Paleoatmospheric pCO$_2$ fluctuations across the Cretaceous–Tertiary boundary recorded from paleosol carbonates in NE China

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**Abstract**

A dramatic change in atmospheric composition has been postulated because of global carbon cycle disruption during the Cretaceous (K)–Tertiary (T) transition following the Chicxulub impact and Deccan Trap eruptions. Here, pedogenic carbonates were collected from drill core of a borehole (SK-1 (N)) straddling the Late Cretaceous and early Paleocene strata in the Songliao Basin, northeast China, to reconstruct atmospheric CO$_2$ concentrations using a paleosol paleobarometer. Our estimates for atmospheric pCO$_2$ from paleosol carbonates range between 277 ± 115 ppmv and 837 ± 164 ppmv between 67.8 Ma and 63.1 Ma. One large (~66.5 Ma) and several small CO$_2$ spikes (~64.7–64.2 Ma) during the latest Maastrichtian to earliest Danian are reported here and incorporated with previously published pCO$_2$ estimates also estimated from paleosol carbonates. These CO$_2$ spikes are attributed to one-million-year-long emplacement of the large Deccan flood basalts along with the extraterrestrial impact at the K–T boundary.

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1. Introduction

The K–T boundary was marked by one of the largest mass extinctions during the past 500 million years (Peters, 2008), and several hypotheses have been proposed to explain the mass extinction at the K–T boundary. The impact hypothesis was introduced to account for the mass extinction (Alvarez et al., 1980), and increasing numbers of scientists attribute the mass extinction to the Chicxulub impact event (Hildebrand et al., 1991; Kring, 2007; MacLeod et al., 2007; Miller et al., 2010; Schulte et al., 2010). Global environmental consequences of the impact included release of large quantities of water, dust, and climate-forcing sulfuric and nitric acidic gases (Retallack, 1996), extensive combustion of biomass or fossil organic matter (Wolbach et al., 1988; Melosh et al., 1990; Ivany and Salawitch, 1993; Jones and Lim, 2000; Belcher et al., 2009), and mega-tsunami and ejecta debris deposition (Claeys et al., 2002). Alternatively, a continental flood basalt hypothesis has also been used to explain the K–T mass extinction pattern, due to abrupt global cooling resulting from the volatilization release of sulfur dioxide and dust into the atmosphere for single eruptive events in the Deccan flood basalts (Keller et al., 2008; Chenet et al., 2009; Courtillot and Fluteau, 2010), or to later greenhouse warming with increase of atmospheric CO$_2$ once dust, soot and aerosols fell to the ground (Duncan and Pyle, 1988; O’Keefe and Ahrens, 1989; Crowley and Berner, 2001). In addition, multicausal models including impact, volcanic activity, marine regression, and changes in global and regional climatic patterns have been linked to the extinction event (Keller, 2001; Keller et al., 2003, 2009; MacLeod, 2003; Archibald et al., 2010; Keller et al., 2010).

A significant perturbation of the global carbon cycle has been predicted from extinctions themselves, as well as from impact and volcanic eruption near the K–T boundary. It was hypothesized that atmospheric CO$_2$ would rise dramatically across the K–T transition due to massive amounts of CO$_2$ from Chicxulub’s target carbonate-rich lithologies and the projectile (O’Keefe and Ahrens, 1989; Agrinier et al., 2001; Kring, 2007), from widespread large wildfires (Melosh et al., 1990; Wolbach et al., 1990; Ivany and Salawitch, 1993; Durda and Kring, 2004), from intruded or impacted coal or hydrocarbons (Belcher et al., 2005; Harvey et al., 2008; Belcher et al., 2009), from reduction in worldwide marine primary productivity (D’Hondt et al., 1998; Aberhan et al., 2007; Maruoka et al., 2007), and from degassing of mantle volatiles during several short eruptions of the Deccan Trap (Courtillot et al., 1986; Officer et al., 1987; Self et al., 2006; Kring, 2007; Chenet et al., 2009).

Estimated atmospheric CO$_2$ concentrations across the K–T transition are tests of these hypotheses. An abrupt pCO$_2$ fluctuation at the K–T boundary has been examined using both stomatal index of fossil plants (Beerling et al., 2002; Retallack, 2009a) and a paleosol barometer (Nordt et al., 2002, 2003). However, disparity between magnitude and
duration of CO₂ concentration in these studies highlights the need for more records with greater precision and temporal resolution (Arens and Jahren, 2002; Retallack, 2004). In the past, lack of information about key parameters such as soil respiration for the pedogenic CO₂ paleobarometer of Cerling (1991) have limited their precision in determining ancient CO₂ levels, but now a variety of proxies for soil respiration are available (Retallack, 2009b; Breecker et al., 2010; Royer, 2010; Cotton and Sheldon, 2012).

The Songliao Basin of China has thick sequences of Jurassic–Paleogene terrestrial strata (Wan et al., 2007), including carbonate-nodule-bearing paleosols suitable for determination of paleoatmospheric CO₂ (Huang et al., 2010). Our study uses selected carbonate paleosols in northeast China in order to: (1) estimate atmospheric pCO₂ levels across the K–T, 2010). Our study uses selected carbonate paleosols in northeast China in order to: (1) estimate atmospheric pCO₂ levels across the K–T boundary using a paleosol CO₂ paleobarometer and supplement the global database of CO₂ concentrations; and (2) indicate the source(s) of variegated sandstone and gray-green mudstone intercalated with brown mudstone (Wang et al., 2008). Within one of the largest Cretaceous landmasses (Scotese et al., 1988), the Songliao Basin in northeast China covers an area of ~260,000 km² (Fig. 1). The basin is filled predominantly with volcaniclastic, alluvial fan, fluvial, and lacustrine sediments of Late Jurassic, Cretaceous, and Paleogene ages on a pre-Mesozoic basement (Wang et al., 2009). Mesozoic and Cenozoic terrestrial strata are up to 7000 m thick above the base of coal-bearing Wuyun Formation (Chen et al., 2004; Liu et al., 2009). About 10 species of Aquilapolles are observed to indicate late Maastrichtian age of Furao Formation (Chen et al., 2004), and a SHRIMP U–Pb zircon age of rhyolitic crystal tuff, ~9.3 m below the top of the Furao Formation strata is 66±1 Ma, only 0.5 Ma older than the recommended K–T boundary age in the International Stratigraphic Chart (Li et al., 2004). However, the K–T boundary should be close to the depth of 360.6 m given that paucity of pollen and spores within approximate 100 m of section within 360.6 m to 263.4 m (Li et al., 2011; Deng et al., 2013). The geomagnetic polarity timescale for the borehole (SK-1 (N)) was determined by combining magnetostratigraphy, SIMS U–Pb zircon geochronology and lithostratigraphy, and the top of chron 30n in the GPTS (Cande and Kent, 1995) was put at the depth of 342.1 m (Deng et al., 2013). Accordingly, the K–T boundary is estimated at ~340 m in depth of this borehole in NE China.

2. Geological setting

Within one of the largest Cretaceous landmasses (Scotese et al., 1988), the Songliao Basin in northeast China covers an area of ~260,000 km² (Fig. 1). The basin is filled predominantly with volcaniclastic, alluvial fan, fluvial, and lacustrine sediments of Late Jurassic, Cretaceous, and Paleogene ages on a pre-Mesozoic basement (Wang et al., 2009). Mesozoic and Cenozoic terrestrial strata are up to 7000 m thick above the base of coal-bearing Wuyun Formation (Chen et al., 2004; Liu et al., 2009). About 10 species of Aquilapolles are observed to indicate late Maastrichtian age of Furao Formation (Chen et al., 2004), and a SHRIMP U–Pb zircon age of rhyolitic crystal tuff, ~9.3 m below the top of the Furao Formation strata is 66±1 Ma, only 0.5 Ma older than the recommended K–T boundary age in the International Stratigraphic Chart (Li et al., 2004). However, the K–T boundary should be close to the depth of 360.6 m given that paucity of pollen and spores within approximate 100 m of section within 360.6 m to 263.4 m (Li et al., 2011; Deng et al., 2013). The geomagnetic polarity timescale for the borehole (SK-1 (N)) was determined by combining magnetostratigraphy, SIMS U–Pb zircon geochronology and lithostratigraphy, and the top of chron 30n in the GPTS (Cande and Kent, 1995) was put at the depth of 342.1 m (Deng et al., 2013). Accordingly, the K–T boundary is estimated at ~340 m in depth of this borehole in NE China.

3. Methods

3.1. Sample collection and analytical methods

Paleosol carbonate samples were collected from 23 paleosol Bk horizons within the Upper Mingshui Formation (late Maastrichtian–early Paleocene) in the Drill SK-1 (N) at depths between 267.6 m and 480.4 m below the surface (Fig. 2). On a basis of the age of 65.58 Ma for the deposition at the depth of 342.1 m (Deng et al., 2013), the age of the paleosol horizons (A, Ma) for this section were extrapolated from sediment accumulation rate and the depth of the paleosol horizons (D, m) while the sedimentation accumulation rate (S, m/Ma) for the Upper Mingshui Formation was assumed as 30 m/Ma, 60 m/Ma respectively at the depth of less than 342.1 m, between 342.1 m and 530.78 m in combination with paleomagnetic analysis (Deng et al., 2013) (Eq. (1)).

$$A = 65.58 + \frac{D-342.1}{S}.$$  

(1)
Three samples of pedogenic carbonate nodules from each Bk horizon were sampled for stable carbon and oxygen isotopic compositions of pedogenic carbonates. ~5 mg of the micritic carbonate was sampled. These samples were reacted in vacuum with 100% phosphoric acid for at least 4 h at 25 °C, and the resulting CO2 analyzed for carbon and oxygen isotope compositions with a Finnigan MAT 253 mass spectrometer at State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences. The three isotopic values of separated pedogenic nodules for each Bk horizon were averaged to determine intranodule variability. The results are expressed in the notation δ‰ (per mil) relative to Pee Dee belemnite (PDB). Reproducibility of both δ18O and δ13C on standards and unknowns is within ±0.2‰.

### 3.2. Assumptions for atmospheric CO2 estimation

The pedogenic carbonate CO2 paleobarometer was used for estimates of atmospheric CO2 concentrations (Cerling, 1999; Ekart et al., 1999):

\[
P_a = P_r \frac{(\delta^{13}C_i - 1.0046\delta^{13}C_r - 4.4)}{(\delta^{13}C_r - \delta^{13}C_i)}
\]

where \(P_a\) is atmospheric CO2 (ppmv), \(P_r\) is soil-respired CO2 concentration (ppmv) and \(\delta^{13}C_i\), \(\delta^{13}C_r\) and \(\delta^{13}C_l\) are the stable carbon isotopic compositions of soil CO2, soil-respired CO2, and atmospheric CO2, respectively. Variables in this equation are guessed from the following analyses and transfer functions.

The isotopic compositions of respired soil CO2 (\(\delta^{13}C_i\)) is approximated by the \(\delta^{13}C\) of paleosol organic carbon (\(\delta^{13}C_o\)) (Cerling, 1991), accordingly, \(\delta^{13}C_o\) can be substituted for \(\delta^{13}C_i\) in the model equation (Cerling, 1999). Considering the striking fractionation of carbon isotopic composition induced by aerobic decomposition after burial of soils (Ekart et al., 1999; Wynn, 2007), in addition to low levels of paleosol organic carbon, the isotopic compositions of well-preserved fossil terrestrial plants may also be used as a proxy of \(\delta^{13}C_i\) instead of \(\delta^{13}C_o\) (Robinson et al., 2002; Cleveland et al., 2008a). In cases such as this, where insufficient fossil wood was found in each paleosol, an alternative protocol is to estimate the \(\delta^{13}C\) of atmospheric CO2 (\(\delta^{13}C_r\)) through geological time from \(\delta^{13}C\) of planktic foraminifera from high resolution marine sediments (Passsey et al., 2002; Nordt et al., 2003; Retallack, 2009b), and \(\delta^{13}C_r\) was calculated using Eq. (3) from Arens et al. (2000).

\[
\delta^{13}C_r = \frac{\delta^{13}C_o + 18.67}{1.1}
\]

A five-point running average of the \(\delta^{13}C\) values of planktic foraminifera were selected for \(\delta^{13}C\) estimation within 67.8 Ma and 64.9 Ma from Deep Sea Drilling Project (DSDP) core 525A from the South Atlantic (Li and Keller, 1998) and within 64.8 Ma and 63.1 Ma from DSDP 577 from the North Pacific (Shackleton and Bleil, 1985; Zachos et al., 1989; Nordt et al., 2003), and ~7‰ was assumed as the isotopic equilibrium fractionation value between ocean and atmospheric CO2 (Passsey et al., 2002). An assumed value of ~24‰ is used in geological time from 68 Ma calculated from \(\delta^{13}C\) values of planktic foraminifera of DSDP 525A in good agreement with an average value of ~24.2‰ (ranging from ~24.18‰ to ~24.33‰) of terrestrial fossil plants from Sakhalin, Russian Far East (Hasegawa et al., 2003), in the neighborhood of the Songliao Basin, northeast China. The paleomagnetic ages of strata for \(\delta^{13}C\) estimation from DSDP 525A and DSDP 577 were estimated following Cande and Kent (1995). The \(\delta^{13}C\) estimated from planktic foraminifera was adopted for the paleosols at the identical ages inferred from the sedimentation rates.

Two approaches have been currently used to estimate paleotemperature in paleosol formation (Dworkin et al., 2005). One approach derives from the statistical relationship between alkaline index (\(N = (K_2O + Na_2O)/Al_2O_3\), as a molar ratio) to indicate the degree of soil weathering and mean annual temperature (Sheldon et al., 2002), however, this quantification is problematic for soils formed under arid and semiarid climate because \(N\) value is unaltered or may increase with the temperature due to evaporative enrichment of Na and K within this kind of soils (Pan and Huang, 2012). Here, the isotopic composition of soil CO2 (\(\delta^{13}C\)) comes from that of pedogenic carbonate (\(\delta^{13}C_i\)), corrected for temperature (\(T\) in °C) dependent fractionation from Eq. (4) (Romanek et al., 1992). We use isotopic composition of oxygen in pedogenic carbonate (\(\delta^{18}O\)) relation for modern climates to estimate temperatures, despite known diagenetic effects on oxygen isotopic composition of pedogenic carbonate after burial and potential evaporative enrichment effects under arid climates (Cerling, 1984; Quade et al.,...
1989; Cerling and Quade, 1993; Mack and Cole, 2005; Tabor and Montañez, 2005). These dia genetic alterations are considered minimal because of the shallow burial depth of paleosols (<0.5 km) and limited diageneric alteration reflected by pedogenic features (Nordt et al., 2003; Dworkin et al., 2005; Prochnow et al., 2006; Huang et al., 2010). In addition, because the Eq. (5) was derived from modern pedogenic carbonates that likely experienced some degree of evaporative enrichment (e.g., Dworkin et al., 2005), it is unnecessary to assume the total absence of evaporation (Cleveland et al., 2008a).

$$\delta^{13}C_i = \frac{\delta^{13}C_i + 1000}{11.98 - 0.12 \cdot \frac{1}{1000} - 1} - 1000$$  \hspace{1cm} (4)

$$T = \frac{\delta^{18}O_i + 12.65}{0.49}$$  \hspace{1cm} (5)

Partial pressure of respired CO2 in soil (Pp in ppmv) depends dominantly on atmospheric CO2 and CO2 from respiration of roots, animals and microbes. Much higher paleo-atmospheric CO2 concentrations estimated previously from the soil carbonate CO2 paleobarometer than those from other paleo-pCO2 proxies, e.g., stomatal index of fossil plants, was newly attributed to overestimation of Pp (Breecker et al., 2010; Royer, 2010). However, a proposed Pp value of 2500 ppmv for all paleosols was oversimplified (Breecker et al., 2010; Royer, 2010). For the highly significant relationship between respired soil CO2 during late growing season and depth to Bk horizon, Retallack (2009b) established a novel transfer function between Pp and depth to carbonate, and Eq. (6) might be a better solution to reconstruct the partial pressure of respired soil CO2 (Royer, 2010). Another relationship between summer minimum soil-respired CO2 and mean annual precipitation has been proposed for the soils containing pedogenic carbonates (Cotton and Sheldon, 2012) using a correlation of soil productivity with precipitation. This relationship was not used for the following three reasons. First, estimation of Pp using the scheme of Cotton and Sheldon (2012) results in large Pp errors envelopes once errors of paleoprecipitation are compounded with errors in correlation of Pp and precipitation. Second, Cotton and Sheldon (2012) are mistaken in their statement that Retallack (2009a) used mean growing season Pp. Third, use of the very lowest summer Pp values by Cotton and Sheldon (2012) gives near modern concentrations (375–454 ppmv) for middle Miocene pCO2 when applied to data of Retallack (2009b), which is too low to account for observed warmer and wetter Miocene paleoclimate (Retallack, 2009a). For compaction in paleosols, Dc was corrected using Eq. (6) in modern soils (Sheldon and Retallack, 2001).

$$Pp = 66.7Dc + 588$$  \hspace{1cm} (6)

$$Dc = Dc'/\left[0.38 - \frac{62}{27\pi} - 1\right]$$  \hspace{1cm} (7)

where Dc (in cm), Dc' (in cm) and K (in km) are original depth to carbonate nodules, depth to carbonate nodules in paleosol, and burial depth, respectively.

4. Pedogenic carbonate nodules

In most calcareous paleosols, the calcic horizon (Bk horizon) was reddened by dehydration and recrystallization of iron hydroxides to hematite (Fig. 3A-B) (Retallack, 1997, 2001; Budd et al., 2002), but some paleosols are gray in color (Fig. 3C), with little difference in color between upper and lower horizons. In terms of the morphological classification of calcrites (Goudie, 1983; Quast et al., 2006), the collected calcrites mainly appeared in forms of well-rounded to sub-rounded nodular with a diameter of 0.1–3.5 cm (Fig. 3A–F).

Micrite dominates microfabric in the carbonate nodules (Fig. 4A–D), and sparry calcite is constrained to the cracks (Fig. 4B), as is characteristic of pedogenic carbonate (Budd et al., 2002; Deutz et al., 2002; Dworkin et al., 2005; Cleveland et al., 2008b). Micritic aggregates in larger nodules have circumgranular cracks cemented by microsparite (Fig. 4C), as also known from paleosols elsewhere (Kovda et al., 2003). Displacive fabrics also are apparent where splinters of matrix have rotated (Fig. 4D), and these indicate expansion due to soil formation under low confining pressure.

5. Estimation of Cretaceous atmospheric CO2 concentrations during the late Maastrichtian and the early Danian

Calculations of pCO2 values from paleosol carbonates from Drill SK-1 (N) in China, range between 277 ppmv and 837 ppmv from 67.8 Ma through 63.1 Ma (Table 1), and are generally lower than the estimates of the pCO2 range from ~400 ppmv (ca. 1.4 present atmospheric level (PAL)) up to ~1400 ppmv (3.0 PAL) for the interval between 80 Ma and 60 Ma by geochemical and biogeochemical models (Tajika, 1999; Berner and Kothavala, 2001; Wallmann, 2001; Berner, 2006; Fletcher et al., 2008). Also our estimates are lower than previous values of pCO2 calculated from paleosol carbonates (Ekart et al., 1999; Cojan et al., 2000; Nordt et al., 2002), largely because of assumptions by those authors of 4000–6000 ppmv of Pp. If Pp is assumed to be only 2500 ppmv as proposed by Breecker et al. (2010), their pCO2 values decrease to within the range of our estimates (Fig. 5). Also, averaged pCO2 concentrations for our estimation, i.e., ~460 ppmv, during the early Paleocene is comparable with 375–404 ppmv pCO2 estimated from fossil Ginkgo from Helongjiang, NE China (Quan et al., 2010).

The standard errors for atmospheric CO2 estimates, derived from the transfer functions (above-mentioned equations) and analytic error limits, calculated from the transposed equations on a base of Gaussian error propagation used by Retallack (2009b). The standard error of the soil-respired CO2 transfer function (Eq. (5)) reaches ±893 ppmv (Retallack, 2009b), and resulted in a variation within ±75 ppmv and ±269 ppmv of the maximal errors for atmospheric CO2 estimates. The uncertainty from paleotemperature estimates is ±5.8 °C for Eq. (4) producing a range of ±11 ppmv and ±51 ppmv atmospheric CO2. An analytic error of ±0.3% of δ18O, ±0.2% of δ13C and ±0.4% of δ13C gives less than ±0.1 ppmv atmospheric CO2. In general, the errors for all atmospheric CO2 concentration estimate fluctuate between ±78 ppmv and ±271 ppmv using Gaussian quadrature (Table 1). The ultimate errors for the mean atmospheric CO2 concentration at each age range between ±79 ppmv and ±454 ppmv.

Using the paleosol barometer a pCO2 peak had been previously discovered at 65.5 Ma (Nordt et al., 2002) or between 65.5 and 65.0 Ma (Nordt et al., 2003). An unusually high peak of >2300 ppmv CO2 at ~65 Ma was calculated from stomatal index of fossil ferns (cf. Stenochlaena), but this plant model remains poorly understood (Beering et al., 2002). Another high value of 1689±430 ppmv atmospheric CO2 was determined for ~65 Ma from 563 counts of a single leaf of Ginkgo: such low numbers of leaves and counts are statistically of low reliability (Retallack, 2009a). Discounting these extreme values and combining re-calculated pCO2 data estimated from other pedogenic carbonates (Ekart et al., 1999; Cojan et al., 2000; Nordt et al., 2002), a pCO2 curve spanning the Maastrichtian and Danian was composed to examine atmospheric CO2 variation (Fig. 5). A large spike (~840 ppmv) was detected at 66.0 Ma and several small spikes (~550–600 ppmv) at 64.7, 64.5 and 64.2 Ma, respectively.

The critical issue for identifying more spikes is the temporal resolution of atmospheric pCO2 time series. Geochemical or biogeochemical models provide pCO2 estimates for the entire Phanerozoic time at scales of 5–10 Ma, and so reflect major trends, but not short-term excursions (Royer et al., 2001). Many dramatic fluctuations in pCO2 concentration occurred over short-time spans during geological time
Atmospheric pCO2 variations of over 100 ppmv in ~30 ka, were revealed from air trapped within ice cores, largely because of interaction between ocean and atmosphere (Fischer et al., 1999; Petit et al., 1999; Siegenthaler et al., 2005; Lourantou et al., 2010). Four atmospheric pCO2 rises (>100 ppmv) in the duration of <100 ka have been detected since 800 ka BP to the present (Lüthi et al., 2008). In deep time, short-lived (<1 Ma) pCO2 excursions are common, and at least 20 pCO2 spikes have been recognized over the past 300 million years using stomatal index (Retallack, 2009a).

6. Causes for elevated atmospheric CO2 concentrations

Low pCO2 level during mid-Maastrichtian (68.0–67.0 Ma) ranging from 200 ppmv to 300 ppmv are compatible with evidence for a mid-Maastrichtian cool event from variation in sea level and marine δ18O records (Huber et al., 2002; Miller et al., 2003).

A period of relatively high pCO2 persisted for ~1.5 million years (66.5 Ma and 65 Ma), and the atmospheric CO2 concentrations mostly exceeded 500 ppmv (Fig. 5). The high pCO2 level for ~1.5 Ma is in phase with the Deccan eruptions at 67–66.5 Ma (Self et al., 2006; Chenet et al., 2007; Self et al., 2008; Jay et al., 2009). Moreover, the small CO2 spikes within 64–65 Ma (Fig. 5) is in agreement with the third large eruption phase of the Deccan Traps (Chenet et al., 2007; Bryan et al., 2010; Hooper et al., 2010).

The peak atmospheric CO2 level within ~66.0–65.5 Ma may have resulted from both the Deccan Trap eruptions and Chicxulub impact. Self et al. (2006, 2008) estimated that over ~13,000 Gt CO2, was released from Deccan Traps emplacement during ~2 Ma, and the largest emission of CO2 (~5000 Gt) also occurred over a short time-span (66.0–65.5 Ma) (Fig. 5). With respect to the current mass of atmospheric CO2 (~3000 Gt), several single eruptive events spanning tens and hundreds of years, a mass of ~300 Gt degassing during each single eruptive event producing at least 40–80 ppmv in pCO2 increase, is consistent with geochemical models of Caldeira and Rampino (1990) and the calculation from global volcanic emissions for thousands of years during the last deglaciation along with the current volcanic observations (Huybers and Langmuir, 2009). In contrast, Self et al. (2005) and Chenet et al. (2009) found much lower pCO2 release from the Deccan Traps. Though the lavas contained little CO2, vast amounts of CO2 may

Fig. 3. Photographs of paleosols and pedogenic nodules. A) Paleosols and Bk horizon (0971), pen for scale; ~17 cm in length; B) paleosols and Bk horizon (1220), coin for scale; ~2.5 cm in diameter; C) Bk horizon and pedogenic nodules (2940), coin for scale; ~2.5 cm in diameter; D) Bk horizon and pedogenic nodules (1410), coin for scale; ~2.5 cm in diameter; and E and F) pedogenic nodules within Bk horizon (1320 and 1221, respectively), coin for scale; ~2.5 cm in diameter.
have been produced by contact metamorphism surrounding intrusions in carbonate rocks, coal or organic-rich shales (Ray et al., 2008; Ganino and Arndt, 2009; Hegde and Chavadi, 2009).

Presumably the Chicxulub impact at ~65.6 Ma contributed greatly to the input into the atmospheric CO₂ produced from vaporized carbonates increased atmospheric CO₂ by a factor of 2 or more even for over 10^5 years because of the impact onto the carbonate-rich marine sedimentary terrace (O’Keefe and Ahrens, 1989; Beerling et al., 2002). The maximum amount of CO₂ was estimated at 100,000 Gt during the impact event (Takata and Ahrens, 1994). This is an unbelievably large amount, and is best regarded as a theoretical maximum, considering the complex kinetics and thermodynamics of the reactions during the impact events (Agrinier et al., 2001; Ivanov et al., 2002). Subsequent estimation from the numerical models and experiments, ranged from

![Fig. 4. Micrites in the carbonate nodules. A) Micritic fabrics (1320); B) micritic fabrics and sparry calcites in the cracks (298); C) micritic aggregates and circumgranular cracks cemented by microsparite (1350); and D) micrites and displacive fabrics (0971).](image)

### Table 1

Data used to estimate paleoatmospheric CO₂ concentration across the K-T boundary from paleosols.

<table>
<thead>
<tr>
<th>Age [Ma]</th>
<th>Sample no.</th>
<th>Δ¹³C₀</th>
<th>D₀ (cm)</th>
<th>K</th>
<th>D₁ (cm)</th>
<th>P₀ (ppmv)</th>
<th>Δ¹³C₀</th>
<th>Δ¹³D₀</th>
<th>T (°C)</th>
<th>Δ¹³C₀</th>
<th>Δ¹³C₀</th>
<th>P₀ (ppmv)</th>
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<td>4700</td>
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<td>−8.21</td>
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Note: The standard errors of P₀ are calculated using Gaussian error propagation; MP₀ is the mean value of P₀ at a certain age, and the standard errors of MP₀ are assigned to the maximal P₀ error at a certain age.
~300 to >10^4 Gt for the mass of CO2 emission into the atmosphere (Ivanov et al., 1996; Pope et al., 1997; Pierazzo et al., 1998; Kring and Durda, 2001; Beerling et al., 2002), is one to two orders of magnitude lower than that of Takata and Ahrens (1994). Despite disagreement concerning the mass of liberated CO2, it is reasonable that the atmospheric pCO2 level dramatically increased, due to vaporization of target rocks of the Chicxulub impact (Beerling et al., 2002; Premović, 2009).

Extensive wildfires ignited by the ejecta (Wolbach et al., 1990; Kring and Durda, 2001; Beierling et al., 2002), is one to two orders of magnitude lower than that of Takata and Ahrens (1994). Despite disagreement concerning the mass of liberated CO2, it is reasonable that the atmospheric pCO2 level dramatically increased, due to vaporization of target rocks of the Chicxulub impact (Beierling et al., 2002; Premović, 2009).

Extensive wildfires ignited by the ejecta (Wolbach et al., 1990; Kring and Durda, 2001; Beierling et al., 2002) or combustion of hydrocarbons during the impact event (Scott et al., 2000; Belcher et al., 2005; Harvey et al., 2008; Belcher et al., 2009) could introduce large amounts of CO2 into the atmosphere (Kring, 2003, 2007). Nevertheless, the consequence of the impact-generated pulse of thermal radiation from these sources remains uncertain (Belcher et al., 2003; Belcher, 2005; Goldin and Melosh, 2009). Here we do not include the CO2 emissions from above-mentioned processes, although ~10^4 Gt of CO2, roughly equivalent to the mass of CO2 liberated from vaporized target sediments, had been estimated (Kring and Durda, 2001; Kring, 2007).

In concert with the markedly elevated atmospheric CO2 level, global warming, sea level rise and deglaciation should occur after a period of cooling resulting from the huge mass of dust and sulfate aerosols ejected from the impact (Kring, 2007; Huybers and Langmuir, 2009). Though the coupling of atmospheric CO2 concentrations and climate change was suspected (Veizer et al., 2000; Kump, 2002; Shaviv and Veizer, 2003; Donnadieu et al., 2006), ocean temperature estimated from δ18O of foraminifera disagreed with atmospheric pCO2, perhaps due to seawater pH effects (Zeebe, 2001; Royer et al., 2004). However, other studies supported the hypothesis that global warming was driven by increased atmospheric pCO2 level (Crowley and Berner, 2001; Pearson et al., 2001; Retallack, 2002; Royer et al., 2004; Can et al., 2007; Pucéat et al., 2007; Fletcher et al., 2008; Retallack, 2009a; Solomon et al., 2009, 2010). After a Late Cretaceous cooling (Pucéat et al., 2007), a global warming event occurred at the transition between late Maastrichtian and early Danian consistent with the elevated pCO2, supported from the isotopes of numerous global drilling sites (Zachos et al., 1989; Li and Keller, 1998; Huber et al., 2002; Abramovich and Keller, 2003; Ravizza and Peucker-Ehrenbrink, 2003; MacLeod et al., 2005; Westerhold et al., 2011), simulation models (Pierazzo et al., 1998; Dessert et al., 2001; Hunter et al., 2008) and calcareous nanofossil assemblages (Thibault and Gardin, 2010). The seawater temperature estimates range from below 1 °C (Caldeira and Rampino, 1990), to ~2 °C (Pierazzo et al., 1998; Zachos et al., 2001; Huber et al., 2002),
A high-temporal-resolution curve of paleotemperature from the δ18O of foraminifera in a duration corresponding to the K-T boundary is only known from the South Atlantic (Cramer et al., 2009). The δ18O of foraminifera varied coincidently with the fluctuations of atmospheric CO2 levels, even the smaller-scale CO2 spike between 66 Ma and 67 Ma (Fig. 5). Recent progress in the high-resolution Maastrichtian and Paleocene stable isotope record from marine deposits reveals short-term global climate changes (Abramovich et al., 2010; Westerhold et al., 2011), for spikes of CO2 input into the atmosphere less than the occurred near the K-T boundary.

Sea level rise across the K-T boundary is known from sedimentary correlation of boreholes globally (Adatte et al., 2002; Miller et al., 2005a; Komizn, et al., 2008; Miller et al., 2011). Estimates of sea level fluctuation are less than 50 m (Haq et al., 1987; Miller et al., 2003; Van Sickel et al., 2004; Miller et al., 2005a,b; Komizn, et al., 2008; Cramer et al., 2009; Miller et al., 2011). Furthermore, global seawater acidification and decreased CaCO3 burial fluxes were observed at the K-T boundary due to the huge amount of CO2 liberation induced by the Deccan volcanism and Chicxulub impact (Robinson et al., 2009; Premović, 2011) and impact generated nitric and sulfuric acid (Retallack, 1996).

7. Conclusions

Calcareous paleosols have been discovered in a scientific drill core from the Songliao Basin, northeast China. Well developed pedogenic carbonates were collected from the scientific drill core (SK-1 (N)). Here, we measured δ18O and δ13C values of these paleosol carbonates to estimate Cretaceous atmospheric pCO2 levels using Cerling’s (1991) model, as refined by Retallack (2000b).

Together with previous data on estimates of atmospheric pCO2 from 67.8 Ma and 63.1 Ma, we found one large and several small pCO2 spikes when CO2 concentration rose from less than 300 ppm between 68 Ma and 67 Ma to ~840 ppm between 66.5 Ma and 65.5 Ma, then dropped and rose to ~550 ppm between 64.7 Ma and 64.2 Ma.

Inconsistencies between various estimates of atmospheric CO2 using the paleosol barometer can be largely ascribed to varied assumptions of different applications of the paleosol barometer and to differing temporal resolution of different paleosol sequences. Higher high-resolution records from pedogenic carbonates may provide insight into short-term spikes of paleo-atmospheric CO2, as demonstrated here to accompany a mass extinction at the K-T boundary.

Rising pCO2 after 66.5 Ma is consistent with the onset of main Deccan Trap eruptions, and atmospheric pCO2 peaked within 66–65.5 Ma as a result of large eruption of the Deccan Traps in combination of masses of CO2 released into the atmosphere produced from vaporized carbonates due to Chicxulub impact. The small CO2 spikes between 64.7 Ma and 64.2 Ma derived from the CO2-liberation from another phase of the Deccan Traps. Global warming and sea level rise was also associated with these CO2 spikes.

Acknowledgments

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