Synchronous record of $\delta^{13}C$ shifts in the oceans and atmosphere at the end of the Permian

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ABSTRACT

In conjunction with the profound ecologic crisis at the end of the Permian, the most conspicuous geochemical event is the worldwide negative shift in the carbon isotopic composition ($\delta^{13}C$) of both carbonates and sedimentary organic matter. Comparative carbon isotopic analyses of carbonates and the molecular fossils of land plant leaf cuticles from a marine Permian-Triassic transition section in the southern Alps, northeastern Italy, substantiates the concept of synchronous disturbances in oceanic and atmospheric chemistry and, therefore, verifies the primary nature of the end-Permian $\delta^{13}C$ disturbance. The $\delta^{13}C$ excursion appears to be a consequence of the ecological crisis, and the global reservoir of soil organic matter may be the only plausible source of ^{13}C-depleted carbon.

INTRODUCTION

Global extinctions at the end of the Permian reflect the most devastating ecologic crisis of Phanerozoic time (Erwin, 1993, 1994; Hallam and Wignall, 1997). The ecosystem collapse affected not only marine, but also terrestrial biota (Retallack, 1995; Smith, 1995; Visscher et al., 1996). The extinction events are accompanied by conspicuous negative shifts in the

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carbon isotopic compositions of carbonates ($\delta^{13}C_{carb}$) that have been recorded in latest Permian sections throughout the world (Magaritz et al., 1988; Baud et al., 1989; Holser et al., 1989; Erwin, 1993; Bowring et al., 1998; Jin et al., 2000).

End-Permian $\delta^{13}C_{carb}$ shifts are generally interpreted as reflecting a reapportioning of carbon between the Earth's inorganic and organic reservoirs. A thorough appreciation of the nature of the isotopic trends is essential to help us understand the association between changes in end-Permian oceanic and atmospheric chemistry and the ecologic crisis. Because $\delta^{13}C_{carb}$ provides a record of oceanic bicarbonate, the $\delta^{13}C$ shifts are generally interpreted in terms of a prominent global change in the $\delta^{13}C$ values of the surface waters from which the carbonate originated. However, individual end-Permian $\delta^{13}C_{carb}$ profiles from different sections frequently display significant variations in the absolute magnitude of the $\delta^{13}C$ shifts as well as many small-scale fluctuations. These differences are likely to be secondary diagenetic effects, which can mimic primary perturbations in the global carbon cycle (Scholle, 1995).

Complementary to the $\delta^{13}C_{carb}$ record, carbon isotope profiles for both marine (Magaritz et al., 1992; Wang et al., 1995; Wignall et al., 1988; Looy, 2000; Twitchett et al., 2001) and terrestrial (Morante et al., 1994; Krull and Retallack, 2000; Krull et al., 2000) sedimentary organic matter ($\delta^{13}C_{org}$) also display negative shifts at the end of the Permian. This could imply a means of confirming the primary origin of the negative shifts in $\delta^{13}C_{carb}$. However, it appears that $\delta^{13}C_{org}$ trends may not always be a straightforward record of isotopic changes in surficial carbon reservoirs, because shifts in $\delta^{13}C_{org}$ may be caused by variations in the contributions from different sources for the organic matter (Foster et al., 1997). Most of the $\delta^{13}C_{org}$ data available originate from shallow-marine sedimentary rocks, so that $\delta^{13}C_{org}$ values can reflect the carbon isotopic composition of a mixture of marine and land-derived material. Consequently, even when $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ values are measured in the same sections, bulk $\delta^{13}C_{org}$ data are inappropriate for verifying to what extent the end-Permian carbon isotope event represents a dramatic disturbance in the global carbon cycle. In terrestrial sedimentary strata, $\delta^{13}C$ trends for land-plant derived organic matter (Morante et al., 1994; Morante, 1996) and the tusks of vertebrates (Thackeray et al., 1990; MacLeod et al., 2000), could reflect atmospheric change associated with the ecologic crisis. However, substantiation of a suspected synchronism with the marine $\delta^{13}C_{carb}$ trends is hampered by the lack of accurate time controls when attempting to correlate terrestrial and marine Permian-Triassic sedimentary records.

A further complicating factor when interpreting $\delta^{13}C_{org}$ profiles is the significant variation among the ^{13}C content of organic compounds from individual plants. Many of the enzymatic processes involved in secondary carbon metabolism have associated isotope effects, and different metabolites can have different $\delta^{13}C$ values (O'Leary, 1981; Farquhar et al., 1989). Lipids, for example, are generally enriched in ^{12}C; the difference between $\delta^{13}C$ values for whole-leaf carbon and lipids may

be as much as 10‰ (O'Leary, 1981). Dissimilarities in the relative proportions of different plant constituents contributing to and/or preserved in sedimentary rocks can also disturb $\delta^{13}C_{org}$ trends (Van Kaam-Peters et al., 1998).

To remove the uncertainty surrounding the end-Permian $\delta^{13}C$ shifts, a record is required that cannot have been produced by diagenetic alteration of carbonates, or variations in the sources of sedimentary organic matter. In this chapter, we demonstrate that the real and profound nature of the end-Permian global $\delta^{13}C$ shift can be verified by comparing shallow-marine $\delta^{13}C_{carb}$ data with compound-specific carbon isotopic signatures of *n*-alkanes ($\delta^{13}C_{alk}$). These *n*-alkanes are the chemical fossils of leaf cuticles from land plants, transported and incorporated into marine sediments. We document concurrent shifts in $\delta^{13}C_{carb}$ and $\delta^{13}C_{alk}$ values from the same samples, confirming that these data represent an approximately synchronous record of the primary chemical changes occurring in the surface ocean, atmosphere, and terrestrial biosphere during the end-Permian ecologic crisis.

CARBON ISOTOPES, KEROGEN, AND MOLECULAR FOSSILS

We established $\delta^{13}C_{carb}$ and $\delta^{13}C_{alk}$ profiles for the latest Permian sedimentary strata at Val Badia (western Dolomites, southern Alps, northeast Italy) (Fig. 1). In this section, close to the boundary between the Bellerophon Formation and the Werfen Formation, the end-Permian ecosystem collapse is evidenced by the last occurrences of a variety of foraminifera and gymnospermous pollen, as well as an abundance of fungal remains (Cirilli et al., 1998). It is now accepted that the first appearance of the conodont *Hindeodus parvus* should mark the onset of the Triassic in the marine realm (Yin et al., 1996). One of the implications of this definition is that the crisis occurs before, rather than at, the biostratigraphically defined Permian-Triassic boundary. In the western Dolomites, the first occurrences of *H. parvus* are in the basal part of the Mazzin Member of the Werfen Formation (Kozur, 1998). Unfortunately, there are no conodont records available for the Val Badia section.

The $\delta^{13}C_{carb}$ profile for Val Badia displays high Late Permian values (SD600 to SD0-6) that are followed by a sharp drop (SD0-6 to SU30) and a subsequent gradual decline into younger samples (SU30 to SU1300). The abrupt onset of the observed trend is common to coeval sections throughout the southern Alps (Magaritz et al., 1988; Holser et al., 1989) and elsewhere.

By applying gas chromatography–isotope ratio mass spectrometry (GC-IRMS) (Hayes et al., 1990; Van Kaam-Peters et al., 1997), the $\delta^{13}C_{alk}$ profile is constructed on the basis of $\delta^{13}C$ values measured for individual *n*-alkanes that are present in fractionated solvent extracts of sedimentary organic matter in the Val Badia section (Fig. 2). In the thermally mature Val Badia sedimentary rocks (mean vitrinite reflectance values 0.62%), long-chain *n*-alkanes are likely to represent the products
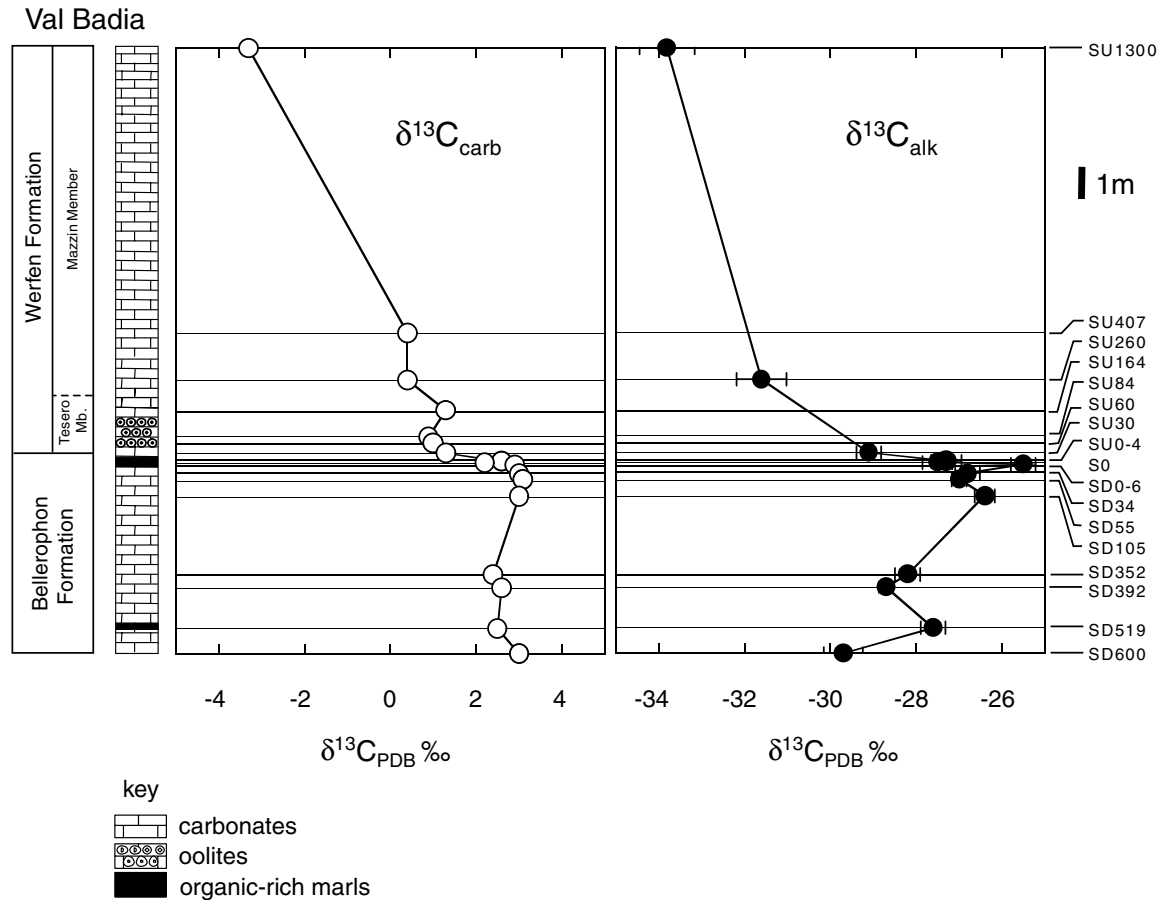
Figure 1. Profiles for $\delta^{13}C_{carb}$ and $\delta^{13}C_{alk}$ obtained from end-Permian sedimentary rocks at Val Badia, western Dolomites, northeastern Italy, illustrating isotopic harmony between these marine and terrestrial carbonaceous materials. For locality, description of lithology, and microfossil content of section, see Cirilli et al. (1998). Sample codes indicate their position (in cm) either above (SU) or below (SD) conspicuous organic-rich marl (S0) situated close to extinction event (Cirilli et al., 1998). Newly defined (conodont based) Permian-Triassic boundary is in basal part of Mazzin Member (see text). $\delta^{13}C_{carb}$ was determined by heating samples under vacuum to 400°C (30 min) before treatment with H_3PO_4 to produce CO_2. CO_2 was introduced into VG SIRA 24 isotope ratio mass spectrometry and ratio of $^{13}C/^{12}C$ measured. $\delta^{13}C_{alk}$ is average of $\delta^{13}C$ values for C_{19} through C_{29} n-alkanes, and was obtained by extracting samples (as in Sephton et al., 1999), and then fractionating extracts (as in Kohnen et al., 1990) to give saturated hydrocarbon fraction. Compound identification was accomplished (as in Sephton et al., 1999), and isotopic measurement of individual n-alkanes was performed (as in Van Kaam-Peters et al., 1997). Each sample was run in triplicate, except for S0, which was run in quadruplicate. Standard deviations (1σ) for data are indicated. All obtained carbon isotope ratios are expressed in usual delta notation relative to international PDB (Peedee belemnite) standard as follows: $\delta^{13}C$ (‰) $= [(^{13}C/^{12}C)_{sample}/(^{13}C/^{12}C)_{PDB} - 1] \times 10^3$. Mb—Member.

of the thermal breakdown of highly aliphatic biopolymers, selectively preserved in kerogen (Tegelaar et al., 1989a). In general, the two principal precursor macromolecules of the *n*-alkanes are cutan, a resistant polymethylenic structure in leaf cuticles (Nip et al., 1986; Tegelaar et al., 1989a, 1989b, 1991), and algaenan, the resistant cell wall material found in a variety of fresh-water and marine algae (Goth et al., 1988; Gelin et al., 1996). The *n*-alkanes from Val Badia display the unimodal distribution patterns characteristic of cutan; a dominance of algaenan would have resulted in a predominantly bimodal distribution.

Palynofacies analysis of the chemically investigated sam-

ples (Fig. 3) confirms earlier observations (Cirilli et al., 1998) that kerogens from the end-Permian sedimentary rocks at Val Badia are overwhelmingly dominated by land-derived material. Structured palynodebris is generally degraded. This category includes mainly tracheal structures, sclerenchymous structures, and cuticular structures reflecting a land plant origin. Although structureless, subordinate opaque palynodebris can also be attributed to land plants (e.g., Cope, 1981). The abundant amorphous organic matter appears to be an end product of the decomposition of the structured palynodebris. Moreover, the amorphous material is nonfluorescent and, because algal organic matter should fluoresce at the measured maturity, a

Figure 2. Gas chromatography traces of saturated hydrocarbon fractions from Val Badia sedimentary rocks. $\delta^{13}C$ values of individual *n*-alkanes are indicated, illustrating isotopic homogeneity within, but significant variation between, samples.
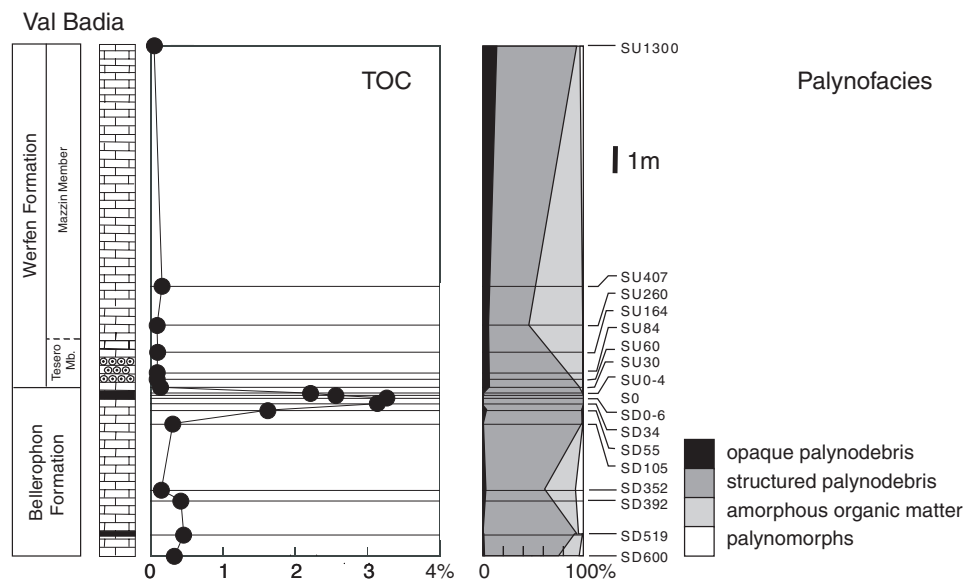
Figure 3. Profiles for percentage of total organic carbon (TOC) (left) and principal palynofacies categories (right), obtained from end-Permian sedimentary rocks at Val Badia, western Dolomites, northeastern Italy. For locality, description of lithology, and microfossil content of section, see Cirilli et al. (1998). Sample codes correspond to those of Figure 1. TOC was determined as dry-weight percentages. Sample preparation for palynofacies took place according to standard procedures of Laboratory of Palaeobotany and Palynology, Utrecht University, including sieving over a 10 μm sieve. Data for palynofacies percentage diagram were obtained by counting at least 200 organic particles per sample. Mb—Member.

marine origin is unlikely. Except for subordinate marine acritarchs in samples from the Mazzin Member, all palynomorphs (pollen, spores, fungal remains) are land derived.

To corroborate the presence of cutan rather than algaenan, we investigated the kerogen samples with flash pyrolysis–gas chromatography (Py-GC) and flash pyrolysis–gas chromatography–mass spectrometry (Py-GC-MS). Two end-member kerogens were detected on the basis of characteristic pyrolysis products; one dominated by aromatic and furan rings (Sephton et al., 1999), the other dominated by long-chain *n*-alk-1-ene/*n*-alkane doublets with a similar distribution pattern, as observed for the extracted *n*-alkanes (Fig. 4A). Comparative analysis of fossil leaf cuticles of *Ortiseia*, a common conifer genus in the Upper Permian of the western Dolomites and other parts of Europe (Poort et al., 1997), confirms that the aliphatic molecules are the pyrolysis products of cutan (Fig. 4B). Subtle variations in the distribution of the pyrolysis products are presumably due to changes in the land plant assemblage, which contributed cuticular material to the sediments.

The homogeneity of the $\delta^{13}C_{alk}$ values makes it possible to construct mean C_{19} to C_{29} *n*-alkane values that accurately represent the carbon isotopic ratios of the aliphatic hydrocarbons in each sample. Throughout the section, the $\delta^{13}C_{alk}$ values appear to be harmonious with the $\delta^{13}C_{carb}$ trend (Fig. 1). Initial high values (SD600 to SD0-6) are followed by a drop (SD0-6 to SU30) and a subsequent gradual decline (SU30 to SU1300).

The concomitant change of $\delta^{13}C_{alk}$ and $\delta^{13}C_{carb}$ to more negative values indicates that the chemical fossils of leaf cuticles from land plants contain an accessible record of the carbon isotopic expression associated with the end-Permian ecologic crisis. This is because the $\delta^{13}C$ signature of fossil land plant material primarily reflects the carbon isotopic composition of atmospheric CO_2. The relatively constant isotopic separation maintained by the $\delta^{13}C_{alk}$ and $\delta^{13}C_{carb}$ values (Fig. 5) corrob-

orates the proposal that a single source of organic matter, i.e., land plants, has contributed to the aliphatic material (cf. Foster et al., 1997). Because secondary diagenetic effects are unlikely to produce isotopic changes in the $\delta^{13}C$ values of two sedimentary carbonaceous phases that agree in both sign and magnitude, the $\delta^{13}C_{alk}$ and $\delta^{13}C_{carb}$ profiles must reflect simultaneous primary disturbances in end-Permian atmospheric and oceanic chemistry.

COUPLING BETWEEN THE CARBON ISOTOPE EVENT AND THE ECOLOGIC CRISIS

The concurrent atmospheric and oceanic decline in $\delta^{13}C$ and its association with biological evidence of the ecosystem collapse at Val Badia support the concept of a causal relationship between the end-Permian ecologic crisis and redistribution of ¹³C-depleted carbon between major carbon reservoirs. Yet, until recently, it was unknown whether ecosystem collapse was a consequence or a cause of changes in global carbon cycling. It is frequently emphasized that the marine extinction is coincident with the carbon isotope event. This observation (e.g., Jin et al., 2000) is likely to be influenced by the condensed nature of many of the carbonate-rich Permian-Triassic transition sections in the Tethys realm, including the boundary stratotype at Meishan, southern China. However, in the greatly expanded siliciclastic Permian-Triassic section of Jameson Land, East Greenland, detailed analysis of the sequence of isotope events and significant quantitative changes in the marine and terrestrial fossil record has now clearly revealed that the marine and terrestrial ecosystem collapse preceded the onset of the negative excursions in the $\delta^{13}C_{carb}$ and $\delta^{13}C_{org}$ record (Looy, 2000; Twitchett et al., 2001). Consequently, the cause of ¹³C depletion cannot be the cause of the ecologic crisis. Scenarios relying on rapid overturn of anoxic deep oceans (Knoll et al., 1996) or

A) Val Badia m/z 55+57
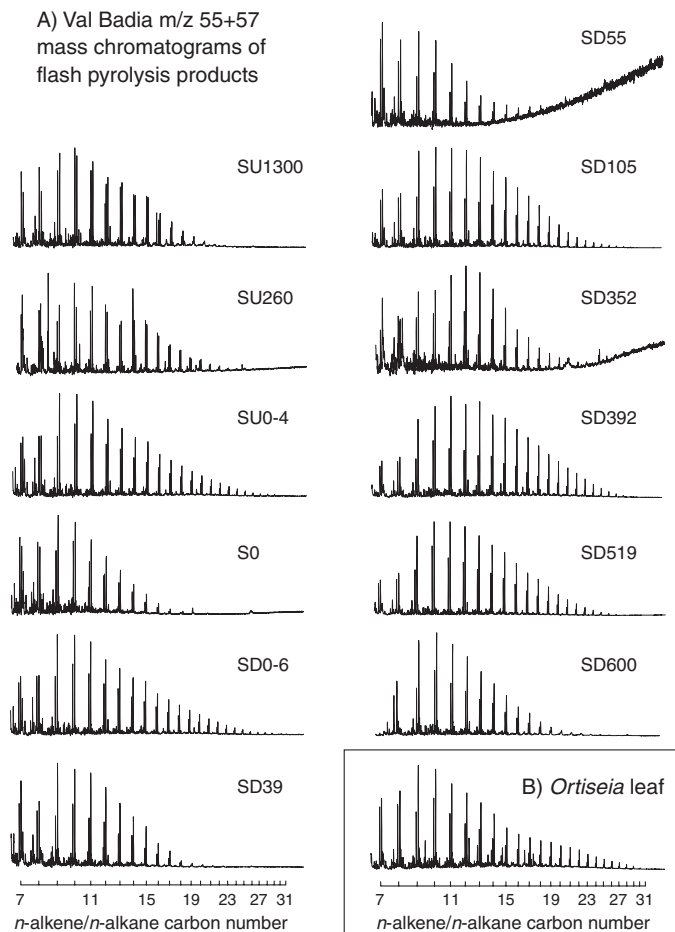mass chromatograms of
flash pyrolysis products

Figure 4. Summed mass chromatograms of mass/charge (m/z) 55 + 57 from Curie point (610°C) flash pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) analyses of (A) kerogens from Val Badia section and (B) isolated leaf of Late Permian conifer genus *Ortiseia*. These mass chromatograms selectively display *n*-alkene and *n*-alkane patterns in pyrolysis products, and comparisons indicate that cutan is dominant aliphatic biopolymer in Val Badia sedimentary rocks. Carbon number retention times of *n*-alkene and *n*-alkane doublets are shown. Py-GC-MS conditions were as in Sephton et al. (1999).

Figure 5. Cross-plots of $\delta^{13}C_{carb}$ and $\delta^{13}C_{alk}$ from Val Badia, northern Italy. Data form single population within which alkanes display relatively constant isotopic relationship with carbonate (x = y − 30.5‰). This correlation indicates that single source of organic matter (i.e., land plants) has contributed to alkane parent material throughout section.

dissociation of oceanic CH_4-hydrate (Erwin, 1993; Morante, 1996) as mechanisms for massive release of light carbon are therefore unsatisfactory.

In order to assess whether specific end-Permian carbon reservoirs could have had the necessary combination of isotopic composition and size to produce the observed perturbations, the release mechanism and origin of the ^{13}C-depleted carbon should be in harmony with both mass-balance and time-frame considerations (Spitzy and Degens, 1985). Following the verification of the primary nature for the initial ~3‰ shift in $\delta^{13}C_{carb}$ observed at Val Badia, this value may be used confidently in quantitative considerations. From estimated sedimentation rates in Greenland, it may be inferred that the initial $\delta^{13}C_{carb}$ decline had a duration of <50 k.y. (Looy, 2000; Twitchett et al., 2001).

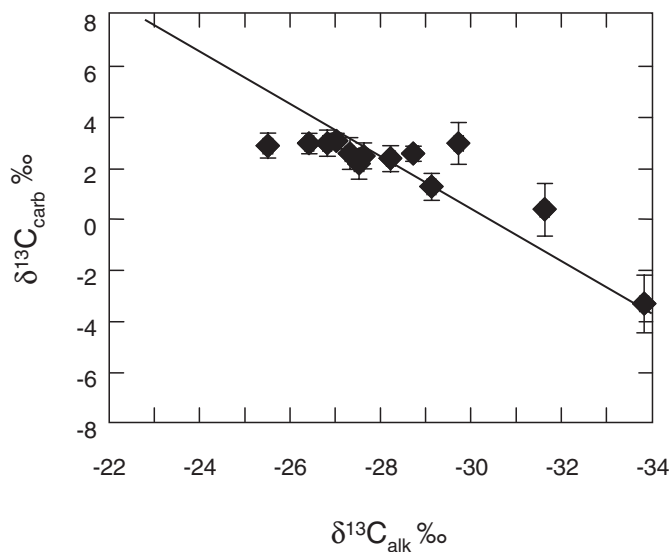Together, these data corroborate the concept that the initial release of ^{13}C-depleted carbon into surficial environments at the end of the Permian was both massive and fast.

Considering the observation that the abrupt initial step of the end-Permian $\delta^{13}C$ excursion follows ecosystem collapse, the global reservoir of soil organic matter with mean $\delta^{13}C$ values of −25‰ may be the only plausible source of ^{13}C-depleted carbon. End-Permian accumulations could have been mobilized as extensive soil erosion followed the massive die-back of woody vegetation that characterized end-Permian ecosystem collapse on land (Visscher et al., 1996; Retallack, 1999; Ward et al., 2000). In the Val Badia section, evidence for increased soil erosion is provided by an elevated total organic carbon content, in combination with the land plant origin of palynodebris categories in the microscopic organic matter assemblage (Fig. 3). The heavily degraded nature of this buried plant debris indicates decomposition on land prior to transport into the marine depositional environment. Because rootlets deteriorating in soils are known to become inertinized and structureless (Cope, 1981), this may also apply to the opaque palynodebris. From a biogeochemical point of view, the unusually high abundance of cyclic diaryl ethers, such as dibenzofuran and its alkyl derivatives, in the Val Badia kerogen could well reflect the rapid redeposition of soil organic matter (Sephton et al., 1999).

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