

## DATING PALEOSOL AND ANIMAL REMAINS IN LOESS DEPOSITS

H C Zhang<sup>1,2</sup> • B Li<sup>1</sup> • M S Yang<sup>1</sup> • G L Lei<sup>1</sup> • H Ding<sup>3</sup> • Jie Niu<sup>1</sup> • H F Fan<sup>1</sup> • W X Zhang<sup>1</sup> • F Q Chang<sup>1</sup>

**ABSTRACT.** Accurate and reliable dating of paleosols, animal remains, and artifacts is of crucial importance in reconstructing environmental change and understanding the interrelationship between human activities and natural environments. Dating different materials in the same sample can help resolve problems such as soil carbon sources and carbon storage state. Conventional radiocarbon dating of soil (inorganic and organic matter) and accelerator mass spectrometry (AMS) dating of animal remains (fossil bones and teeth) result in different ages for materials from the same sample position in a typical loess section at Xinglong Mountain, Yuzhong County, Gansu Province in NW China. Inorganic matter is  $\sim 3400$  yr older than organic matter,  $4175 \pm 175$  cal BP to  $3808 \pm 90$  cal BP. A 1610-yr difference between the  $^{14}\text{C}$  ages of fossils (animal bones and teeth) and soil organic matter suggests that a depositional hiatus exists in the studied profile. The varying  $^{14}\text{C}$  ages of fossils and soil organic and inorganic matter have important implications for paleoclimate reconstructions from loess sections. It is critical to consider the meaning of the variable  $^{14}\text{C}$  ages from different material components from the same sample position in terms of soil organic and inorganic carbon storage, vegetation history reconstruction, archaeology, and the study of ancient civilizations.

### INTRODUCTION

Widely distributed loess deposits, like the Chinese Loess Plateau, are rich in information regarding paleoenvironmental changes since the late Cenozoic (Zhisheng et al. 1990; Kukla et al. 1990; Ding et al. 1994; Porter and Zhisheng 1995; Guo et al. 2000). The Loess Plateau in NW China has long been regarded as a natural laboratory for the study of global climate change, especially the monsoon evolution history in Asia and its correlation with the uplift of the Tibetan Plateau (Zhisheng et al. 2001; Guo et al. 2002).

Study of loess deposits has not only focused the attention of scientists on global and regional environmental and climatological changes, but also land-surface changes and archaeology, since the Chinese Loess Plateau has for many years been a cradle for human evolution and social civilization development (An et al. 2004; Zhou 2004). Loess is an aeolian material that can be directly related to atmospheric circulation. The dust has been used as a tracer of global energy and momentum transportation and as a source of information on the mechanics of climate change (Jickells et al. 2005; Wang et al. 2005). Loess deposits not only contain organic matter, which is considered one of the main contributors to carbon circulation in the soil-biosphere-atmosphere system, but are also rich in inorganic carbonate, which also plays an important role in terms of carbon storage (Zhang 1993; Houghton 2003; Wang et al. 2003; Zhang 2004; Wang et al. 2005). Loess is one of the most suitable soils for farming, and as a result, human activities have drastically disturbed loess deposits over a long period. These land-use and land-surface changes can release the carbon stored in the soil, changing the natural carbon equilibrium and resulting in an increase in the  $\text{CO}_2$  content of the atmosphere, thus promoting global warming effects (Cao and Woodward 1998; Cox et al. 2000; Guo and Gifford 2002; Knorr et al. 2005; Bellamy et al. 2005; Powlson 2005).

It is difficult to establish a high-resolution chronology for loess sections (Liu et al. 1994; Yin et al. 1997; Schramm et al. 2000), although organic matter and animal remains in loess deposits provide suitable materials for dating. Conventional radiocarbon dating and accelerator mass spectrometry

<sup>1</sup>National Laboratory of Western China's Environmental Systems, MOE; College of Earth Sciences and Environments, Lanzhou University, Lanzhou 730000, China. Also: Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences (CAS), Nanjing 210008, China.

<sup>2</sup>Corresponding author. Email: zhanghc@niglas.ac.cn.

<sup>3</sup>College of Graduate Studies, Chinese Academy of Sciences (CAS), Beijing 100049, China.

(AMS) are the most common methods used to provide absolute ages for loess-paleosol sequences of the Late Pleistocene and associated climate events. This article presents AMS and conventional dates of paleosol and animal remains in a loess profile from NW China and discusses the significance of the differing ages of various materials from the same sampling position.

## STUDY AREA

Yuzhong Basin is a rhomb-shaped basin aligned in a NE–SW direction (Figure 1). The basin itself is surrounded by mountains and hills, with Xinglong Mountain, the only forest-covered mountain in the area, to the southwest and Bei Mountain to the northeast. The hills to the northwest and southeast are covered by loess-fluvial deposits. The elevation changes from more than 3500 m asl at Xinglong Mountain to as low as 1800 m asl in the central part of the basin. The south basin is higher than the north basin due to the nearby Xinglong Mountain. The Dahe (Big River), a seasonal river strongly influenced by water extraction for agricultural usage, flows through the lowest part of the basin in a SE to NW direction and then joins the Yellow River (Figure 1). Temperatures range from 18.3 °C in July to –7.4 °C in January, with an annual mean temperature of 6.4 °C. Annual mean precipitation from 1951 to 1980 was only 388 mm, reflecting the area's semi-arid continental climate.

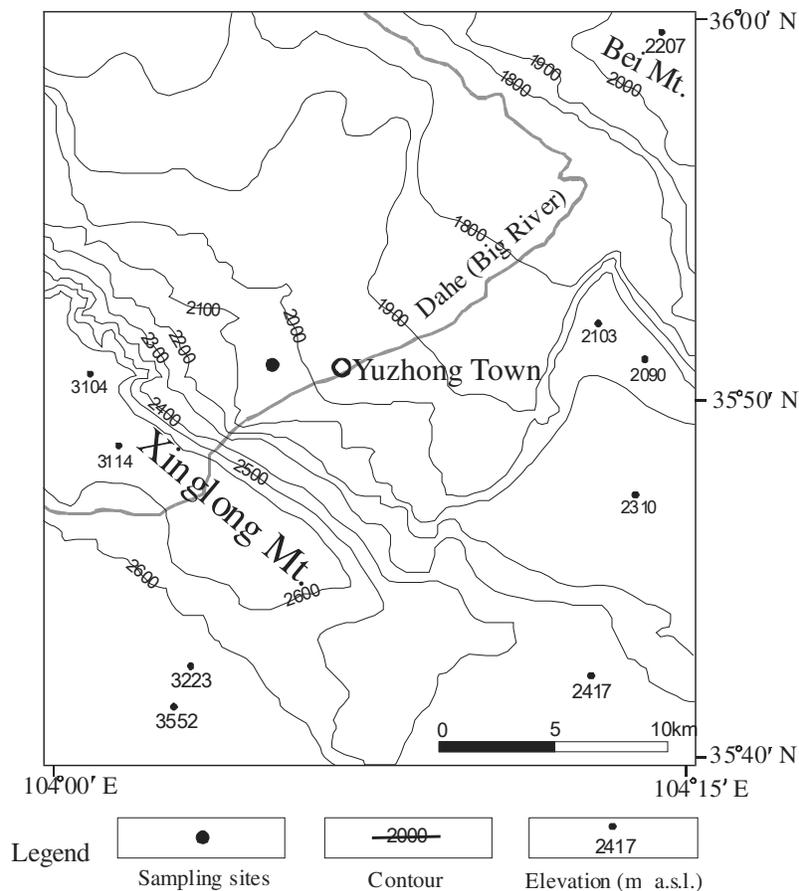


Figure 1 Map of the study area and sampling site

## MATERIALS AND METHODS

The investigated profile (35°49'N, 104°05'E) is located on the loess-pluvial fan of Xinglong Mountain in Yuzhong County, Gansu Province, China. The profile possesses a distinguishable paleosol-loess sequence that should provide useful information regarding paleoenvironmental changes in the area.

The studied section is 4.6 m thick. The upper 200 cm is a natural outcrop, while the lower part is a manually excavated profile. Numerous animal bones and fossil teeth of sheep and horse were found at a depth between 80 and 100 cm in the section, together with remains of ceramics and other artifacts (Figure 2). The artificially broken bones indicate that people not only consumed animal meat but also extracted marrow from the bones. From the well-prepared section, a total of 460 samples were taken at 1-cm intervals. All samples were kept in bags to prevent contamination. In order to test the reliability and accuracy of different dating methods (i.e. conventional  $^{14}\text{C}$  and AMS methods at different laboratories), the ages of various components from the same sampling position were tested. The ages of the materials (e.g. organic and inorganic matters in the same tested sample) and the age differences of soil and mega-fossils at the same sampling position are discussed. Conventional  $^{14}\text{C}$  analyses were conducted at the  $^{14}\text{C}$  Laboratory in National Laboratory of Western China's Environmental Systems (MOE), Lanzhou University, China (lab code Lug; half-life:  $5568 \pm 40$  yr) and Leibniz Institute for Applied Geosciences (GGA-Institut), Hannover, Germany (lab code Hv). AMS dates were conducted at Leibniz Laboratory for Radiometric Dating and Stable Isotope Research at Kiel University in Germany (lab code Kia). The grain size of all 460 samples was analyzed using a Mastersize2000<sup>TM</sup> laser grain-size analyzer.



Figure 2 a) The original cliff where a small piece of bone (arrow point) was discovered during a student excursion; b) the students on the field trip. After the cliff was cleaned, large amounts of fossil bones and teeth, ceramics, and artifacts were found (circled area). The dotted line marks the boundary between upper artificial material and the lower original loess-paleosol sequence; c) the fossil bones and teeth of sheep and horses; d) artifact (stone tool) used to smash the bones for marrow.

## RESULTS AND DISCUSSION

All  $^{14}\text{C}$  and AMS dates measured are listed in Table 1. It is clear that the ages of various materials/components from the same sample are different from one another. Among the dated materials, ages of fossil animal bones and teeth are the youngest, and the age of organic carbon in soil is younger than that of inorganic carbon. The age of fossil bones obtained by conventional  $^{14}\text{C}$  is almost the same as that by AMS, but slightly younger than the conventional method obtained from Hannover. The dates represent the real ages of different components in the tested sample.

Table 1 Dating results of different materials from the same sampling position.

Lab code	Matter	Method	<sup>14</sup> C age/BP	δ <sup>13</sup> C	cal BP
Lug-04-49	Inorganic carbon	<sup>14</sup> C	6306 ± 80		7395 ± 85
Lug-04-49	Organic carbon	<sup>14</sup> C	3682 ± 70	−23.6	4175 ± 175
Hv-25091	Organic carbon	<sup>14</sup> C	3520 ± 70		3808 ± 90
	(average)				(3990)
Hv-25092	Bone	<sup>14</sup> C	2410 ± 90	−23.3	2526 ± 130
Lug-03-89	Bone	<sup>14</sup> C	2248 ± 50		2245 ± 95
Kia 23774	Teeth (collagen)	AMS	2235 ± 30	−16	2240 ± 90
	(average)				(2380)
Kia 23774	Teeth (insoluble fraction)	AMS	1815 ± 40	−17	1760 ± 60

The fossil bones are 2410 ± 90 BP (2526 ± 130 cal BP) and 2248 ± 50 BP (2245 ± 95 cal BP) using conventional <sup>14</sup>C. The collagen of fossil teeth dated to 2235 ± 30 BP (2240 ± 90 cal BP), while the remaining insoluble fossil teeth produced a date of 1815 ± 40 BP (1760 ± 60 cal BP) by AMS. Thus, the date of fossil bone using the conventional <sup>14</sup>C method is similar to the AMS date of fossil teeth collagen. The youngest age for insoluble residue of fossil teeth suggests that this fraction had been slightly contaminated by external <sup>14</sup>C of a more recent age, resulting in a younger age (by ~620 yr) than that of the collagen fraction. During the sample preparation procedure, 30.8 mg of collagen and 3.7 mg of carbon residue were collected from 737 mg of fossil teeth. The dominance of the teeth collagen fraction ensures more accurate results. These data were obtained from 2 laboratories (in China and Germany) using both conventional <sup>14</sup>C and AMS dating as a test of accuracy.

The age of fossil bones/teeth represents the time of animal death (whether the animals were killed by humans or died of natural causes). When the sheep and horses died, their remains were usually buried in loess/fluvial deposits and the bones fossilized with time. Because the moisture content in loess is very low, the fossils remain dry and this limits decay. Thus, there is almost no carbon exchange between the fossils and the surrounding soil material.

Loess is composed mainly of quartz, feldspar, mica, calcite (carbonate), clay minerals (e.g. kaolinite, illite), and organic matter. Among them, calcite (carbonate) also contains <sup>14</sup>C formed during the reaction  $\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{+2} + 2\text{HCO}_3^-$ . Calcite has a very complex origin—e.g. it may come from the source area together with dust (loess material) and/or it may be precipitated by rainfall or from pedogenic processes. Calcite/carbonate formed during the latter 2 processes can be regarded as an in situ “secondary mineral.” Theoretically, the age of such minerals represents the soil formation time. Unfortunately, it is impossible to separate this secondary mineral from the original source. To offset this problem, inorganic matter is also dated. The result is a mixed inorganic test sample that is usually older than the sample’s formation age; this is the “dead carbon” effect and can be described as follows. When dating soil inorganic matter, we assume that  $I = I_0 e^{-\lambda t}$ , where  $I$  represents the <sup>14</sup>C concentration influenced by dead C, which directly affects dating accuracy. The age can be revised by the following method when considering or counting the dead-C proportion: if the dead-C proportion is  $X$ , the formula for dating is  $I = I_0(1-X)e^{-\lambda t}$ . If we know the age of the sample tested, then the dead-C proportion will be  $X = [I_0/\exp(-\lambda t)]I_0 = 1 - I/I_0[\exp(-\lambda t)]$ . Taking into account the dead-C proportion and comparing the age obtained from inorganic matter (6306 ± 80 BP) with that of soil organic matter (3682 ± 70 BP [4175 ± 175 cal BP] and 3520 ± 70 BP [3808 ± 90 cal BP]), we estimate that the age of soil inorganic carbon is about 3200–3500 yr older than the soil formation age, if organic matter formed during soil formation.

In loess-paleosol sequences, especially in soil/paleosol layers, the origin of organic matter is also very complex. It primarily includes 1) plant and animal remains decomposed by microorganisms during the pedogenic processes and 2) organic matter transported by flowing water or by wind blowing from surrounding, and possibly older, deposits. These factors influence the initial  $^{14}\text{C}$  concentration of organic matter and the dating results for soil/paleosol.

The organic carbon (humics and humic acid) in the soil material is  $3682 \pm 70$  BP ( $4175 \pm 175$  cal BP) and  $3520 \pm 70$  BP ( $3808 \pm 90$  cal BP), which is on average 1610 yr older than that of the fossil bones/teeth and represents the age of mixed organic carbon in soil. In soil and paleosol layers of loess sequences, most of the microorganisms formed during the pedogenic processes, as there are few microorganisms in material of aeolian origin. Therefore, as discussed previously, the age determined by soil/paleosol organic matter is assumed as the time of soil/paleosol formation. Nevertheless, the organic component in the soil/paleosol is variable and its origin is complex. It is not easy to distinguish them or separate the organic matter, even when we know that the material from the same source has identical chemical characteristics.

The age of paleosol organics (humic and humic acid) is 1610 yr older than that of fossils. If the age of organic matter represents the soil formation time and the age of fossil bone and teeth represents the time of human activity, then from about 3990 to 2380 cal BP there was almost no loess accumulation in the area, and at least 1 deposition hiatus occurred in the studied section.

Grain-size analyses show that the content of fine material (clay  $<2 \mu\text{m}$ ) increased greatly from a depth of 150 cm upwards in the section. A maximum clay content is reached at a depth of  $\sim 120$  cm, while the content of coarse material (grain size  $>63.0 \mu\text{m}$ ) decreased rapidly (Figure 3). This phenomenon implies that there was a change taking place at the time from a cold, dry, windy climate to a mild, humid climate, resulting in weakening wind strength and decreasing dust transportation. Other studies indicate that the period between 5000 and 3000 cal BP was an abnormal global climate phase in the Holocene when global climate fluctuated drastically (Zhang et al. 1998, 2000; Mayewski et al. 2004). Ice-core records from Dunde in Qilian Mountain, south of the Tengger Desert in the upper Yellow River, suggest that the climate in NW China was very unstable during this period, and frequent, violent floods influenced the population stability and social development (Yang and Xia 2001; Xia and Yang 2003; An 2004).

## CONCLUSIONS

This study suggests that with the use of suitable materials and analysis of appropriate components, it is possible to obtain reliable and accurate absolute  $^{14}\text{C}$  ages of samples in loess-paleosol sequences. The most important strategy is to work on carefully selected sections that were continuously deposited and to make measurements on suitable materials. Should artifacts or other human/animal relics appear, it is necessary to test the ages of each material because the section studied might contain hiatuses due either to discontinuous material accumulation or disturbances by human activity. Thus, caution is necessary when interpreting these results, since the tested ages of the artifacts or human/animal relics might be different from that of the surrounding deposits.

The age of inorganic matter in the tested sample is  $6306 \pm 80$  BP ( $7395 \pm 85$  cal BP), which is about 3200–3500 yr older than the estimated soil formation age ( $4175 \pm 175$  and  $3808 \pm 90$  cal BP) obtained by  $^{14}\text{C}$  testing soil organic matter. This difference implies that the majority of inorganic carbon (calcite/carbonate) was formed well before the soil formation or well before the loess material had been deposited. Inorganic and organic carbon fractions form at different times and have different origins and sources. These fractions should be separated when calculating carbon sink-

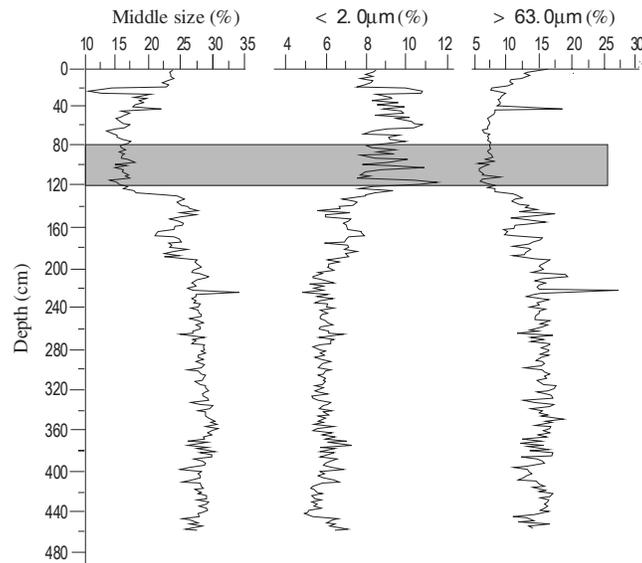


Figure 3 Grain-size distribution along the section; the shaded area denotes the sampling position.

source/releasing amounts. This study has important implications for carbon equilibrium and storage state in the biosphere-lithosphere, since  $\text{CO}_2$  has been inevitably blamed for greenhouse gas effects that result in unprecedented global warming.

The  $^{14}\text{C}$  age of soil organic carbon represents the pedogenic period, which at the time was mild-humid with weakening winds and declining dust transportation when compared to the previous harsh climate. Such pleasant climate conditions were favorable for human activity and animal development. However, during the transition from a harsh to mild-humid climate—as recorded by the ice-core records from Dunde and the lacustrine-fluvial deposits in the southern Tengger Desert and upper Yellow River (Yang and Xia 2001; Xia and Yang 2003)—the unstable climate resulted in unpredictable conditions that sometimes precipitated environmental disasters, including frequent and violent floods that induced famine and massive population migration, thus negatively influencing the population stability and social development.

The appearance of the fossil bones and teeth of sheep and horses indicates that at the time the climatic conditions were suitable for animal development. The artifacts and artificially broken bones indicate human activity in the area, which is consistent with ancient civilization development in recent arid-semiarid NW China. The almost 2000-yr time difference between fossil bones and soil organic matter in the paleosol reveals very low loess deposition rates and a possible depositional hiatus between ~2240 and 4180 cal BP. This result has 2 important implications. First, it demonstrates that the age of organic matter in soil/paleosol might not be the same as artifacts or human relics, as is so often regarded in scientific literature. Second, the time difference implies that a depositional hiatus may exist in the loess-paleosol sequence that has been used for paleoclimate reconstruction. This type of loess-paleosol sequence is usually treated as a continuous deposit; thus, previous interpretations of climate proxies and climate reconstructions might be misleading or wrong.

## ACKNOWLEDGMENTS

This study was supported by the NSFC (40371117), the Hundred Talent Project by the Chinese Academy of Sciences (CAS), and the State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environments (SKLLQG0514). Special thanks to Dr P Grootes and Dr M Frechen for dating the samples and providing detailed discussions of the results that guaranteed the reliability of all dates. The authors thank Prof W M Edmunds and C P Dalton for checking the English, and an anonymous reviewer for valuable suggestions and comments that improved the paper.

## REFERENCES

- An CB, Feng Z, Tang L. 2004. Environmental change and cultural response between 8000 and 4000 cal yr BP in the western Loess Plateau, northwest China. *Journal of Quaternary Science* 19(6):529–35.
- Bellamy PH, Loveland PJ, Bradley RI, Lark RM, Kirk GJD. 2005. Carbon losses from all soils across England and Wales 1978–2003. *Nature* 437:245–8.
- Cao M, Woodward FI. 1998. Dynamic responses of terrestrial ecosystem carbon cycling to global climate change. *Nature* 393:249–52.
- Cox PM, Betts RA, Jones CD, Spall SA, Totterdell JJ. 2000. Acceleration of global warming due to carbon-cycle feedbacks in a coupled climate model. *Nature* 408:184–7.
- Ding Z, Yu Z, Rutter NW, Liu T. 1994. Towards an orbital time scale for Chinese loess deposits. *Quaternary Science Reviews* 13:39–70.
- Guo LB, Gifford RM. 2002. Soil carbon stocks and land use change: a meta analysis. *Global Change Biology* 8:345–60.
- Guo Z, Biscaye P, Wei L, Chen X, Peng S, Liu T. 2000. Summer monsoon variations over the last 1.2 Ma from the weathering of loess-soil sequences in China. *Geophysical Research Letters* 27(12):1751–4.
- Guo ZT, WF, Hao QZ, Wu HB, Qiao YS, Zhu RX, Peng SZ, Wei JJ, Yuan BY, Liu TS. 2002. Onset of Asian desertification by 22 Myr ago inferred from loess deposits in China. *Nature* 416:159–63.
- Houghton RA. 2003. Revised estimates of the annual net flux of carbon to the atmosphere from changes in land use and land management 1850–2000. *Tellus B* 55: 378–90.
- Jickells TD, An ZS, Andersen KK, Baker AR, Bergametti G, Brooks N, Cao JJ, Boyd PW, Duce RA, Hunter KA, Kawahata H, Kubilay N, laRoche J, Liss PS, Mahowald N, Prospero JM, Ridgwell AJ, Tegen I, Torres R. 2005. Global iron connections between desert dust, ocean biogeochemistry, and climate. *Science* 308(1):67–71.
- Knorr W, Prentice IC, House JI, Holland EA. 2005. Long-term sensitivity of soil carbon turnover to warming. *Nature* 433:298–301.
- Kukla G, An ZS, Melice JL, Gavin J, Xiao JL. 1990. Magnetic susceptibility record of Chinese loess. *Transactions of the Royal Society of Edinburgh: Earth Sciences* 81:263–88.
- Liu JQ, Chen TM, Cai LZ. 1994. Dating and reconstruction of the high resolution time series in the Weinan loess section of the last 150,000 years. *Quaternary Science (China)* 3:193–202. In Chinese.
- Mayewski PA, Rohling EE, Stager JC, Karlén W, Maasch KA, Meeker LD, Meyerson EA, Gasse F, van Kreveld S, Holmgren K, Lee-Thorp J, Rosqvist G, Rack F, Staubwasser M, Schneider RR, Steig EJ. 2004. Holocene climate variability. *Quaternary Research* 62: 243–55.
- Porter SC, Zhisheng A. 1995. Correlation between climate events in the North Atlantic and China during the last glaciation. *Nature* 375:305–8.
- Powlson D. 2005. Will soil amplify climate change? *Nature* 433:204–5.
- Schramm A, Mordechai S, Goldstein SL. 2000. Calibration of the  $^{14}\text{C}$  time scale to >40 ka by  $^{234}\text{U}$ - $^{230}\text{Th}$  dating of Lake Lisan sediments (last glacial Dead Sea). *Earth and Planetary Science Letters* 175:27–40.
- Wang S, Tian H, Liu J, Pan S. 2003. Pattern and change of soil organic carbon storage in China: 1960s–1980s. *Tellus B* 55:416–27.
- Wang YQ, Zhang XY, Arimoto R, Cao JJ, Shen ZX. 2005. Characteristics of carbonate content and carbon and oxygen isotopic composition of northern China soil and dust aerosol and its application to tracing dust sources. *Atmospheric Environment* 39:2631–42.
- Xia ZK, Yang XY. 2003. Preliminary study on the flood events about 4 ka BP in north China. *Quaternary Science* 6:667–74. In Chinese.
- Yang XY, Xia ZK. 2001. Summarizing the environmental archaeology development in China. *Progress in Geography* 6:761–8. In Chinese.
- Yin JH, Pen G, Jiao WQ. 1997. A preliminary study on the radiocarbon dating of different organic fractions separated from peat. *Seismology and Geology* 3:227–80.
- Zhang HC. 1993. The carbonate stable carbon and oxygen isotopes of the Jiuzhoutai loess profile and their climate significance. *Journal of Lanzhou University* 29(3):232–40. In Chinese.
- Zhang HC, Ma YZ, Li JJ. 1998. Preliminary research on Holocene paleoclimatic change in the southern Tengger Desert. *Chinese Science Bulletin* 44(16):550–5. In Chinese.
- Zhang HC, Ma YZ, Wünnemann B, Pachur H-J. 2000. A Holocene climatic record from arid northwestern

- China. *Palaeogeography, Palaeoclimate, Palaeoecology* 162:389–401.
- Zhang GL, He Y, Gong ZT. 2004. Characteristics of organic carbon distribution in anthropogenic soils and its implication on carbon sequestration. *Quaternary Science (China)* 2:149–59. In Chinese.
- Zhisheng A, Tunghseng L, Yanchou L, Porter SC, Kukla G, Xihao W, Yingming H. 1990. The long-term paleomonsoon variation recorded by the loess-paleosol sequence in central China. *Quaternary International* 8: 91–5.
- Zhisheng A, Kutzbach JE, Prell WL, Porter SC. 2001. Evolution of Asian monsoon and phased uplift of the Himalaya-Tibetan Plateau since Late Miocene times. *Nature* 411:62–6.
- Zhou QY, Huang H Ch, Pang JL. 2004. Study in the relationship between pedogenic environment changes and human impact in the Holocene soil of the loess plateau in the upper reaches of Jing He. *Arid Land Geography* 4:43–51. In Chinese.