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Terrestrial acidification during the end-Permian biosphere crisis?

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ABSTRACT

Excessive acid rainfall associated with emplacement of the Siberian Traps magmatic province is increasingly accepted as a major contributing factor to the end-Permian biosphere crisis. However, direct proxy evidence of terrestrial acidification is so far not available. In this paper, we seek to determine the probability that relative proportions of extractable monophenolic components from soil-derived organic matter in marine sediments provide a molecular proxy for estimating soil acidity. Intermittently

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low and high ratios of vanillic acid to vanillin detected in latest Permian and earliest Triassic deposits of the Southern Alps, Italy, support concepts of pulses of severe acidification (pH <4) during the main phase of the biosphere crisis.

INTRODUCTION

Recently, three-dimensional (3-D) chemistry-climate simulations underlined the plausibility that both acid rainfall and ozone-layer breakdown could have contributed to the global biosphere crisis and associated extinctions at the end of the Permian Period (Black et al., 2014). Induced by massive acidic and halogenic gas emissions related to the Siberian Traps magmatism, modeled pulses of acid rain with pH values as low as 2 appear to be particularly intense across the Northern Hemisphere, whereas increased UV-B radiation resulting from stratospheric ozone destruction would occur on a more global scale. Concrete evidence for chronic environmental mutagenesis caused by increased UV-B flux may be provided by the worldwide proliferation of tetrads of lycopsid microspores in end-Permian spore/pollen records (Visscher et al., 2004). Harmful effects of acid rain have been hinted at, or proposed in theory, to explain pronounced ecosystem destabilization on land (e.g., Benton and Newell, 2014). Yet, despite the profound negative impact of acid rain on chemical and biological ecosystem processes, credible proxy indicators for excessive end-Permian terrestrial acidification are so far lacking.

Effects of acid rain are particularly intense in soil systems. Field observations and experimental studies demonstrate increased solubilization of plant-toxic metal ions, in particular Al^{3+}, as well as leaching of Ca, Mg and other plant nutrients from soils with limited buffering capacity (e.g., Tomlinson, 2003). As a result of chronic acidity stress, root development and functioning is inhibited and nutrient uptake is reduced, so that

aboveground vegetation becomes predisposed to illness and mortality (e.g., Matzner and Ulrich, 1985). Belowground biota and biotic processes are also adversely affected (e.g., Francis, 1986). Acidity is a factor in regulating the structure of microbial communities in soils. Notably bacterial community composition is dominantly driven by pH rather than temperature or other environmental variables, with lowest levels of diversity and richness observed in acid soils (Fierer and Jackson, 2006). By contrast, fungal communities are less strongly controlled by pH, but at values below 4.5 fungal growth in soils frequently decreases (e.g., Rousk et al., 2009). A wide variety of soil biochemical processes depend on catalytic properties of extracellular enzymes secreted by bacteria and fungi. Enzymatic activity is largely related to pH (Sinsabaugh et al., 2008), so that excessive soil acidification may lead to denaturation and inactivation of enzyme proteins (e.g., Frankenberger and Johanson, 1982).

Extracellular enzymes play a crucial role in the formation and turnover of soil organic matter (SOM), mediating stepwise conversion of complex plant-derived polymers, such as cellulose and lignin, to more simple organic and inorganic constituents. Fungi are the principal agents in initial depolymerization of plant litter, but most intermediate degradation products may also be metabolized by bacterial enzymes (Sinsabaugh, 2010). The apparent pH dependency of enzymatic activity in soils bears the potential of a pH-controlled distribution of degradation products in SOM. Particularly, lignin-derived compounds should be taken into consideration. Lignin requires an intricate suite of oxidative enzymes for its decomposition. White-rot fungi are long known to initiate breakdown with the aid of peroxidase enzymes, but following cleavage of the C–

C, ester, and ether bonds that connect the structural units of lignin, phenolic degradation products are decomposed by both soil fungi and soil bacteria (e.g., Bugg et al., 2011).

A significant intermediate step in various enzymatic decomposition pathways of lignin and other polymerized plant phenolics is the common production of vanillin (Bugg et al., 2011). This monophenolic aldehyde (4-hydroxy-3-methoxybenzaldehyde) may be converted to vanillic acid (4-hydroxy-3-methoxybenzoic acid) by aldehyde-oxydase enzymes (e.g., Crawford et al., 1982) and further to protocatechuic acid (3,4-dihydroxybenzoic acid), before soil microbes accomplish aromatic ring cleavage. Once the free, monophenolic compounds are sorbed onto the matrix of the entire SOM, the concentration of extractable vanillic acid usually exceeds that of vanillin (e.g., Whitehead et al., 1982). Bacterial culture studies have confirmed that enzymatic oxidation of vanillin and other aromatic and aliphatic aldehydes is a pH-sensitive process, generally with optimum pH values above 5 (e.g., Kunc, 1971). In view of this sensitivity, analysis of variations in relative proportions of vanillin and vanillic acid extracted from SOM may offer the possibility to detect major changes in soil acidity.

Organic matter is regularly preserved in paleosol profiles across the Permian-Triassic boundary and has been successfully analyzed for carbon-isotope signatures ($\delta^{13}C_{org}$) that may provide proxy information on redox conditions, soil development, and microbial degradation (e.g., Krull and Retallack, 2000). However, individual SOM molecular components were so far not identified from latest Permian paleosols. Alternatively, despite effects of selective preservation, transfer and redistribution of soil materials by erosion offers the possibility to trace relevant information on the nature of SOM by analyzing the organic matter content of shallow-marine sediments. In

accordance with widespread end-Permian demise of woody vegetation (e.g., Looy et al., 2001), strongly increased erosion rates are illustrated by a wealth of sedimentological information from fluvial systems (e.g., Newell et al., 2010) and shelf deposits (e.g., Algeo and Twitchett, 2010). Enhanced soil erosion is substantiated by the common occurrence in marine sediments of soil-derived organic debris (Sephton et al., 2005b) and soil-borne resting structures of filamentous fungi (Visscher et al., 2011). At the molecular level, latest Permian sedimentary organic assemblages are frequently marked by an unusual enrichment of polycyclic aromatic hydrocarbons (PAHs; inclusive of alkylated and oxygenated PAHs) (e.g., Sephton et al., 1999; Watson et al., 2005; Shen et al., 2011). These are likely to reflect rapid transport and burial of soil-derived materials (Sephton et al., 2005a). Anoxic sedimentary conditions and restricted thermal maturation may have prevented further biotic and abiotic conversion of the organic molecules.

Of all the marine end-Permian deposits so far analyzed, solvent-extractable organic matter from thermally immature marls in a section near Vigo Meano in the Southern Alps of northern Italy revealed the most diverse molecular composition (Watson et al., 2005), including abundant alkylated naphthalenes alongside xanthones and dibenzofurans. Dibenzo-*p*-dioxin was detected for the first time in Paleozoic samples, underlining the unusual preservation of the organic assemblage. In view of the remarkable abundance and diversity of aromatic compounds, we revisit the Vigo Meano assemblage to investigate the presence of soil-derived monophenolic components that could offer promise for verifying end-Permian terrestrial acidification scenarios.

The section investigated is exposed along the ‘Strada alle Gorghe’ (46°07′43.4”N, 11°08′09.0”E) near the village of Vigo Meano, 5 km north of Trento. Organic-rich

samples originate from an 80-cm-thick marl unit, and three successive thin, marly interbeds in the overlying oolitic grainstones (Fig. 1). When lithostratigraphically correlated with the nearby Masi Saracini section and other Permian-Triassic transition sequences in the Dolomites (e.g., Farabegoli and Perri, 2012), the marl unit represents the Bulla Member of the Bellerophon Formation, while the oolites belong to the Lower Tesero Member of the Werfen Formation.

The age of the Bulla and Lower Tesero Member is constrained by conodont biostratigraphy (e.g., Farabegoli et al., 2007; Farabegoli and Perri, 2012). The Bulla Member and the lower part of the Lower Tesero Member represent the late Changhsingian *Hindeodus praeparvus* Zone. Within this interval a variety of distinctive Permian brachiopods, foraminifera, and calcareous algae become extinct. Concomitant terrestrial crisis is reflected by a pronounced diversity decline of pollen and spores of land plants and the proliferation of fungal remains (e.g., Cirilli et al., 1998). In the Bulla reference section, the first appearance of *Hindeodus parvus* marks the Permian-Triassic boundary at 1.30 m from the base of the Lower Tesero Member. The globally recognized end-Permian negative excursion in the carbon-isotopic composition of marine carbonates ($\delta^{13}C_{carb}$) straddles the boundary between the Bulla and Lower Tesero Members (e.g., Kraus et al., 2013).

The conodont records, complemented with sequence-stratigraphic analysis, indicate that the Bulla and Lower Tesero members could respectively correlate to the end-Permian beds 25–26 and the Permian-Triassic boundary bed 27 of the global stratotype section and point (GSSP) for the Permian-Triassic boundary at Meishan, China (Farabegoli et al., 2007; Farabegoli and Perri, 2012). Beds 25–27 witness the main

marine extinctions (Wang et al., 2014) and are now radiometrically ($^{206}Pb/^{238}U$) bracketed between 251.941 ± 0.037 Ma and 251.902 ± 0.024 Ma (Burgess et al., 2014).

In addition to molecular characterization of extractable aromatic compounds, we analyzed samples from the Vigo Meano section for total organic carbon (TOC), Rock-Eval parameters and carbon-isotope signatures ($\delta^{13}C_{org}$) of bulk organic matter. Together with analytical procedures, results of the additional analyses are detailed in the GSA Data Repository[1].

POLYCYCLIC AROMATIC COMPOUNDS

Molecular characterization of the extracted apolar organic fractions confirms the abundance of PAHs, alkylated PAHs, and oxygenated PAHs already detected during previous organic-geochemical work on the Vigo Meano marls (Watson et al., 2005). The fraction is notably characterized by a variety of alkylated naphthalenes, phenanthrenes, biphenyls, xanthones, and dibenzofurans; the presence of dibenzo-*p*-dioxin was also confirmed. The enrichment of PAHs observed in the Vigo Meano marls can be traced throughout the Southern Alps (Sephton et al., 1999, 2005b) and has since been documented from marine Permian-Triassic transition sequences in Greenland, Spitsbergen and Canada (e.g., Nabbefeld et al., 2010), China (e.g., Shen et al., 2011), and Australia (Grice et al., 2007). Considering their co-occurrence, it seems plausible that the varied PAHs have derived from comparable sources. A largely or entirely terrigenous origin is commonly accepted, but considerable controversy exists with respect to their formation.

At present, wildfires are the single most important natural source of PAHs. The pyrosynthetic compounds are formed by thermal decomposition and subsequent

recombination of organic molecules. It is conceivable that end-Permian PAHs were produced by ubiquitous vegetation burning, particularly when found co-occurring with charred wood remains (Shen et al., 2011). But also the role of intrusive magmatism should be considered (e.g., George, 1992). In contrast to negligible emissions by present-day volcanoes, subsurface combustion of Late Paleozoic Siberian coal deposits as well as Neoproterozoic-sourced oil accumulations formed an almost unlimited source of organic ingredients for the formation of volcanogenic PAHs. Sorbed to volcanic dust and aerosols, winds may have distributed the compounds over great distances.

Whether produced by wildfires or by volcanic activity, pyrogenic PAHs accumulate in soils via atmospheric fallout (Wilcke, 2000). In modern erosion-deposition systems characterized by high rates of soil erosion and associated organic carbon runoff, PAH distribution patterns demonstrate that enrichment of PAHs in marine sediments is mainly the result of SOM influx (e.g., Ma et al., 2008).

VANILLIN AND VANILLIC ACID

The extracted polar fraction of the Vigo Meano organic assemblages yielded modest amounts of free vanillin and vanillic acid. Fugacity modeling, predicting the potential distribution of free vanillin to principal environmental compartments, suggests that only negligible quantities (0.031%) will be distributed to sediments (Table DR1 in the Data Repository). It is plausible, therefore, that the free vanillin in marls of the Bulla and Lower Tesero Members reflects excessive SOM influx. Free vanillin and vanillic acid are readily biodegradable, even under anaerobic conditions (e.g., Healy and Young, 1979). Yet, our findings imply the almost complete cessation of biodegradation and other diagenetic processes that could have transformed the compounds to CO_2 or CH_4 during

transport and burial. Although there is experimental evidence that sorbed organic chemicals may sometimes escape biodegradation (Pritchard, 1987), the microbial growth conditions that prevented breakdown of vanillin and vanillic acid have still to be unraveled.

Quantitative changes within the section are observable through the ratio of vanillic acid to vanillin [acid/aldehyde – $(Ad/Al)_v$ ratio] (Fig. 1; Table DR2). In only two samples does the amount of vanillic acid exceed that of vanillin, resulting in relatively high $(Ad/Al)_v$ values (>1). In marked contrast, most other samples are characterized by very low ratios (<0.1).

Vanillin and vanillic acid show similar hydrophobicity, having partition coefficients (log P_{ow}) of 1.188 and 1.334, respectively (http://www.chemspider.com). Despite the possibility of partial desorption of the molecules during transport, one may assume that the measured $(Ad/Al)_v$ values in sediments still approximate the ratios of free vanillic acid and vanillin originally sorbed onto the SOM matrix. $(Ad/Al)_v$ values <0.1 can thus be regarded as pronounced deviations from the usually high relative proportion of sorbed vanillic acid in soils (Whitehead et al., 1982).

Microbiological information relevant to a possible calibration of $(Ad/Al)_v$ ratios to pH values is limited. However, in agreement with the notion that enzymatic oxidation of vanillin is a pH-sensitive process (Kunc, 1971), results of pH experiments in the food industry, where vanillin (‘vanilla’) is extensively used as a flavoring ingredient, are particularly informative (Anklam et al., 1997). By analyzing pasteurized milk samples under different pH values (3.5–9.5, adjusted by adding HCl or NaOH solution), progressive enzymatic degradation of vanillin and formation of vanillic acid could be

observed above a pH value of 4. Enzymes had their highest level of activity toward vanillin at pH 8.0. At pH levels <4, no significant amounts of vanillic acid were formed (Fig. DR1). These observations support earlier conclusions of simulated acid rain experiments suggesting that specific soil microbial populations, such as vanillin degraders, will be preferentially inhibited by acid rain of pH levels around 3 (Bewley and Stotzky, 1984). We consider, therefore, that the predominantly low $(Ad/Al)_v$ ratios recognized in the organic matter record from the Bulla and Lower Tesero members could be interpreted in terms of SOM influx from acidified soils with a pH <4. Since intermittent high ratios correspond to soils with normal acidity (pH in the range 5–6.5), severe soil acidification must have occurred in pulses.

CONCLUDING REMARKS

As a working hypothesis, we conclude that low $(Ad/Al)_v$ ratios in the Vigo Meano section provide proxy evidence for pulses of terrestrial acidification during the main phase of the end-Permian biosphere crisis. Further organic-geochemical research may reveal to what extent similar $(Ad/Al)_v$ signals can be detected in other Permian-Triassic transition sequences. In order to build a more robust actualistic framework for accurate interpretation and calibration of the end-Permian molecular records, baseline information is needed for the distribution of free vanillin and vanillic acid in modern marine sediments with significant input of soil-derived organic matter, as well as supporting results from acidified-soil studies and laboratory experiments.

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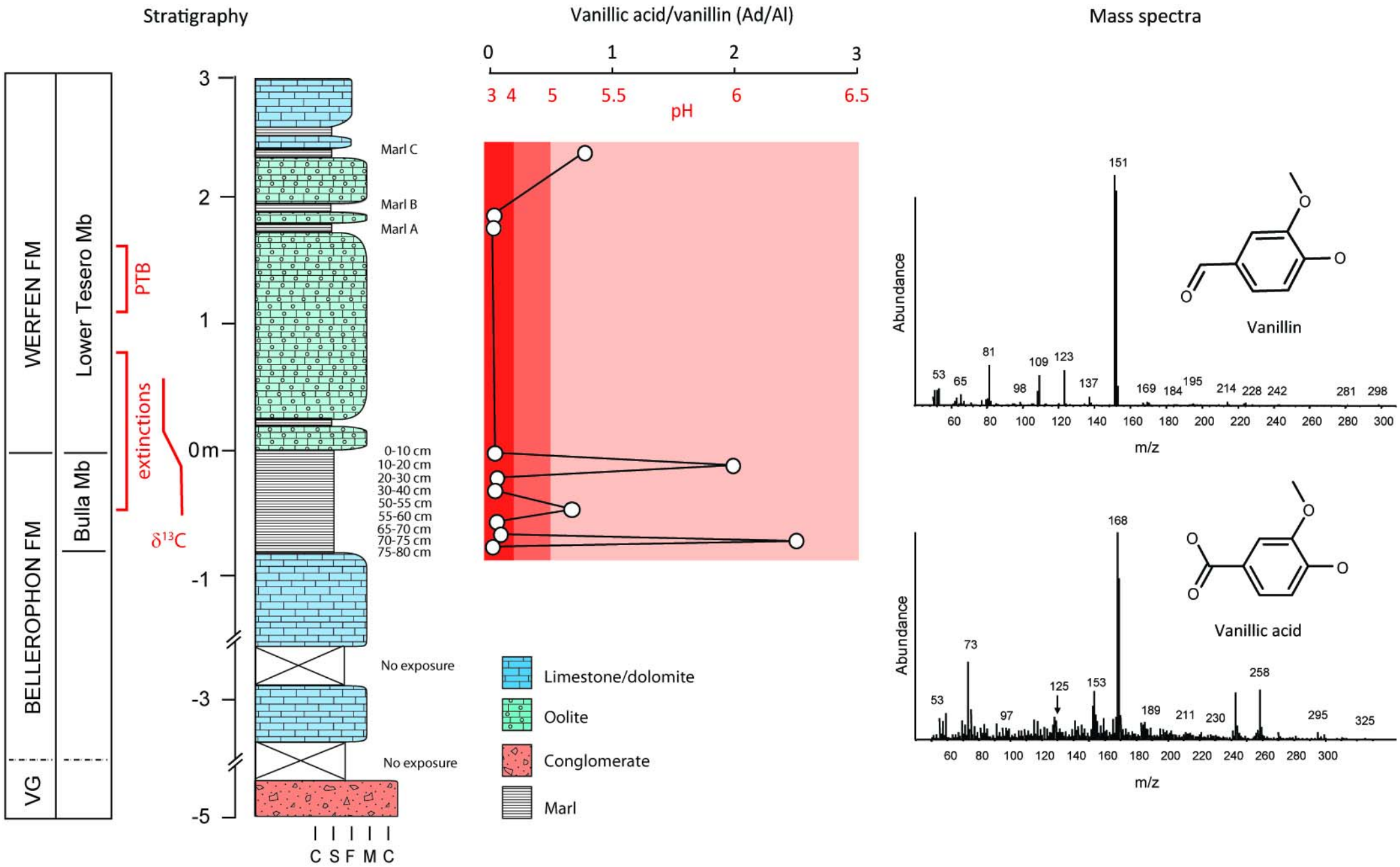
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FIGURE CAPTION

Figure 1. Ratios of vanillic acid to vanillin [acid/aldehyde – (Ad/Al)v ratios] in latest Permian and earliest Triassic organic matter assemblages from the Vigo Meano section, providing proxy evidence for pulses of soil acidification (pH <4). For calibration of (Ad/Al)v values to pH values see the Data Repository (Fig. DR1 [see footnote 1]). VG—Val Gardena Formation; PTB—approximate position of the Permian-Triassic boundary; extinction—interval of principal marine extinction and floral turnover in the Southern Alps; $\delta^{13}C$—position end-Permian negative carbon-isotope shift in the Southern Alps.

[1]GSA Data Repository item 2015059, experimental methods, geochemical data sets, and relationship of molecular proxy to acidity, is available online at www.geosociety.org/pubs/ft2015.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.


Stratigraphy
Vanillic acid/vanillin (Ad/Al)
Mass spectra
WERFEN FM
BELLEROPHON FM
VG
Lower Tesero Mb
Bulla Mb
PTB
extinctions
δ13C
3
2
1
0m
-1
-3
-5
Marl C
Marl B
Marl A
0-10 cm
10-20 cm
20-30 cm
30-40 cm
50-55 cm
55-60 cm
65-70 cm
70-75 cm
75-80 cm
No exposure
No exposure
C S F M C
0
1
2
3
3 4 5 5.5 6 6.5
pH
Limestone/dolomite
Oolite
Conglomerate
Marl
Abundance
m/z
151
Vanillin
168
Vanillic acid