

**DATA REPOSITORY**

**Terrestrial acidification during the end-Permian biosphere crisis?**

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**SUPPLEMENTARY MATERIAL**

In addition to data sets, this supplementary material contains brief explanatory notes on applied methods.

**EXPERIMENTAL METHODS**

**RockEval**

Samples were analyzed for total organic carbon (TOC) and standard RockEval parameters (RE6).

## **Stable isotopes**

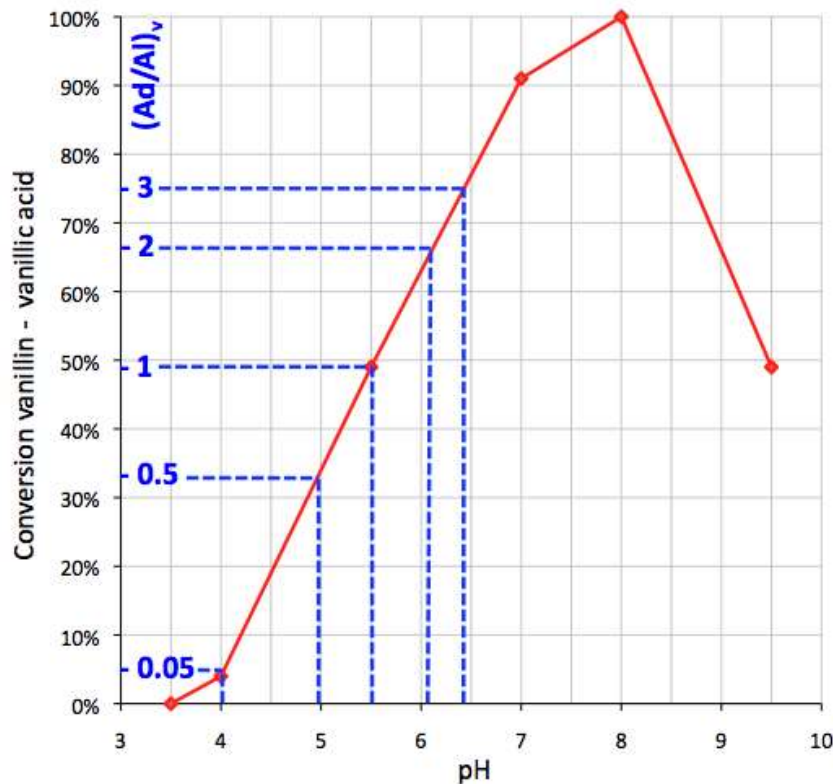
Approximately 1.5 mg of each samples were placed in silver cups and acidified several times with drops of 10% HCl. The samples were then combusted to carbon dioxide which was analysed on a Finnigan MAT Delta E stable isotope ratio mass spectrometer.

## **Organic geochemistry**

Each sample (1.0 g) was homogenized, and then ultrasonically extracted three times using 10 ml of a dichloromethane/methanol mixture (97:3). The extracts were fractionated by silica gel chromatography and elution solvents comprising n-hexane (aliphatic fraction), n-hexane-dichloromethane (1:1, v/v) (aromatic fraction without oxygen-containing compounds), dichloromethane (oxygen containing aromatic compounds) and dichloromethane-methanol (1:1, v/v) (polar compounds). Compound detection of the aliphatic hydrocarbons was performed with an Agilent Technologies 6890 gas chromatograph (GC) coupled to an Agilent Technologies 5973 quadrupole mass selective detector gas chromatograph-mass spectrometer (GC-MS) using a HP-ULTRA-2 fused-silica capillary column (50 m × 0.20 mm i.d. coated with 0.11 µm cross-linked 5%-diphenyl–95%-dimethyl siloxane as stationary phase) and He as carrier gas. The samples were injected using a splitless injector held at at 280°C. The column was heated from 50°C to 300°C at 5°C min<sup>-1</sup> followed by an isothermal period of 10 min. The mass selective detector was operated in the electron impact mode at 70 eV, source temperature of 250 °C, emission current of 1 mA and multiple-ion detection with a mass range from 50 to 500 amu. Compound identifications were based on comparison of GC retention time, mass spectrometric fragmentation patterns and literature mass spectra.

Quantification of vanillin and vanillic acid was achieved by integration of the relevant peaks in the mass chromatograms. To account for variability in ionisation efficiency standards were analysed and the relative responses of vanillin to vanillic acid established at 1:0.69.

Integration data were corrected to account for ionisation efficiency. Vanillic acid to vanillin ( $(Ad/Al)_v$ ) ratios were calibrated to pH values by using the experimental relation between enzymatic oxidation of vanillin to vanillic acid and pH in pasteurized milk described by Anklam et al. (1997).



**Figure DR1.** Calibration  $(Ad/Al)_v$  to pH.

**N.B.**  $(Ad/Al)_v$  ratios based on extracted, free vanillin and vanillic acid monomers should not be confused with  $(Ad/Al)_v$  ratios obtained via the alkaline CuO oxidation technique (Hedges and Ertel, 1982). When organic materials containing lignin polymers are reacted with CuO, a variety of phenolic oxidation products are released, among which the  $(Ad/Al)_v$  ratio provides a widely applied measure of the degree of microbial degradation of remnant lignin polymers in soils and young sediments (e.g. Thevenot et al., 2010). Upon CuO oxidation, most fresh vascular plant tissues yield  $(Ad/Al)_v$  ratios in the range of 0.1–0.2, while values in the range of 0.2–4 are usually indicative of degradation.

## Theoretical distribution of vanillin

**Table DR1.** Potential environmental distribution of vanillin (%), calculated using a generic level-1 fugacity model (from UNEP Screening Information Data Set, available at <http://www.chem.unep.ch/irptc/sids/OECDSEIDS/121335.pdf>)

Environment	vanillin (%)
Water	98.5
Air	0.066
Soil solids	1.41
Sediment solids	0.031
Suspended sediments	0.00098
Fish	0.00008

## DATA

**Table DR2.** TOC, RockEval, carbon-isotope, and (Ad/Al)<sub>v</sub> data for the Vigo Meano section.

Sample	TOC (wt %)	S1 (mg/g)	S2 (mg/g)	S3 (mg/g)	HI	OI	PI	Tmax (°C)	δ <sup>13</sup> C <sub>org</sub> (‰)	(Ad/Al) <sub>v</sub>
Marl C									-20.95	0.76
Marl B									-26.24	0.01
Marl A									-26.59	0.01
0 to 10									-25.89	0.03
10 to 20	0.82	0.03	0.44	0.61	54	74	0.06	431	-27.95	2.00
20 to 30									-27.70	0.04
30 to 40	0.83	0.03	0.71	0.66	86	80	0.04	434	-27.93	0.01
45 to 55									-25.38	0.67
55 to 60									-24.97	0.03
65 to 70	0.34	0.02	0.43	0.53	126	156	0.04	432	-22.20	0.09
70 to 75	1.15	0.04	1.19	0.78	103	68	0.03	431	-26.09	2.52
75 to 80	1.01	0.02	0.46	0.67	46	66	0.04	427	-24.67	0.00

## Total organic carbon analyses

Gross geochemical indicators (Table DR2) may reveal general information on the amount of sedimentary organic materials, their source and their level of post-burial thermal maturation. TOC contents of the marly unit at Vigo Meano range from 0.34 wt% to 1.15 wt% with the

highest values observed at the base. Rock-Eval hydrogen and oxygen indices (HI, 46-126 mg HC/g TOC; OI, 74-156 mg CO<sub>2</sub>/g TOC) are consistent with a predominantly terrestrial origin (Type III) for the organic carbon.  $T_{\max}$  data indicate that the organic matter has not yet entered the oil window.

Measured  $\delta^{13}\text{C}_{\text{org}}$  values fluctuate between -27.95‰ and -20.95‰, without apparent trend. In the Southern Alps the conspicuous end-Permian negative excursion in the carbon-isotopic composition of carbonates ( $\delta^{13}\text{C}_{\text{carb}}$ ) straddles the boundary between the Bulla and Lower Tesero Members (e.g. Kraus et al., 2013). In organic matter assemblages from the Val Badia section in the western Dolomites, a concurrent shift was demonstrated in compound-specific carbon-isotope signatures of *n*-alkanes ( $\delta^{13}\text{C}_{\text{alk}}$ ) indicative of leaf cuticles of land plants (Sephton et al., 2002). Bulk  $\delta^{13}\text{C}_{\text{org}}$  values measured at Vigo Meano fluctuate between -27.95‰ and -20.95‰. Because these fluctuations do not match the distinctive negative  $\delta^{13}\text{C}_{\text{alk}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  trends, they may reflect variation in source organic matter rather than global changes in atmospheric <sup>13</sup>C content.

Land plants using C<sub>3</sub> photosynthesis have  $\delta^{13}\text{C}$  values ranging from -35‰ to -20‰. Although Late Permian values <-26‰ would not exclude a marine organic fraction (e.g. Luo et al., 2014), the Vigo Meano isotope record matches the high influx of land-plant materials in latest Permian seas, recognized across the Southern Alps (e.g. Kraus et al. 2013). If this influx is soil-dominated, fluctuating  $\delta^{13}\text{C}_{\text{org}}$  values could well indicate supply of eroded SOM from different depth levels. In modern soil profiles, isotopic fractionation during long-term SOM decomposition commonly results in progressive <sup>13</sup>C enrichment with depth (e.g. Wang et al., 2008).

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