{15}\text{N}$  signature of this palynomorph may be a useful, unaltered indicator of baseline isotopic change in future palaeoclimate studies. The greatly reduced sample size accepted by the nano-EA-IRMS makes this technique a viable complement to bulk sediment analyses.

The results, using the nano-EA-IRMS, demonstrate that the  $\delta^{15}\text{N}$  signature of the bulk organic samples differ significantly from that of the isolated *Tasmanites* spp. Three distinct isotopic relationships were observed from the three different sample localities. These include parallel changes in the  $\delta^{15}\text{N}$  values of bulk samples and extracted *Tasmanites* spp., variation in the  $\delta^{15}\text{N}$  of bulk samples, with no corresponding change recorded in *Tasmanites* spp., and opposing  $\delta^{15}\text{N}$  changes recorded between the bulk samples and the extracted *Tasmanites* spp. This inconsistent isotopic variation further emphasises the complexity of the nitrogen cycle. Possible explanations for the observed variation include changes in the rate of N-fixation and denitrification due to climate change, incomplete nitrification, and variation in the bulk organic content.

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### 1. Introduction

Changes in bulk sedimentary  $\delta^{15}\text{N}$  values have become a useful measure of palaeoclimate change, and have been shown to correlate well with recent glacial–interglacial  $\delta^{18}\text{O}$  curves observed in Greenland ice-cores (Altabet et al., 2002). However, significant alteration of the stable nitrogen isotope signal, attributed to diagenesis, has been documented close to the sediment–water interface during early burial. This is a particular problem where sediment accumulation rates are low, whereas areas of high sediment accumulation rates, such as continental margins, appear to record negligible change between the sinking flux  $\delta^{15}\text{N}$  and bulk sedimentary  $\delta^{15}\text{N}$  (Robinson et al., 2012). Significant lateral differences in bulk sedimentary  $\delta^{15}\text{N}$  (>2‰) have also been found within downcore records located a mere 15 km apart in the South China Sea (Kienast et al., 2005). Studies have also shown that the inorganic N fraction contained within clay minerals in

sediments can be relatively significant, leading to a mixture of inorganic and organic  $\delta^{15}\text{N}$  values in bulk samples (Carman et al., 1996; Freudenthal et al., 2001; Schubert and Calvert, 2001; Kienast et al., 2005).

Bulk samples contain a variety of organic material. Trophic enrichment typically leads to a 3–4‰ enrichment in  $\delta^{15}\text{N}$  for each trophic step up the food chain (DeNiro and Epstein, 1981; Minagawa and Wada, 1984). The trophic enrichment factor of an ecosystem is assumed to stay constant through time, but the base-line does not. Primary producers provide the initial step within a trophic system, therefore, base-line  $\delta^{15}\text{N}$  changes, brought about by environmental change, may be recorded by primary producers. Bulk marine sediments mainly consist of marine primary producers, however, terrestrial material and higher trophic level organisms can contribute a significant proportion, dependent upon benthic conditions, palaeogeographic conditions and sediment accumulation rates (Meyer and Kump, 2008).

In an effort to provide a better overall record of past changes in sedimentary  $\delta^{15}\text{N}$ , a targeted approach, using discrete and quality controlled sedimentary N fractions are being analysed more routinely. The  $\delta^{15}\text{N}$  of N bound in diatoms (e.g., Sigman et al., 1999; Crosta and Shemesh, 2002; Robinson et al., 2004), foraminifera (e.g., Altabet and Curry, 1989; Ren et al., 2009) and chlorophyll degradation products

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(e.g., Sachs and Repeta, 1999; Ohkouchi et al., 2006) have all been analysed as a means of overcoming some of the concerns related to bulk sedimentary  $\delta^{15}\text{N}$ . This study describes the analysis of the stable nitrogen isotope signal of the palynomorph, *Tasmanites* spp. (80–200  $\mu\text{m}$ ), and the extraction techniques used to successfully separate samples of this palynomorph (60–120 specimens) from bulk Upper Devonian (Famennian) shales from Kentucky, USA, which are dominated by amorphous organic matter (AOM). Abundant occurrences of prasinophytes, such as *Tasmanites* and *Leiosphaeridia*, often coincide with black shale formation and reduced abundance of normal marine phytoplankton (Prauss and Riegel, 1989). It is therefore suggested that these isolated palynomorphs may provide a high precision record of  $\delta^{15}\text{N}$  change within the photic zone during extreme oceanographic change, recording the initial stage of nutrient N uptake within the marine trophic system. *Tasmanites* are also found deposited in marine sediments of lower organic composition (TOC < 0.5%), such as grey shales, providing a consistent stratigraphic dataset over a range of depositional conditions.

## 2. Materials and methods

### 2.1. Materials

Samples of Upper Devonian shales were obtained from three localities in northeastern Kentucky, USA (Fig. 1). Outcrop samples were obtained along highways I64W (N38°10.810' W83°34.081', the Three Lick Type Section, approximately 14 km west of Morehead, samples shown correlate to the lower Cleveland Member of the Ohio Shale), KY10E (N38°35.748', W83°20.566', 2 km east of Vanceburg, upper Cleveland Member of the Ohio Shale), and KY801N (N38°9.128' W83°33.098', at the junction with KY1722, Cleveland Member of the Ohio Shale). The shales are composed of varying quantities of silt (quartz, feldspar, chlorite and mica) and clay particles (illite and kaolinite), carbonaceous matter, pyrite and minor amounts of carbonate (Schwietering, 1979). The organic fraction (TOC 7–12%, Perkins et al., 2008) is dominated by amorphous organic matter (AOM), with the remainder being composed of a mixture of prasinophytes, acritarchs, fish remains, terrestrial plant material and spores.

The Cleveland Member of the Ohio Shale is contemporaneous with glacial deposits located in high palaeo-latitudes (Perez-Leyton, 1991; Díaz-Martínez et al., 1999; Melo and Loboziak, 2003; Wicander et al., 2011; Strel et al., 2012). A 3 tonne dropstone has also been documented near the top of the Ohio Shale unit in Kentucky, interpreted to be the result of alpine glaciation on the adjacent Acadian Mountains (Lierman and Mason, 2007; Clayton et al., 2010). Stratigraphic resolution within the Cleveland Member has been difficult to determine due to a fairly

uniform palynomorph assemblage. The three chosen sections are therefore not stratigraphically correlated and may overlap each other.

Samples of the Lower Permian Quamby Group at Latrobe, Northern Tasmania, Australia, often referred to as the Tasmanite Oil Shale, were obtained in order to perform preliminary chemical treatment experiments. This sample was chosen due to the abundance of large *Tasmanites* and their ease of extraction from the rock matrix, a friable mix of quartz, illite, chlorite and jarosite, without the use of chemical treatments.

Palynomorphs are generally highly resistant to most forms of decay, including routine acid extraction techniques, and are widely distributed in sedimentary rocks, indicating that they may be excellent sedimentary archives of organic carbon and nitrogen. *Tasmanites* spp. (Fig. 2b) is a thick-walled, spherical palynomorph, belonging to the prasinophyte algae (Tappan, 1980; Guy-Ohlson, 1996). The fossil phycomata commonly found in dispersed sediments are representative of the non-motile cyst forming phase of the life cycle (Guy-Ohlson, 1988), and the carbon distribution (n-alkanes/alkene doublets) within these algal cysts is consistent with the resistant biopolymer, algaenan (Dutta et al., 2006). Cyst formation in *Pachysphaera*, the modern equivalent to *Tasmanites*, has been tentatively associated with the lunar cycle (Guiry, 2015).

Ackmann et al. (1970) suggested that modern prasinophyte blooms are related to the enrichment of the water column by nitrogen and phosphates. The availability and isotopic signature of nitrogen varies as a result of redox conditions, often brought about by climate and palaeogeographic change (Meyer and Kump, 2008). Therefore, fossil prasinophytes such as *Tasmanites*, are potentially excellent records of nutrient conditions which change due to environmental factors. *Tasmanites* also have significant value because they are a widely occurring and much longer ranging genus (Proterozoic–Recent) (Wicander and Playford, 2008) than many of the other commonly investigated sedimentary N fractions (pelagic foraminifera and diatoms). *Tasmanites* are also relatively large when compared to other common palynomorphs, permitting easier extraction from the rock matrix, whilst also requiring a smaller number of extracted specimens per sample for stable isotope analysis.

### 2.2. Preliminary chemical testing

A range of chemical treatments were carried out on the Tasmanite Oil Shale, to ascertain what effect the procedures would have on the carbon and nitrogen isotope composition of the palynomorph, *Tasmanites*, prior to the extraction of *Tasmanites* from the Upper Devonian Kentucky samples.

Part of the Tasmanite Oil Shale sample was used as a control sample, to which the isotopic ratio of all of the treated *Tasmanites* samples could

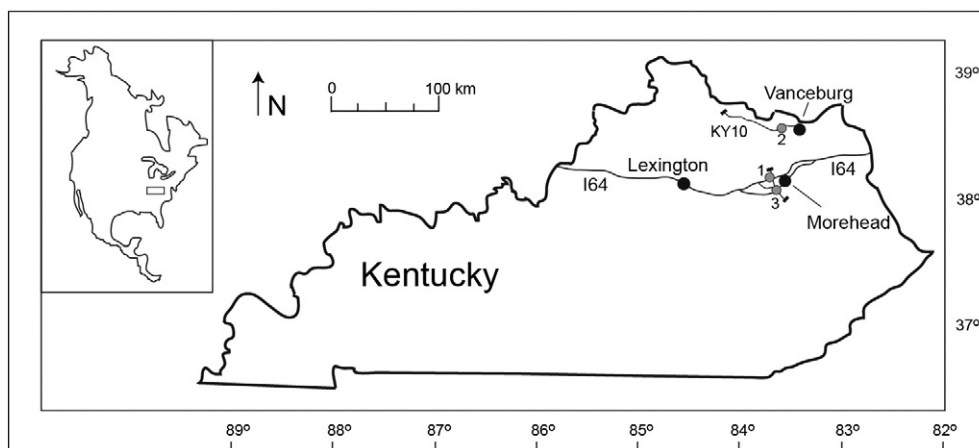


Fig. 1. Upper Devonian black shale sample localities, Kentucky, USA. 1. I64W, lower Cleveland Member of the Ohio Shale, 2. KY10E, upper Cleveland Member of the Ohio Shale, 3. KY801N, Cleveland Member of the Ohio Shale.

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