Stable isotopes of carbon from basaltic rocks and their possible relation to atmospheric isotope excursions

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Abstract

Repeated short-time negative excursions from the general trend of organic carbon isotopes occur at, and shortly after, the Permo-Triassic and Cretaceous–Tertiary mass extinctions. The cause of these excursions is unexplained since an extinction event can only explain one excursion at each boundary. At the P/T boundary one negative excursion occurs shortly before the boundary proper followed by one at the boundary, followed by several excursions that can be correlated in both marine and terrestrial environments over larger geographical distances. Also at the K/T boundary negative excursions in organic carbon, which can be correlated, occur after the boundary in both marine and terrestrial settings.

As both mass extinctions occurred contemporaneously with major continental flood basalts, the present study focuses on the possible effect of eruption of flood basalts on the atmospheric carbon isotopic budget. The carbon isotopic compositions of forty different basalts, from the time span of Albian to the Recent, and predominantly continental flood, were measured.

The isotopic composition of the CO_2 gas released by basalts is generally accepted as being rather heavy (−5‰ PDB) based on observations from Hawaii. This is in strong contrast to the observed values in this study, which showed that the gas released had an average isotopic value of around −23‰ PDB. Acid digestion by HF left a residue of elemental carbon with isotopic values in the range of −24 to almost −28‰ PDB. This corresponds to the carbon released during stepped heating experiments in the temperature range from 200 to 600 °C. Since basalt in a molten state has a temperature of >600 °C and since the most negative carbon (i.e. the elemental carbon) is released below that temperature, it suggests that the most isotopically negative component is not present as elemental carbon above temperatures of 600 °C. In view of the recorded isotopic composition of −24‰ for gas collected at a temperature between 700 and 800 °C from Mauna Loa, it seems that the generally assumed −5‰ is unrepresentative for flood basalts. It is therefore possible that high intensity volcanic episodes have caused the repeated negative excursions. It is further suggested that the short-time non-secular isotopic variation pattern of organic carbon through time may be a record of volcanic activity. The episodic nature of volcanism precludes it from being causally related to the secular variations.

Elemental carbon from four different kimberlites yielded carbon isotopic values similar to those from basalts. It is suggested that the Boudouard reaction ($2CO = C + CO_2$) may be responsible for the formation of the elemental carbon.

1. Introduction

Across the two largest mass extinctions in earth history (the Permo-Triassic and Cretaceous–Tertiary) various authors have reported excursions (departures of

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values from the average trend) in carbon isotopes (e.g. Baud et al., 1989; Margaritz et al., 1992; Hansen et al., 1996, 1999, 2000; Wit et al., 2002; Tong et al., 2003; Payne et al., 2004). The isotopic excursions were registered either in carbonate material or in non-carbonate carbon ("organic carbon") or both.

This paper reports measurements of the isotopic composition of carbon from a variety of basalts, finding much greater negative values than hitherto accepted. In the light of these findings, it advocates the possibility that negative carbon isotopic excursions of short duration are caused by emanation of isotopically light CO_2 from continental flood basalts that were active at both mass extinctions.

2. Geological background

Some studies of stratigraphic carbon isotopic fluctuations make no distinction between excursions of short duration as opposed to long time phenomena. The longer term excursions, such as the gradual fall during the Miocene and Pliocene (e.g. Zachos et al., 2001) were designated secular variations by Veizer et al. (1980). In addition, other and much shorter variations were reported. The latter may be of a duration of only 10,000–20,000 years (Hansen et al., 2000) and are thereby fundamentally different from the secular varia-
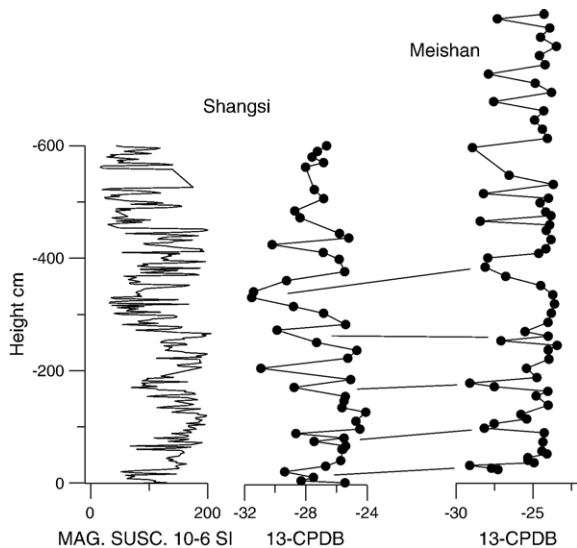

Fig. 2. Organic $\delta^{13}C$ along with variation pattern of magnetic susceptibility from the Permo-Triassic boundary at Jimsar, Xinjiang Province, NW China, along with $\delta^{13}C$ from the corresponding interval at Nelben, Germany. Two lines of suggested correlation between negative $\delta^{13}C$ excursions are shown. The lower excursion takes place in Upper Permian time, while the second excursion is at the Permo-Triassic boundary. Jimsar data from Hansen et al. (2000). Original data from Nelben.

tions. Tong et al.'s (2003) record of carbonate carbon isotopes from Chaohu show two secular patterns (a long-lasting, negative deviation through the Lower Olenegian followed by an equally long positive deviation), where the two together cover the lower half of the Olenegian. This stands in contrast to the very short negative excursion at the Permo-Triassic boundary. The marine Lower Triassic from Shangsi and Meishan show a series of short negative excursions in organic carbon that are different from the secular variations (Fig. 1). Short-time excursions are likewise found across the Permo-Triassic boundary in terrestrial sediments at Nelben, Germany, and Jimsar, NW China (Fig. 2). At the marine Cretaceous–Tertiary boundary at El Kef, Tunisia, and in terrestrial deposits at North Horn, UT, USA, a series of short-time excursions are present (Fig. 3). Many of the excursions can be correlated over large geographical distances. The present paper is related to the short-time excursions and not to the longer secular variations.

A common suggestion of the cause for a negative carbon isotopic excursion at the K/T extinction level is the collapse of the marine ecosystem or in other words a major extinction event (Hsü and McKenzie, 1985). This explanation relates to the fact that death of the planktonic part of the ecosystem will leave behind

Fig. 1. Variation pattern of magnetic susceptibility along with fluctuations in $\delta^{13}C$ in marine lowermost Triassic sediments from Shangsi, W China along with $\delta^{13}C$ from the corresponding interval at Meishan, SE China. The lines are suggested correlation of negative excursions. The pattern of magnetic susceptibility allows estimates of the duration of the excursions following the interpretation in Hansen et al. (2000). Data from Hansen et al. (2000).
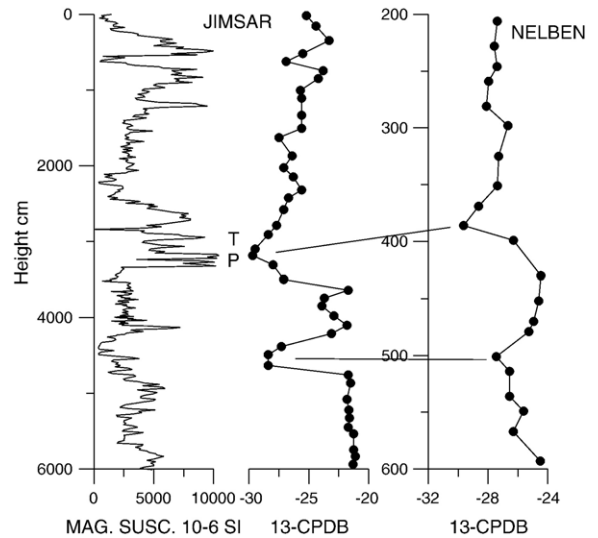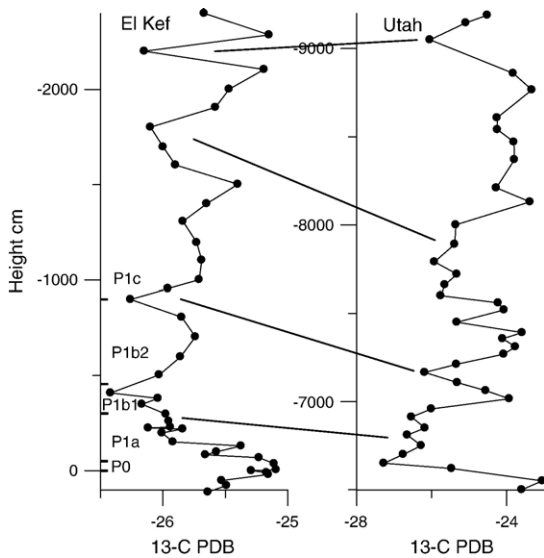
Fig. 3. Organic δ^{13}C across the Cretaceous–Tertiary boundary from marine sediments at El Kef, Tunisia, and terrestrial deposits of North Horn Formation, UT, USA. P0, P1a, etc., are planktonic foraminiferal biozones from Keller (1988). The four lines represent suggested correlation between negative excursions.

raised amounts of ^{12}C in the upper water mass from the decay of organic material as well as cessation of the CO_2 pump (i.e. the carbonate secreting planktonic organisms) which continuously transports $CaCO_3$ to the sea floor. The raised amount of ^{12}C causes a depression of the relative amount of ^{13}C resulting in a negative carbon excursion. Per se, this explanation is sound and reasonable. The disappearance of the carbonate-producing organisms can be observed in the sediments and should be coincident in time with the negative carbon isotopic excursion. When, however, more than one isotopic excursion is found one may ask the rhetoric question: How many times within a shorter period of geologic time can we expect mass-extinctions without a corresponding paleontological signature in the sediments? However, repeated negative excursions over relatively short geological time intervals must be coincident with extinctions that can be observed in the sediments or this explanation cannot be true. It may be added that Hansen et al. (1986) found that the negative excursion in organic carbon (dinocyst skeletons) at the K/T boundary at the locality Nye Kløv in Jylland, Denmark, occurred 15 cm earlier than the disappearance level of coccoliths. This observation leaves some doubt as to the validity of the Hsü and McKenzie scenario (Hansen et al., 1986).

Wit et al. (2002) suggested release of methane gas-hydrates as the cause of repeated isotopic excursions across the Permian–Triassic boundary. This explanation

calls for repeated heating of the colder regions of the globe in order to release the methane, although it could also be related to regressions reducing the pressures in shallow shelf seas. The isotopic composition of the methane is negative in the range of −57‰ to −73‰ (Kvenvolden, 1995). It is, however, a precondition that ocean temperatures were cold enough to allow formation of gas-hydrates in relatively shallow water in sufficient amounts (see discussion in Payne et al., 2004; Grard et al., 2005).

The stratigraphy in the work by Payne et al. is based on conodonts from a section which is at the edge of a Permo-Triassic platform complex in SW China. Here, an Upper Permian conodont is present, while the *H. parvus* (marker of the P/T boundary) occurs 40–50 meters higher. At Meishan (the P/T boundary stratotype section in SE China) the negative organic carbon isotopic excursion starts before the P/T boundary level (Hansen et al., 2000; Fig. 12) and does not even reach into bed 27 (the boundary bed). The negative excursion covers around 185 cm. The corresponding negative excursion interval in Payne et al. has a thickness of 21.5 m at Dajiang and 26 m at Dawen. If Payne et al. are correct in their identification of the negative excursion as representing the Permo-Triassic boundary, the accumulation rate must have been enormous even relative to the terrestrial section at Jimsar (NW China) and Nelben, Germany (see Fig. 2). Payne et al. are referring to work by Tong Jinnan et al. (2003) who showed carbonate carbon isotopes from the Chaohu section, which showed a negative excursion of 1–1.5 m across the P/T boundary. At Chaohu the organic carbon negative excursion starts before the P/T and lasts for about one meter (Fig. 4). As the biostratigraphical constraints are rather poor in the lower part of Payne et
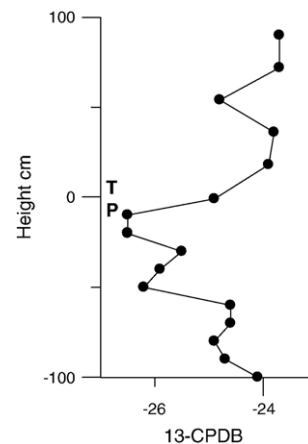

Fig. 4. Variation of organic δ^{13}C versus dept across the Permo-Triassic boundary at Chaohu, Anhui Province, SE China.

al.'s sections and the ubiquitous bentonites and black collapse-layer have not been reported, it is an obvious possibility that the two sections in question are incomplete with respect to the Permo-Triassic boundary. As both negative long-time excursions occur in sediments described as thrombolites, one suspects that the negative excursion could be caused by microbial activity associated with the formation of thrombolites.

The repeated nature of the negative short time excursions calls for a mechanism that episodically releases large amounts of light carbon to the atmosphere. Such a phenomenon could well be volcanism. However, textbooks on stable isotopes (Hoefs, 1973; Faure, 1977) preclude this, since it appears to be accepted generally, that basalts release carbon with an isotopic composition around −5‰ PDB (e.g. Erwin, 1993; Grard et al., 2005). Such carbon is isotopically much too heavy to cause negative excursions.

The general acceptance of the heavy value is based on observations from Hawaii. However, an earlier observation reports an isotopic composition of −24± 2‰ of the CO_2 released by the eruption of Mauna Loa in 1950 (Naughton and Terada, 1954; Friedman et al., 1987). Studies of carbon stable-isotopes of gas from geothermal springs in the Central Andes and northern Chile and Bolivia demonstrated a much wider range of values of total carbon between −20.9‰ and −0.6‰ (Spiro et al., 1997) as opposed to the values from Kilauean fumaroles that are rather stable around −3‰ (Friedman et al., 1987). It poses the question whether the observations from Kilauea are representative for large basalt eruptions.

The present study presents the results of an investigation of the trapped carbon components, mainly from continental flood basalts, in order to elucidate the question of the isotopic composition of the carbon gasses released during eruption of basaltic magmas.

3. Materials and methods

Samples from continental flood basalt provinces such as Kerguelen, Deccan Traps, East Greenland and the Faeroes were available for study. These samples were supplemented by a series of basalts from Denmark, Iceland, France, Germany, Azores, Hawaii, Arizona, and, in addition, samples of kimberlites from Norilsk (Russia), Kimberley (South Africa), Godthåbs-fiord (West Greenland) and Panna (India).

The samples were crushed to a grain size smaller than 200 μm using an agate mortar to avoid contamination. A few grams of the crushed sample were placed in a Pt-boat and after evacuation heated to 1050 °C in an
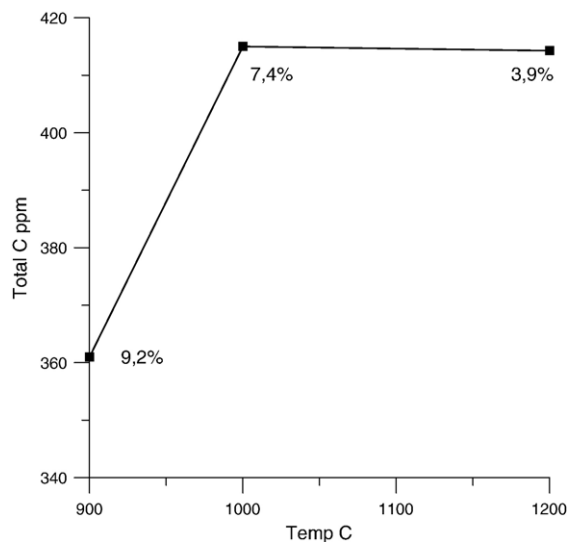

Fig. 5. Plot of carbon yield against temperature in a powdered sample of Deccan tholeiitic basalt (Rajamundry, Khateru, India, flow 3). Each point is based on 10 determinations. Process time: 4 min. The numbers next to the data points register the coefficient of variation of the sample population.

oxygen flow with He as carrier gas. The resulting CO_2 was collected and measured in a Finnigan MAT 251 stable-isotope mass spectrometer with a precision of ±0.04‰. Total carbon was measured in an Eltra Metalyt total C/S analyser at a combustion temperature of 1200 °C. Experiments showed that the carbon yield in the latter equipment did not show significant differences in the temperature range from 1000 to 1200 °C for a heating period of 4 min (Fig. 5). Javoy et al. (1978) found that 1000 °C is sufficient to extract essentially all carbon from a basaltic sample.

In a series of experiments, sub-samples were digested by HF–HCl and the residual carbon was concentrated and pipetted into small Al-jars that were placed in a Pt-boat. They were treated like the samples for total carbon isotopic measurement as described above.

In three cases, the amounts of elemental carbon left after acid digestion were quantitatively estimated by utilizing the yield of the mass-spectrometer calibrated against aliquots of a quantitative standard. The values are probably slightly too low, since it was difficult to avoid adsorption of elemental carbon to the walls of the Teflon containers used for HF digestion of samples.

4. Results

The results for amounts of total carbon, for isotopic composition of bulk (total) carbon and elemental

Table 1
Results of determination of bulk carbon content, bulk carbon isotope composition and isotopic composition of residual carbon after acid digestion

| Sample graphite	Total C (ppm)	$\delta^{13}C_{total}$ (‰ PDB)	$\delta^{13}C$ (‰ PDB)
Girad F4-1 India	593	−19.4	−26.61
Girad F4-2	375	−18.71	−26.77
Girad F4-3	277	−20.22	
Girad F4−4	57	−24.65	
Girad F3-1	299	−24.01	
Girad F3-2	164	−22.4	
Girad F3-3	128	−18.75	
Bergi	227	−22.8	
Ampara-1, Bihar	432	−22.91	−24.79
Rajmahal-2	478		
Anjar-top-5, Gujarat	472	−21.55	
Kholdoda	452	−24.07	
Katheru, Rajamundry	320	−15.49	
Katheru-2	332	−19.05	−25.6
Katheru-3	255	−22.54	
Katheru-4	185	−20.4	
Mo-Clay +28, Denmark	400		−27.21
Mo-Clay +30			−26.18
Faeroes-15	601	−27.13	
Faeroes-10	275	−27.3	
Faeroes-8	1400	−16.29	−25.5
Faeroes-4	367	−26.2	
Faeroes-1	1211	−20.04	
Santa Fe Pit, AZ, USA			−22.25
Stockum, Germany	269	−21.15	
Le Broc, Massif Centrale, France	372	−24.03	
Iceland-29	131	−25.57	
do-30	155	−24.13	−26.35
do-31	116	−25.61	
do-32	55	−24.68	
do-33	121	−24.69	
do-34	152	−25.68	
do-35	119	−25.66	
do-36	91	−27.11	
do-37	247	−21	
GGU 69521 Helgenæs, East Greenland	538	−22.99	
GGU 215713 Pyramiden, Sect. 117	260	−19.56	
do 215705	302	−25.01	
GGU 215653 Steno Glacier	308	−25.45	
do 215659	462	−25.71	
Kimberlite, Kimberley, S. Africa			−25.32
Kimberlite, Panna, India	6817		−27.45
Kimberlite, Sdr-Strømfjord, West Greenland	18 269		−26.29
Hekla, Island 1991			−27.86
MORB. Kolbeinsey, GM. 26-001			−26.19
San Miguel, Azores			−25.91
Terciera, Azores			−22.05
Mauna Ulu, HI, USA			−23.08
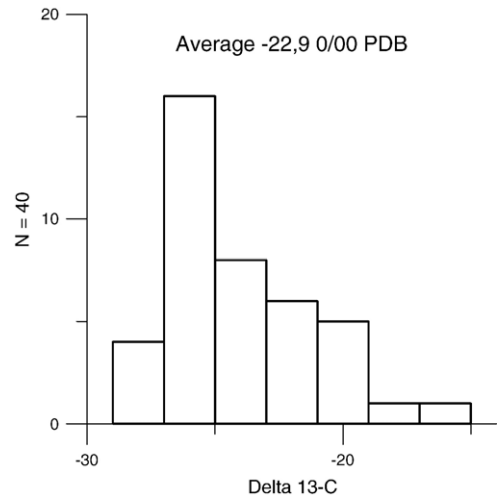
Fig. 6. Carbon isotope composition from bulk determinations of basalts listed in Table 1.

carbon isolated through acid digestion are recorded in Table 1. Details of the samples are presented in Appendix A. The isotopic values for total carbon (bulk) range from −14‰ to −26‰ PDB. The main part of the values falls in the interval from −22‰ to −26‰ and the average of all samples is −22.9‰ PDB (Fig. 6). In three examples, the amount of elemental carbon was quantified, and correction of the isotopic value of total carbon thereby became heavier by 0.7‰, 0.9‰ and 2.2‰, respectively.

All isotopic compositions of elemental carbon after acid digestion fall within the range of −24.1‰ to −27.8‰ $\delta^{13}C$ PDB irrespective of the origin. Kimberlites or basalts (Fig. 7) give essentially the same results.
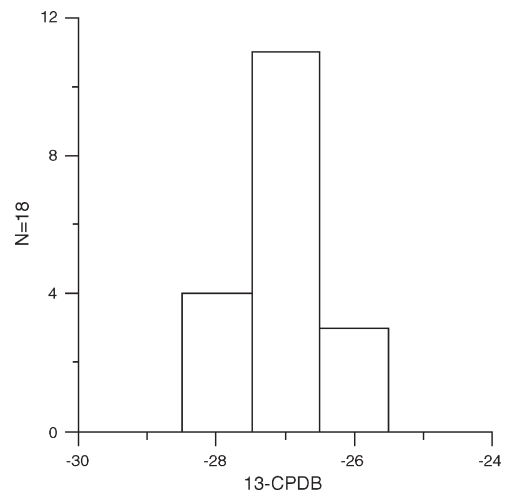

Fig. 7. Isotopic composition of carbon residues after digestion by HF and HCl.

5. Discussion

According to Hoefs (1973) the isotopic compositions of carbon compounds in nature fall into several categories.

(1) the most negative exist in methane and methane-related compounds
(2) the next less negative values are found in elemental carbon
(3) still less negative are CO and CO_2 compounds
(4) the most positive values are found in carbonates.

Fuex and Baker (1973) made a pioneering investigation of carbon isotopes from a variety of igneous rock types. They distinguished between carbonate and non-carbonate carbon. These authors found non-carbonate isotopic composition of mafic and ultramafic rocks from −22.2‰ to −27.1‰. Studies by other authors (data in Kyser, 1986) were conducted on submarine basalt from Loihi Seamount, Hawaii. Isotopic values of total carbon after bulk fusion were in the same range (Fig. 8).

Gerlach and Graeber (1985), Gerlach (1986) and Gerlach and Taylor (1990) divided eruptive activity of Kilauea, Hawaii, into types I and II. These authors pointed out, that apparently the magma chamber under Kilauea giving rise to type II (as registered in e.g. fumaroles) is isotopically fractionated and the magma chamber rarely receives "fresh supplies" from below. Therefore, the carbon isotopic values reported could well be fractionated resulting in the loss of the lighter isotope and thereby unrepresentative for rapidly erupt-
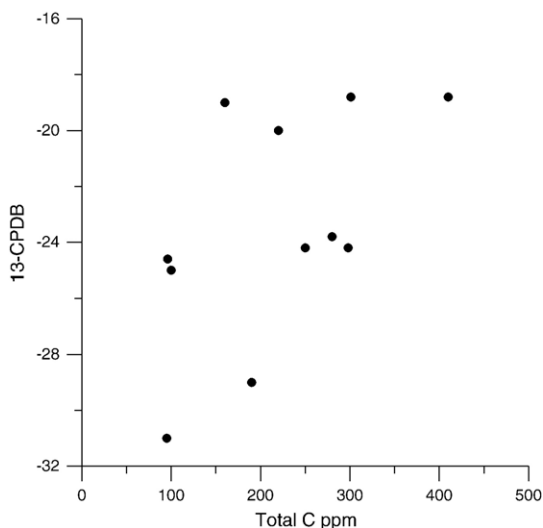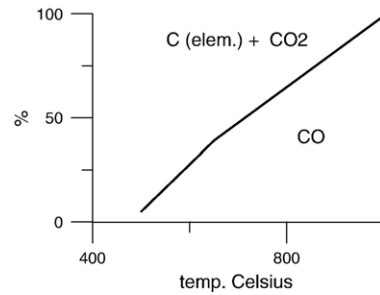

Fig. 9. The Boudouard reaction at 1 atm.

ing flood basalts. The fumaroles from Kilauea seem to vary slightly through time with values around −3‰ (Friedman et al., 1987). Type I degassing, by contrast, has a more direct and less fractionated eruptional history resulting in isotopic composition of the CO_2 gas around −24‰ ±2‰ (Naughton and Terada, 1954; Friedman et al., 1987).

Today the eruption temperature of basalt is around 1100–1200 °C. The solidifying temperature (*solidus*) is around 200 °C lower (Schmincke, 2004). When the basaltic magma after eruption passes the temperature interval from 1000 to 600 °C (or lower), the Boudouard process takes place. At 1000 °C and 1 atm pressure, carbon gas is present as CO only (Boudouard, 1901; Jensen, 1965, p. 394). With falling temperature, the CO splits into elemental carbon and CO_2 (Fig. 9). The carbon is left in the rock as either small flakes or aggregates of beta-graphite, or as coating of the walls of vesicles. Thus, it leads to formation of hollow graphite spheres of poor crystallinity (Figs. 10 and 11). Mathez and Delaney (1981) discussed in detail the process and

Fig. 8. Carbon isotopes determined from bulk fusion of tholeiites and alkali basalts from Loihi seamount, Hawaii. Data from Kyser (1986).
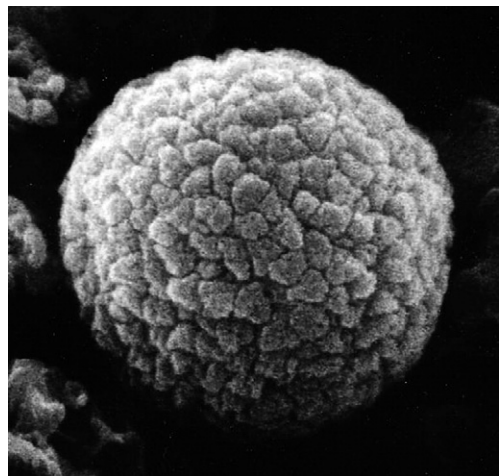

Fig. 10. Poorly crystallized elemental carbon left after HF digestion of basaltic ash bed +28, Eocene, Denmark. Diameter of the spherule = 5 μm.
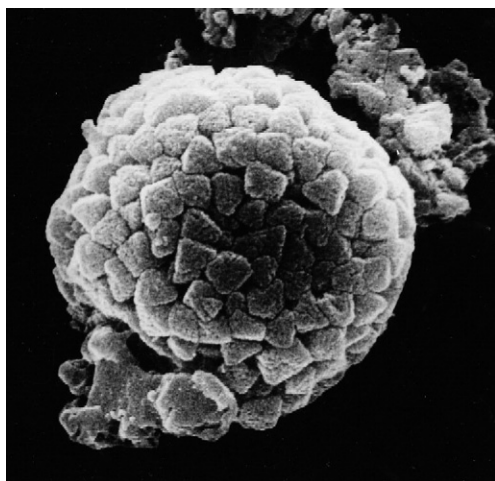
Fig. 11. Hollow, elemental carbon spheres from basaltic ash bed +30, Eocene, Denmark. Diameter of spherule = 7 μm.

its relevance for the formation of elemental carbon in submarine basalts.

The Boudouard process is also active in recent volcanic activity as documented by the Hekla eruption, Iceland, January 1991 (Hansen, 1994). At that occasion, Hekla had a small eruption. Iceland was covered by snow and it was further snowing during the eruption. Thus, a complete ash layer snowed down and was left sandwiched in the snow. An aliquot was treated by ultrasonic vibrations, and the light fraction was concentrated and finally treated with HF followed by HCl. The resultant carbon particles have a grain size of 100–200 nm (Fig. 12).

The carbon left in the basalts is that which just did not escape to the atmosphere. Degassing takes place until solidification, but the major part of the gas escapes right at the extrusion moment (Sigvaldason, 1974).

In the three cases where isotopic corrections were made for the quantified elemental carbon it leads to small changes in the isotopic composition of total carbon in the analyzed rocks. Fuex and Baker (1973) analysed carbonate from a series of mafic rocks and obtained rather heavy isotopic values (2.9‰ to −10.3‰). In the present case, no correction was made for a possible carbonate component, and a correction would lead to even more negative values for total carbon. However, in order to minimize the amount of secondary carbonate, the vesicle-rich upper parts of the basaltic flows were generally avoided.

The result of the bulk determination of carbon isotopes of 40 different samples from flood basalts and volcanic plugs resulting in an average value of −23‰ PDB indicates that the widely accepted value for magmatic carbon of around −5‰ PDB may not be correct. The latter value is based on determination of CO_2 in vesicles where the elemental carbon was left out of consideration. The latter is released during heating to 600 °C and therefore will not be present as elemental carbon at temperatures higher than 600 °C in a basaltic flow. It further follows that the elemental carbon is precipitated in the rock in the low temperature range.

It is further noteworthy, that bulk isotopic composition found in the volcanic plugs are not different from those of flood basalts. The presence of hollow elemental carbon spheres in the acid residues proves that carbon precipitation took place after the formation of the gas vesicles. The carbon spheres are delicate, hollow structures which do not withstand mechanical deformation. Their perfect preservation indicates that the elemental carbon formed later than the molds (i.e. the gas vesicles). Thus, the carbon isotopic value is that at the temperature when the magma had not yet solidified. In consequence, the bulk determinations of carbon isotopic composition show the value of the gas which just did not escape.

The early determinations of carbon isotopic compositions in submarine basalts (Mattey et al., 1984) were suspected of being influenced by surface contamination with kerogeneous matter causing the negative isotopic values of carbon released at low temperature. This can safely be ruled out for subaereal basalts which yield similar negative isotopic values.

Perhaps fractionation leading to enrichment of ^{12}C in the elemental carbon accounts for the differences between the bulk composition and that of the graphite in the vesicles. However, we do not have the entire story,
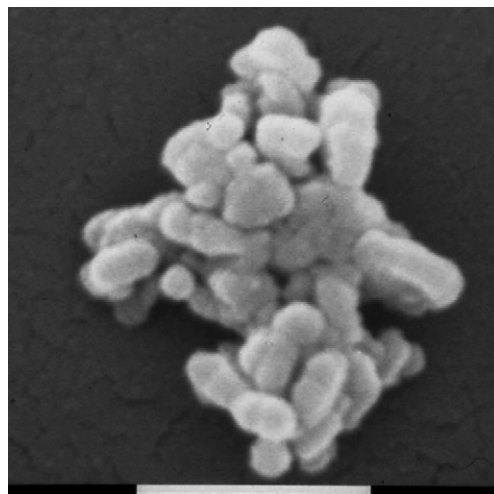

Fig. 12. Elemental carbon particles from the Hekla eruption, 1991. Scale bar = 1 μm.

as apart from the elemental carbon and gas in the vesicles, there may also be one or more components in the form of dissolved carbon in the minerals (or glass). The present study does not have enough determinations of the amount of elemental carbon to allow an evaluation of the possible dissolved carbon isotopic composition as only three samples were studied quantitatively with respect to the elemental carbon. Furthermore, the wet chemical procedures used in the present study leave some doubt as to the accuracy of the determinations, which probably yield low values. Therefore, the question as to the isotopic composition of a third component has to be left open.

In the case of the subaereal basalts, the Boudouard process most likely caused the precipitation of the elemental carbon, and it may further be concluded that the process leads to fractionation causing the depleted carbon and leaving the gas phase enriched in heavy carbon.

Horita (2005) reviewed different experiments related to early atmospheric composition among others the formation of carbonaceous deposits and the fractionation of carbon isotopes relevant for the processes at mantle and crust conditions. However, the results of the studies are not conclusive. In contrast, Javoy et al. (1978) reported experimental evidence for fractionation between CO_2 and carbon dissolved in basaltic magma. These authors found a fractionation ranging from 4.0‰ to 4.6‰ in favor of CO_2.

5.1. The repeated negative excursions

Since the K/T boundary occurs 185 Ma later than the P/T boundary, the preservation of rocks and fossils is generally better at the former. Furthermore, the younger boundary has a biological system which is more easily compared to the recent one than that of the older boundary. For instance, at the older boundary, planktonic foraminifera and coccolithophoriids were not present and the calcareous planktonic system around the P/T boundary is not well understood. For these reasons, we focus here primarily on the K/T boundary.

Two questions need to be addressed: what was the isotopic composition of atmospheric CO_2 in uppermost Cretaceous time and what was the concentration of CO_2?

Both questions can be answered with some degree of certainty. The isotopic composition of plant material (i.e. soot and charcoal) in uppermost Cretaceous time (where only fractionation by the C3 photosynthetic process needs to be considered) suggests that the isotopic composition of the atmospheric CO_2 carbon

was around −3‰ PDB as seen in a long series of analysis from, for instance, terrestrial sequences in Utah (Hansen et al., 1996). The fractionation by the C3 process is −20‰ or more (Raven, 1998).

The second question is harder to answer. However, the marine paleo-temperatures as determined from oxygen isotopes in aragonitic fossils from central west Greenland (Buchardt and Weiner, 1981) show that ocean water was at around 16 °C in Upper Maastrichtian time at a paleo-latitude of 62°N. In order to explain these high ocean temperatures much higher concentrations of atmospheric CO_2 than today are required since there is no evidence that solar radiation was higher at that time.

It has been found that coccoliths and foraminifera experience difficulties in maintaining their carbonate skeletal parts at pH 7.5 (McLean, 1985a,b; Riebesell et al., 2000; Geisen et al., 2004). The atmospheric system rapidly adjusts to injections of carbon, while the ocean is a large and sluggish system where only the uppermost mixed part adjusts fairly rapidly to atmospheric conditions through mechanical mixing. This zone extends to a maximum depth of 50 m (generally the deepest wave-base). It again implies that only organisms residing in the mixed part of the ocean are rapidly affected when the atmosphere changes. It means that marine animals with carbonate larval shells that spend their early life in the high productivity shallow part of the ocean are those that primarily go extinct in addition to the carbonate-secreting plankton.

The pH of the oceans decreases with increasing atmospheric CO_2 as shown in Fig. 13 (D. Dyrssen, personal communication, 1985). From this model, it appears that, at an atmospheric CO_2 concentration of 1745 ppm, the top of the ocean will reach a pH of 7.5. This is in good agreement with the value reported in Royal Society (2005, p. 13). At this pH, the carbonate pump that predominantly consists of coccoliths and
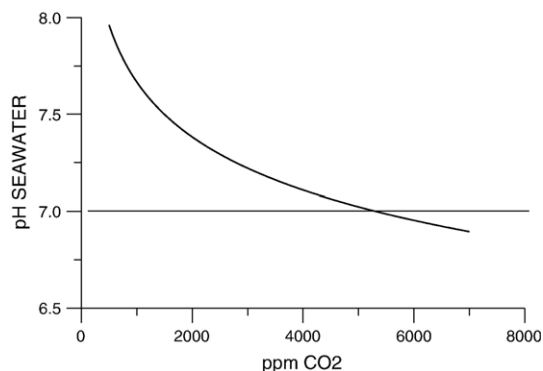
Fig. 13. Relationship between atmospheric pCO_2 and pH in top ocean water at 20 °C (Dyrssen, personal communication).

foraminifera cease their carbon uptake and thereby starts a CO_2 avalanche (i.e. stop their removal of CO_2 from the oceanic mixed layer). Therefore, a threshold value of 1745 ppm exists, which, when exceeded, causes the biological system to collapse. This situation was visualized by Hansen (1990) as an "upside down CCD (calcite compensation depth)", which led to precipitation of carbonate in the uppermost part of the ocean.

Could such a collapse be attributed to the degassing of continental flood basalts? The two largest reported continental flood basalt provinces are the Deccan Traps and the Siberian Traps (Mahoney and Coffin, 1997; Reichow et al., 2002). The latter surpasses a volume of 3 million km^3 while the former is about half the volume of the Siberian Traps. Within the accuracy of radiometric dating (Vandamme et al., 1991; Mundil et al., 2001) these volcanic events are apparently simultaneous with the two largest mass-extinctions in earth's history. This may be coincidental, but the present author thinks that this is very unlikely.

In order to model the possibility of flood basalt CO_2 degassing causing both a 4‰ negative isotopic anomaly and an oceanic collapse with an atmospheric CO_2 concentration of 1745 ppm, it is necessary to consider the calculations by Leavitt (1982).

Leavitt's formula for volcanic degassing is

$$mCO_2 = \frac{sdgvd}{mwCO_2}$$

mCO_2	is the number of moles of CO_2 released
s	is the weight fraction of CO_2 in the magma
dg	is degassing fraction during eruption
v	is the volume of erupted material
d	is the density of the erupted material
$mwCO_2$	is the molecular weight of CO_2 (=44).

In Leavitt's formula there are two variables: The degassing fraction and the weight fraction of CO_2. McLean (1985a,b) and Caldeira and Rampino (1990) accepted a value of 0.6 for the degassing following Sigvaldason (1974). The weight fraction of CO_2 was fixed at 0.5% by McLean (1985a,b) while Caldeira and Rampino used the original 0.2% estimate by Leavitt. Schmincke (2004) mentions up to 0.7 but warns that it is impossible to give a reliable estimate for the CO_2 contents for different magmas and that CO_2 may be transported as free gas in addition to that in the magma. In the present case the weight fraction is assumed to be 0.5% and the degassing fraction 0.6.

Prior to the K/T boundary the CO_2 is already high, but still not at a level where the top of the ocean reaches

a pH of 7.5. The collapse takes place at an atmospheric concentration of 1745 ppm CO_2 which corresponds to 2.8×10^{17} mol CO_2. The resulting isotopic composition is −7‰ PDB (i.e. a 4‰ negative carbon isotopic excursion imposed on the background value of −3‰ PDB) where

x	the number of moles of CO_2 with −3‰ prior to the collapse.
y	the number of moles of CO_2 with −23‰ needed to cause a negative excursion of 4‰ and reaching an atmospheric concentration of 2.8×10^{17} mol.

This leads to

$$x(-3) + y(-23) = (x + y)(-7)$$

From Dyrssen we read that $x+y$ is 2.8×10^{17} mol $CO_2 \sim 1745$ ppm.

From standard mathematical manipulation we arrive at:

$$x = 2.2 \times 10^{17}$$

$$y = 5.6 \times 10^{16}$$

In other words: if the Upper Cretaceous atmospheric concentration of CO_2 prior to the K/T boundary anomaly (following this model) was 1380 ppm then the required volume of basalt degassed would be 18.6% of an assumed Deccan Traps total volume of 1.5×10^6 km^3. If the degassing fraction were higher than 0.6 and the weight fraction of CO_2 is higher than 0.5%, the required volume would be correspondingly smaller and the same applies if the negative excursion is smaller than 4‰.

Observations in the Deccan Traps volcanic field through many years by the present author have demonstrated, that many of the volcanic flows are thick (>30 m) and are single flow sheets with an apparent continuous occurrence for 100 km or more (Hansen et al., 2005). The erupted magma apparently was of very low viscosity and the production rate must have been very high. One of the effects of short time, high eruptional activity could well be occurrences of negative, atmospheric carbon isotopic excursions of short duration with clear isotopic effects on the terrestrial system and in the mixed upper oceanic layer.

It is here suggested that episodic activity of continental flood basalts may cause short time changes in the atmospheric carbon isotopic composition rapidly affecting plant life and resulting in the observed

negative organic carbon isotopic excursions of short duration.

This paper deals only with the aspects of atmospheric carbon and rapidly adjusting shallow oceanic conditions. The main oceanic reservoir is much too large to be seriously affected and will not react to minor light isotope injections into the atmosphere from continental flood basalts unless the threshold value of pH for calcareous plankton is affected. The secular variations in carbon isotopic composition with durations of millions of years (both positive and negative) are not relevant in the context of the present paper.

Appendix A

The samples from the Faeroe Islands were collected by Jensen (1978, 1979), from the lower basalt series at Suderø. They stem from the second uppermost flow in the lower basalt series and represent five different levels across the 12.5-m-thick flow. The age is around the Paleocene–Eocene transition.

Eleven samples from a drill core in a sub-fossil basalt flow were kindly placed at my disposal by Dr. S. Jakobsson, Icelandic Museum of Natural History, Iceland. The samples carry the registration numbers 21428–21438 and originate from a drill core through the Thjorsa lava. It is a tholeiitic, plagioclase–porphyric basalt. The age is Postglacial (around 8000 years). The 11 samples cover an interval of 29 m.

Five samples from the East Greenland Eocene basalt province were placed at my disposal by the Geological Survey of Greenland. The samples were collected by Dr. S. Watt and carry the registration numbers GGU 96521 (Helgenæs), 215705 and 215713 (both from Pyramiden), 215653 and 215659 from the Steno Glacier section. The samples are tholeiitic basalts and are described in Larsen et al. (1989).

Samples from the Kerguelen basalt province of Albian age were collected in the province of Bihar, India. One sample is from 3 km south of Ampara; five additional samples originate from the Rajmahal Hill. The samples were collected with the help of Dr. A. Sarkar. The basalts are tholeiitic.

Four samples originate from the outlier of the Deccan Traps volcanic field in the Rajamundry area, central east Peninsula India, at the Kateru basalt quarry. They are tholeiitic (Rao et al., 2002).

One sample is from Kholdoda, central India, collected five meters above the bottom of the lowermost flow on top of the K/T boundary. Another sample originates from the locality Bergi in an identical position relative to the K/T boundary. Eight samples originate from the Deccan Traps flows at Girad. They are from the top flow (>60 m) and from flow 3 (around 30 m thick). All are single flows of tholeiitic basalt. The geographic position of the localities is recorded by Hansen et al. (2005).

From the Mo Clay, basaltic ash beds +28 and +30 were sampled from a large calcareous concretion (a "Cement-stone"). The age is Lower Eocene. The rock type was characterized as tholeiitic Fe–Ti basalts (Pedersen and Jørgensen, 1981).

A young alkali–basalt that was chemically analyzed by Geological Survey of Greenland was sampled at the Santa Fe basalt quarry, AZ, USA.

Samples of the Tertiary basalts at Stockum, Germany, and Le Broc, Massive Central, France, are both alkali basalts.

Two subfossil basalt samples originate from the Azores (San Miguel and Terciera) and were collected by Dr. S. Björck.

The youngest sample consists of basaltic scoria from the Mauna Ulu field, Hawaii, collected by the author.

A specimen of MORB from the Kolbeinsey Ridge GM. 26-001 was donated by the Geological Museum, Copenhagen.

Dr. M. K. Soni, Geological Survey of India, kindly supplied a sample from the kimberlite at Panna, Central India. Dr. B. Hageskov donated a specimen from a kimberlite from Sdr. Strømfjord, West Greenland. Two kimberlites from respectively Kimberley (South Africa,

GM 1938-153) and Siberia (Russia, GM 1987-95) were placed at my disposal by the Geological Museum, Copenhagen.

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