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Use of Rubidium to Date Loess and Paleosols of the Louchan Sequence, Central China

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Rb concentrations, analyzed at 20-cm intervals from the Luochuan sequence of loess and paleosols, are sensitive to the loess–paleosol alternation controlled by monsoon climate. Because it is geochemically immobile, Rb can be well preserved in the loess–paleosol sequence after deposition, and its concentration depends mainly on properties of the winter monsoon-blown dust and on intensity of the summer monsoon-induced pedogenesis. A curvilinear relation has been developed between the measured Rb-concentration and the apparent sedimentation rate for the last glacial–interglacial cycle. This relation provides a time scale that corresponds well with the presently accepted ages for paleomagnetic reversals of Brunhes/Matuyama and Jaramillo events. With allowance for reduced Rb concentrations caused by early Pleistocene climate, the Rb-based time scale is also consistent with the boundary ages of other major paleomagnetic reversals of the past 2.58 myr. © 2000 University of Washington.

Key Words: **Rb distribution; sedimentation rate; Quaternary time scale; Loess Plateau; East Asian monsoon.**

INTRODUCTION

Loess deposits and intercalated paleosols on the Loess Plateau in central China span the past 2.5 myr and provide a continuous proxy record of variations in the East Asian monsoon climate (An *et al.*, 1990, 1991). Geological and biological evidence indicates that the Chinese loess represents deposition of dust transported by northwest winter monsoon winds, whereas the intercalated paleosols formed under strengthened summer monsoon conditions at times of reduced dust influx (An *et al.*, 1991).

To study the details of climate history registered in the loess and to correlate them with other global climatic time series, it is essential to establish a detailed time scale for the Chinese loess sequence. Most time scales for the loess have been based on the orbital tuning or on the correlation with the marine isotopic stages (Ding *et al.*, 1994; Lu *et al.*, 1999). For example, magnetic susceptibility intervals have been used to approximate geological time by linear interpolation between ages of the Pleistocene paleomagnetic reversals (Kukla *et al.*, 1988). By comparing with cooling events in the northern Atlantic, Porter and An (1995) used thermoluminescence-determined time points to calculate a time scale for the upper 12-m-depth part of the sequence. More recently, a new method for assessing Quaternary time has been established based on the grain size characteristics in the Luochuan loess–paleosol sequence (Vandenberghe *et al.*, 1997). This method represents important progress toward establishing a detailed time scale that is nearly independent of astronomic tuning.

Some recent studies have shown that Rb concentration differs between loess and paleosols in the loess sequence in China (Gallet *et al.*, 1996; Chen *et al.*, 1996) and can indicate variations of the East Asian monsoon strength (Chen *et al.*, 1999). In this paper, we develop the Rb-based age model through the last glacial–interglacial cycle based on Rb concentrations and apparent sedimentation rates. Then we use the model to extrapolate a time scale for the remaining, lower part of the

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Luochuan loess–paleosol sequence, which includes the Brunhes/Matuyama and Matuyama/Gauss magnetostratigraphic polarity reversals.

Rb DISTRIBUTION AND PALEOCLIMATE

Analyzed samples were collected at 20-cm intervals from the classic section of Luochuan on the well-studied Chinese Loess Plateau (Liu, 1985; Kukla and An, 1989; An *et al.*, 1990, 1991) (Fig. 1). This profile consists of three units, the Malan, Lishi, and Wucheng formations (Kukla and An, 1989). Deposits of Tertiary age (the Red Clay) are found at the base of the section. Rb concentrations were determined by X-ray fluorescence, which allows rapid, precise, and fully automated measurements (Leake *et al.*, 1969). Results show that the value of Rb concentration in the section is higher in paleosols and lower in the loess (Fig. 2), with average values of 109 and 97 ppm, respectively. We also analyzed Rb concentrations in different grain size fractions from the last glacial loess unit (L1) and the last interglacial paleosol unit (S1) in Luochuan. These analyses show that Rb concentrations in both loess and paleosols vary inversely with grain size (Fig. 3).

Rb is a typical dispersed element that is not associated with any specific Rb mineral (Wedepohl, 1970) but is present in K-containing minerals, such as mica, K-feldspar, and clays. The Rb concentration can be as high as 1600 ppm in K-feldspar (Wedepohl, 1970), and Rb/Sr ratios in illite can be up to 6.46 (Chaudhuri and Brookings, 1979). Therefore, the variation of Rb concentrations in the loess and paleosol samples can be explained by differences in the mineral composition and grain size of the wind-blown dust, which are both related to the winter monsoon strength. For instance, during glacial periods, dust carried by strong winds of the Mongolian anticyclone (Pye and Li, 1989) carried quartz, feldspar, and carbonates that give relatively high sedimentation rates and low Rb concentrations in the loess. In contrast, both sedimentation rate and grain size were reduced when weaker winds during interglacial periods carried smaller particles, such as clay minerals (Ji *et al.*, 1999a, 1999b), thus leading to higher Rb content in paleosols.

Rb is mainly retained in the weathering zone by adsorption or exchange onto clays (Nesbitt *et al.*, 1980). Such retention of Rb can be confirmed by low concentration, low distribution coefficient, and short residence time in ground water (Taylor and McLennan, 1985). Like K, Rb may not be removed from a weathering section until extensive K-feldspar alteration occurs (Nesbitt *et al.*, 1980). Mineralogical and chemical studies show that pedogenisis in the loess–paleosol sequence on the Loess Plateau includes decalcification and mechanical migration of fine particles without much chemical alteration of silicate minerals (Rutter *et al.*, 1991; Han *et al.*, 1998). Our result from acid leaching experiments for both loess and paleosol samples further confirms that Rb is strongly bound to particles; movement of Rb due to leaching can be virtually excluded (Chen *et al.*, 1998). But enhancement of Rb concentrations in soil horizons can occur during pedogenic weathering processes because, as suggested by Brimhall and Dietrich (1987), the removal of soluble species in the weathering profile leads to an increase in the concentrations of relatively insoluble components. So Rb enrichment can be expected to occur in paleosols due to the removal of Na- and Ca-containing minerals, such as carbonates.

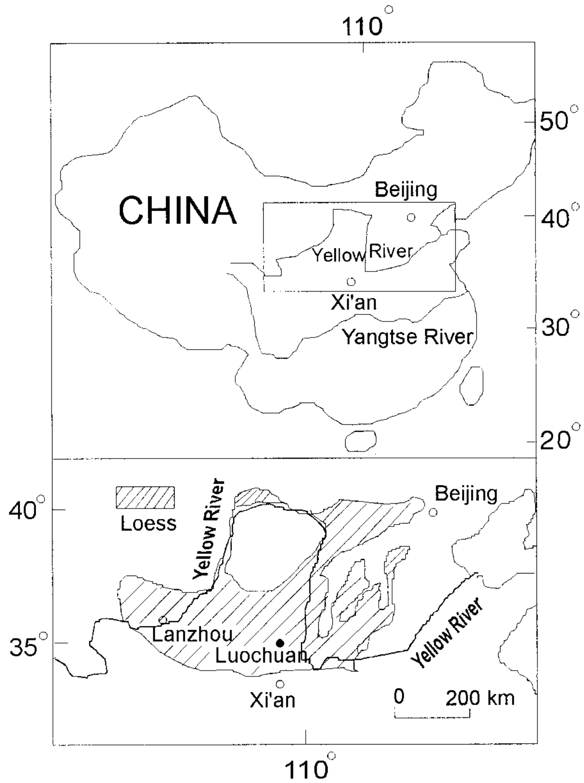

FIG. 1. Location of Luochuan section on the Loess Plateau of China.

The Rb distribution patterns in the Luochuan section imply that: (1) Rb concentrations in the loess and paleosols are strongly related to grain size and, hence, the dust accumulation rates that are largely determined by the winter monsoon strength; (2) Rb derived from the eolian source region may be well preserved in loess–paleosol sections, although its enrichment may occur as a result of postdepositional weathering of soluble species; (3) variations of Rb concentrations are correlated with changes of the paleomonsoon system in China through deposition and pedogenesis of the dust. Details of this correlation appear below.

RELATION OF Rb CONCENTRATIONS TO SEDIMENTATION RATES

The average dust accumulation rate during glacial periods on the Loess Plateau is about 0.1 mm/yr, possibly two or three times higher than during interglacial periods (Liu, 1985; Maher, 1998). After deposition, as the loess is exposed to water

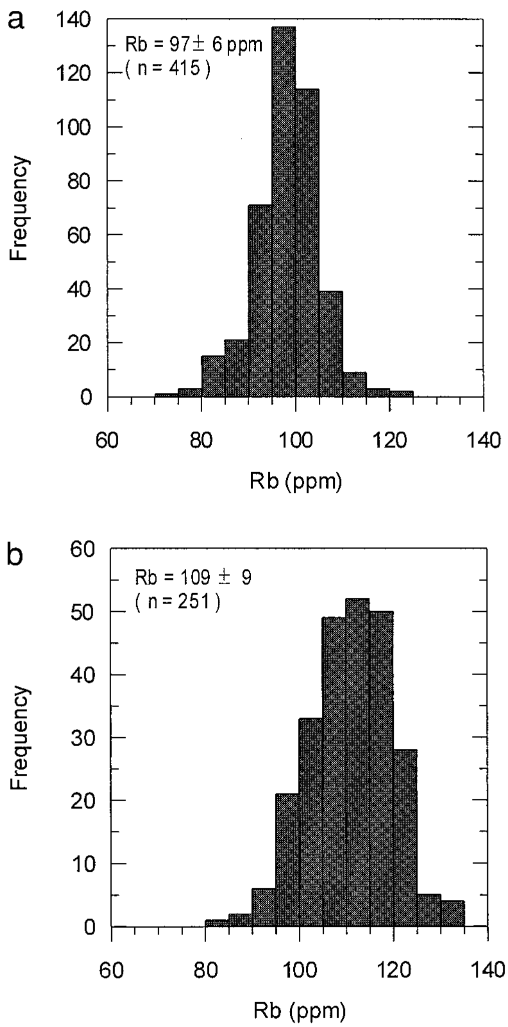

FIG. 2. Histograms of measured Rb concentrations in loess (a) and paleosol (b) samples from the Luochuan profile: Rb, mean values of rubidium concentrations; *n*, sample numbers analyzed.

and atmospheric gases, minerals within the loess decompose selectively and at varying rates. If the weathering zone reaches a depth of 1 m from the ground surface, as suggested by Maher (1998), the residence time for the loess within the zone will be about 10,000 yr (at an accumulation rate of 0.1 mm/yr) and even longer for the paleosols. So the pedogenic processes that produced paleosols must have been active during the accumulation of loess (Verosub *et al.*, 1993). In other words, loess deposition and pedogenesis were competing processes at all times, and the presence of a paleosol only indicates that the latter was predominant (An *et al.*, 1990; Verosub *et al.*, 1993). Hence loess can be viewed as a kind of soil, although a very immature one (An *et al.*, 1990).

It can be deduced that the initial dust accumulation rate has been changing in the loess–paleosol sequence at all times because of changes in thickness of the loess and paleosol units as a result of weathering or pedogenesis. That is, the measured sedimentation rate (defined as the ratio of present-day layer thickness to duration of deposition) from both loess and paleosol units is not equal to the original or true dust accumulation rate, but it contains apparent changes caused by pedogenesis. Because the initial dust accumulation rate is determined by the strength of the winter monsoon (Ding *et al.*, 1994; Porter and An, 1995; Vandenberghe *et al.*, 1997), and the pedogenesis on the Loess Plateau is controlled by the oscillation of the summer monsoon (An *et al.*, 1991; Han *et al.*, 1998), the changes in apparent sedimentation rate register the alternating rise and decline in the intensity of East Asian summer and winter monsoons.

Rb distribution in the Luochuan loess–paleosol sequence indicates that the measured Rb concentrations (C_{Rb}) in loess or paleosol samples are determined by both initial Rb concentrations in dust ($C^{\mathrm{i}}_{\mathrm{Rb}}$) and pedogenic contribution (ΔC_{Rb}), which can be expressed as

$$C_{\mathrm{Rb}} = C^{\mathrm{i}}_{\mathrm{Rb}} + \Delta C_{\mathrm{Rb}}. \tag{1}$$

Because Rb is of inert geochemical behavior during pedogenesis, ΔC_{Rb} depends only on the lost percentage (L) of the soluble constituents in the dust, that is,

$$\Delta C_{\mathrm{Rb}} = C^{\mathrm{i}}_{\mathrm{Rb}} \cdot L/(1 - L). \tag{2}$$

Thus, pedogenic contributions can be calculated from amounts of materials removed from the loess. For example, if 20% of the carbonates in loess are totally removed during pedogenesis, Rb concentrations in paleosols increase by 25%. Equations (1) and (2) yield

$$C_{\mathrm{Rb}} = C^{\mathrm{i}}_{\mathrm{Rb}}/(1 - L). \tag{3}$$

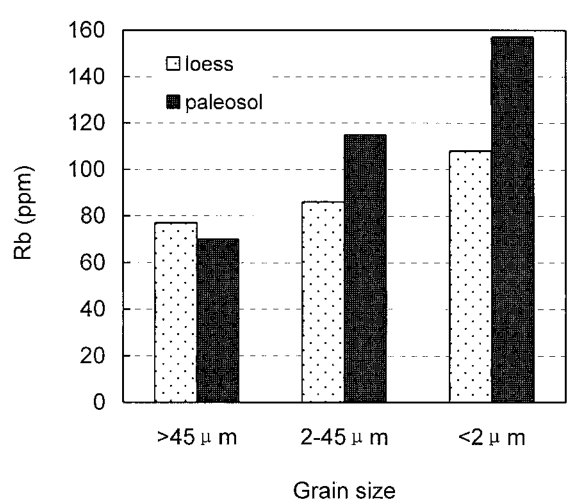

FIG. 3. Rb concentrations in different grain-size fractions (i.e., <2 μm, 2–45 μm, >45 μm) of loess (L1) and paleosol (S1) from the Luochuan section.

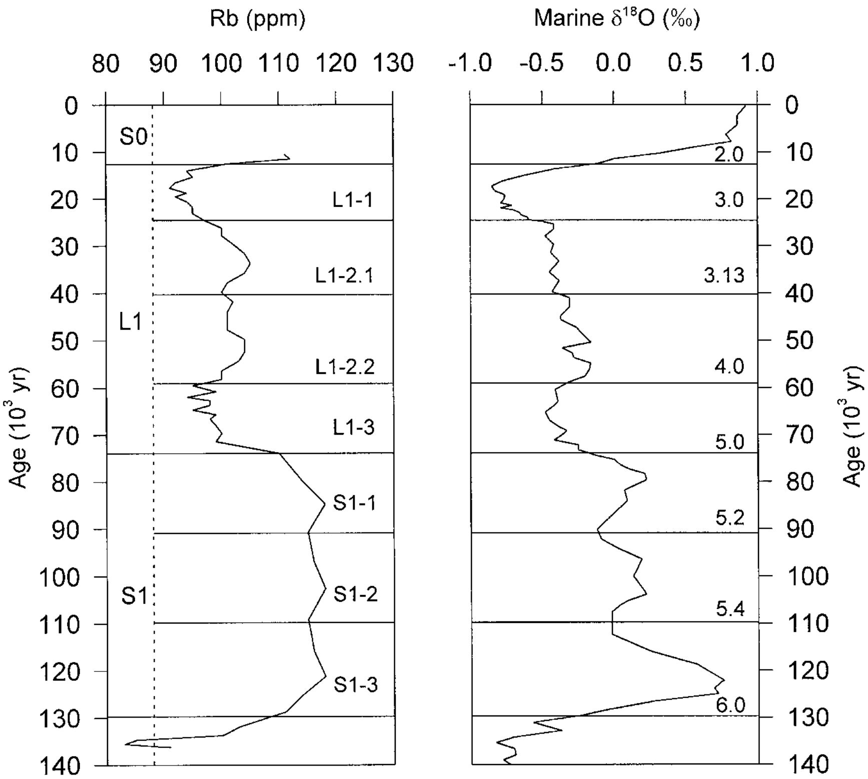

FIG. 4. Rb concentration variations of Luochuan section for the last 130,000 yr, compared with the orbitally tuned oxygen isotope curve (Martinson *et al.*, 1987): S0, Holocene soil; L1, loess of the Malan Formation composed of four intervals (L1-1, L1-2.1, L1-2.2, and L1-3); S1, paleosol of the Lishi Formation subdivided into three intervals (S1-1, S1-2, and S1-3).

This equation indicates that the measured C_{Rb} is quantitatively related to the initial Rb concentration ($C^{\mathrm{i}}_{\mathrm{Rb}}$) and the pedogenic effect (L), both of which are highly correlated with paleoclimate on the Loess Plateau.

As mentioned earlier, Rb is strongly attached to fine grains in dust carried by winter monsoon winds from the desert. During interglacials, weaker winter monsoons produced more fine-grained fractions in the initial dust with relatively high Rb concentrations. Rb is further enriched by summer monsoon-induced pedogenesis that removes soluble materials. Conversely, during cold and dry glacial periods, stronger winter monsoon winds carry coarser dust onto the Loess Plateau, resulting in relatively low initial Rb concentrations. When the summer monsoon was relatively weak, the dust also suffered less weathering, and less consequent increase in Rb concentration.

To look for a relationship between sedimentation rate and Rb concentration, we selected the uppermost part of the sequence (the last 130,000 yr) for regression analysis. We made this selection for several reasons: (1) The Rb distribution curve of the section correlates strongly with the orbitally tuned δ^{18}O curve from Martinson *et al.* (1987) (Fig. 4). (2) This section has been dated by thermoluminescence (Forman, 1991) and has also been correlated with other high-resolution climatic records (Porter and An, 1995; An and Porter, 1997). This previous work enables us to select the ages for calculating sedimentation rates of seven intervals in the section. (3) The section includes different sedimentation rates of dust accumulation under different climatic conditions such as the last glacial maximum, the last interglacial, and mild glacial (marine oxygen isotope stage 3) conditions. Therefore, we assume that the selected section is representative for establishing a relation between Rb concentrations (C_{Rb}) and sedimentation rates (SR) in the sequence.

We calculated the sedimentation rate for seven intervals within the last interglacial–glacial cycle based on their thickness and duration of deposition (Fig. 4). Through correlation analysis we obtain the relation between C_{Rb} (ppm) and SR (mm/yr) as follows:

$$\mathrm{SR} = 141.5e(-0.0712C_{\mathrm{Rb}}). \tag{4}$$

The correlation coefficient is very high ($R^2 = 0.97$) (Fig. 5). Using this Rb concentration model, we calculated SR for some typical loess and paleosol units which were deposited in climate extremes on the plateau (Guo *et al.*, 1998). Comparison of the results with the sedimentation rates obtained based on the oxygen isotope stages model (see Table 1) indicates that the values of SR derived from the two models are not only consistent with each other but also agree well with a generally

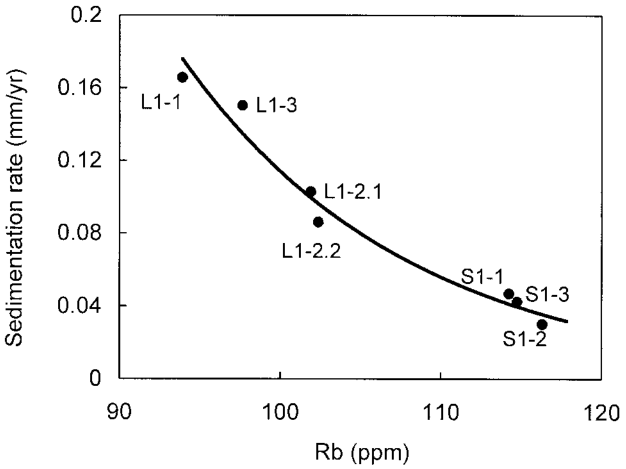

FIG. 5. Relationship between Rb concentration and apparent sedimentation rate in the upper part of the Luochuan section. Labels for the seven intervals are the same with those in Figure 4.

accepted order of the changes in East Asian monsoon circulation during these typical climatic periods (Liu, 1985; Kukla, 1987).

TIME SCALE BASED ON THE Rb DISTRIBUTION

Based on exponential equation (4), the age (T_n) of an individual interval (n) can be calculated as

$$T_n = T_0 + \sum^{n} a_i/\mathrm{SR}_i, \qquad (5)$$

where T_0 is the known age of the bottom of the paleosol (S_0) which corresponds to the marine oxygen isotope stage 2 (Martinson *et al.*, 1987), and where a_i and SR_i respectively represent the thickness (mm) and the sedimentation rate (mm/yr) of each measured interval i. Equations (4) and (5) combined allow a Quaternary time scale to be computed.

The computed ages correspond well with the magnetostratigraphic ages derived from the Brunhes/Matuyama boundary (0.78 myr; Singer, 1995) and the Jaramillo reversals, deviations of which are less than 1% (Table 2). This result means the relationship between the Rb concentration and the sedimentation rate found in the upper part of the Luochuan profile is representative of the entire Lishi Formation.

However, the Rb-based ages in the Wucheng Formation differ substantially from the paleomagnetic ages. For example, the age for the end of the Olduvai is calculated as 1.478 myr, about 0.292 myr younger than its magnetostratigraphic age. However, the magnetostratigraphic dating of the Wucheng Formation has not been checked by magnetic susceptibility (Kukla *et al.*, 1988), and it conflicts with ages inferred from grain-size trends (Vandenberghe *et al.*, 1997). Huissteden *et al.* (1997) used a grain-size model to recalculate ages of the Luochuan loess sequence, including an allowance for compaction. But compaction accounts for only 0.05–0.08 myr of the difference from the paleomagnetic ages.

Comparing Rb concentrations in the Wucheng Formation with those in the younger loess sequence, we found that Rb distribution in the Wucheng Formation deviates gradually from the general trend of the whole section (Fig. 6). So there might exist a systematic reduction of Rb concentration in the Wucheng Formation. If there are no changes in dust source area and in atmospheric circulation, perhaps Rb-enriched clays or other minerals migrated during or after dust deposition in the early Pleistocene. X-ray diffraction analyses show that amount of Rb-rich minerals such as illite, mica, and chlorite in the Wucheng Formation are less common than in the Lishi Formation (Fig. 7). This lower amount of fine-grained minerals may be related to early Pleistocene climate conditions, which have been inferred to be moister and warmer (Liu, 1985; Kukla and An, 1989). Such conditions would have led the complex paleosols in the Wucheng Formation to suffer more intensive weathering than those in the Lishi and Malan Formations (Derbyshire *et al.*, 1995). We believe that these climate con-

TABLE 1
Sedimentation Rates (SR) of Loess and Paleosol Units from the Luochuan Section

Loess and paleosol units	Thickness (m)	Oxygen isotope stage model: Corresponding $\delta^{18}O$ stages	Duration (10^3 yr)	SR1 (mm/yr)	Rb concentration model: Rb (ppm)	SR2 (mm/yr)
L1	7.6	2 ~ 4	59	0.13	99	0.12
S1	2.6	5	57	0.05	113	0.05
S4	2.7	11	61	0.04	116	0.04
S5	5.2	13 ~ 15	142	0.04	120	0.03
L9	9.2	22 ~ 24	59	0.16	95	0.16

Note. Nomenclature of the loess and paleosol units follows Kukla and An (1989). Correlation of the loess and paleosol units with the oxygen isotope stages follows Liu (1985) and Kukla (1987). Duration of the oxygen isotope stages is from Imbrie *et al.* (1984) and Ruddiman *et al.* (1986). SR1 is defined as the ratio of layer thickness to duration while SR2 is calculated from Rb concentration.

TABLE 2
Comparison of Calculated Ages of Magnetic Reversals in Luochuan Section and Defined Ages

Magnetostratigraphic boundary	Defined age (10^3 yr)	Calculated age (10^3 yr)	Percentage age deviation (%)
Brunhes/Matuyama	780	781	0.1
Top Jaramillo	990	985	0.5
Base Jaramillo	1070	1066	0.4
Top Olduvai	1770	1782	0.7
Base Olduvai	1950	1894	2.9
Matuyama/Gauss	2580	2532	1.9

Note. Magnetostratigraphic boundaries defined by Kukla and An (1989). Ages defined by Shackleton *et al.* (1990), Langereis *et al.* (1994), and Singer (1995).

ditions were favorable for soil erosion that caused clay high in the soil profile to be transported by running water. Such erosion may have reduced Rb concentrations in the Wucheng Formation.

To adjust for loss of Rb by erosion, we tentatively applied a correction, like the method used by Vandenberghe *et al.* (1997), to Rb concentrations in the Wucheng Formation. Here a second-order polynomial has been fitted to the shift of the Rb concentration with depth in the Wucheng Formation to restore the general trend in Rb distribution in the section. A compensatory value for the Rb concentration for each layer in the Wucheng Formation has been obtained and added to the measured value. The final time scale shows a good approximation to the Olduvai reversals (Shackleton *et al.,* 1990) with a difference of less than 0.06 myr from the paleomagnetic reversals (Table 2 and Fig. 6). The established time scale can be extrapolated into the Pliocene (the Red Clay). The difference between the calculated age and the expected age of the Gauss/Matuyama boundary (2.58 myr; Langereis *et al.,* 1994) is 0.048 myr. This dating obviates a hiatus that Vandenberghe *et al.* (1997) placed between the Quaternary loess sequence and the Pliocene Red Clay.

CONCLUSIONS

1. Rb concentrations in the Luochuan loess–paleosol sequence are sensitive to loess–paleosol alternation and are inversely proportional to sedimentation rate. The Rb distribution record thus provides a proxy indicator of East Asian monsoon circulation.

2. The apparent sedimentation rate and the measured Rb concentrations have a curvilinear relationship in the well-dated

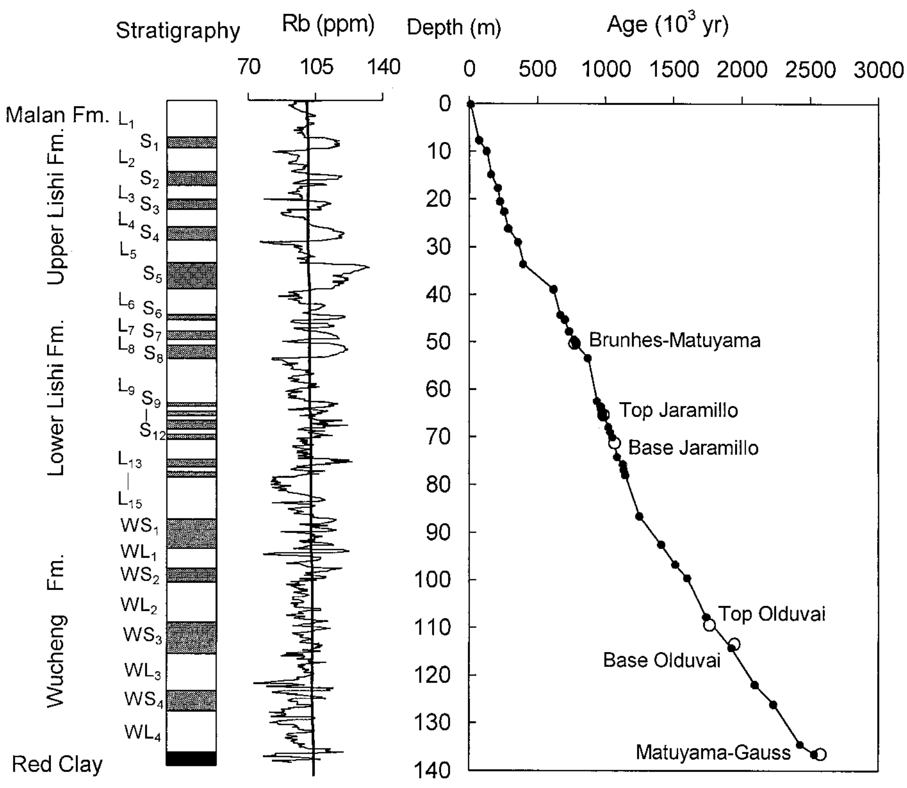

FIG. 6. Depth–age curve derived from the Rb concentration model compared with the paleomagnetic reversals: L, loess units of the Malan and Lishi Formation; S, paleosol units of the Lishi Formation; WL and WS, loess and paleosol units of the Wucheng Formation. Rb distribution in the Wucheng Formation deviates progressively from the general Rb trend (the long solid line) in the Luochuan section.

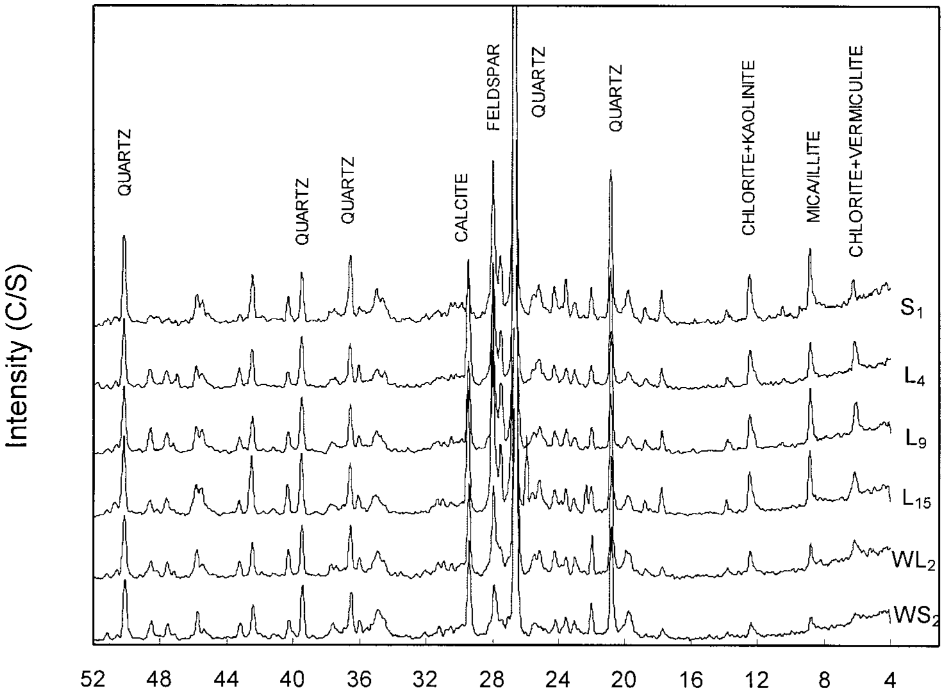

FIG. 7. X-ray diffraction spectra (Cu$K\alpha$) of bulk samples from the Luochuan section. Mica/illite and chlorite are less abundant in the Wucheng Formation (samples WL2 and WS2) than in the Lishi Formation (samples S1, L4, L9, L15).

upper part (the last glacial–interglacial cycle) of the sequence. This relationship can be used to extrapolate ages to the lower boundary of the Lishi Formation. The calculated ages compare well to the paleomagnetic ages of the Brunhes/Matuyama boundary and the Jaramillo reversals.

3. With allowance for Rb removed from the Wucheng Formation, the time scale approximates the presently accepted ages for the Olduvai reversal and the Gauss/Matuyama boundary.

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