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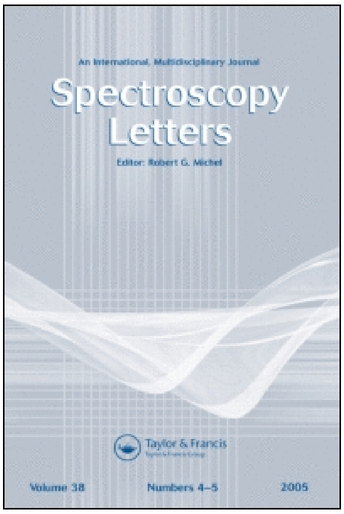

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^{57}Fe-Mössbauer Studies on Loess-Palaeosol Samples from the Luochuan Section, Loess Plateau of Central China

Yu Zhi[ab]; Chen Jun[a]; Ji Junfeng[a]
[a] Department of Earth Sciences, Institute of Surface Geochemistry, State Key Laboratory of Mineral Deposit Research, Nanjing University, Nanjing, China [b] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing, China

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^{57}Fe-MÖSSBAUER STUDIES ON LOESS-PALAEOSOL SAMPLES FROM THE LUOCHUAN SECTION, LOESS PLATEAU OF CENTRAL CHINA

Zhi Yu[1,2,*] Jun Chen[1], Junfeng Ji[1]

[1] Institute of Surface Geochemistry, State Key Laboratory of Mineral Deposit Research, Department of Earth Sciences, Nanjing 210093, Nanjing University, China
[2] Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing 210093, Nanjing University, China

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INTRODUCTION

Information about ancient climate can be obtained by the study of loess-palaeosol sequences that relate to the periodic changes in palaeoclimate conditions[1-3]. Various parameters, such as carbonate contents, ratio of iron valence state $Fe^{3+}/(Fe^{3+}+Fe^{2+})$ or Fe^{3+}/Fe^{2+}, magnetic properties, ^{10}Be concentration, record of $\delta^{18}O$ in deep-sea sediment, and Rb/Sr ratios are used to interpret traces of palaeoclimate. In particular, magnetic properties of loess-palaeosol have been recently linked as stratigraphic definition and correlation with paleoclimatic reconstruction[4-5]. The source of magnetic susceptibility for Loess-palaeosol is most attentive since its correlation with loess weathering is still not united for some loess-palaeosol sequences, including those of the Chinese Loess Plateau, Tajikistan, the Czech Republic, Siberia, Alaska, and Argentina. The first three sequences, showing maximal value of susceptibility

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associated with the most developed paleosol, are absolutely opposite to the latter three sequences. Previous investigations for loess-palaeosol from the Luochuan area, Loess Plateau of Central China, and been successfully made by descriptions for profiles of magnetic susceptibility, such as mica/chlorite ratios, and Rb/Sr ratios, indicating the trace of palaeoclimate, for instance the winter wind strength or the East Asian monsoon.[6-10] The relationships between magnetic susceptibility and those parameters are indirect, but induced by the same factor, the generation of loess-palaeosol.

The loess-palaeosol magnetism is in general originated from iron compounds since iron oxides, showing varieties of magnetic behaviors, such as ferromagnetic maghemite or magnetite, antiferromagnetic hematite or goethite and paramagnetic lepidocrocite, ferrihydrite and other iron-bearing minerals, are often associated with loess-palaeosol weathering. Consequently, studies for iron compounds in loess-palaeosol become more attractive, worthwhile and meaningful, while it may help us to have better understanding of the development process of loess-palaeosol. To distinguish the magnetism in loess-palaeosol from other kinds of iron-bearing minerals has been a very interesting topic for geophysicists since the discovery of correlation between magnetic susceptibility and weathering of loess. Mössbauer spectroscopy has proved to be a very useful tool for the investigation of iron compounds and iron-bearing minerals[11]. Magnetic hyperfine structure, iron valence and spin states in minerals are easily detected using the Mössbauer technique. An advantage to using Mössbauer spectroscopy in studies of loess-palaeosol is that it can analyze amorphous, poorly crystallized minerals or ultrafine grain particles of soils, prior to powder X-ray diffraction. The application of the Mössbauer effect on mineral science has been reviewed in several articles[12-13].

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EXPERIMENTAL

The samples studied were from the upper part of the Luochuan section which is well studied[1-3], included the early Holocene (S0) paleosol, the L1 loess (or Malan Loess = last glaciation), and the S1 (last-interglacial) paleosol. A detailed description of these samples was given in previous papers [8-10].

The Mössbauer effect measurements were performed at room temperature using a conventional constant acceleration spectrometer (Austin S-600) in transmission mode with a ^{57}Co/Pd source (at room temperature). All isomer shifts (I.S.) are reported with respect to the ^{57}Co/Pd source (at room temperature). The spectra were analyzed using a least-squares fitting procedure with Lorentzian lines in the MOSFUN program. In order to compare Mössbauer effect (absorption intensity) for the series of samples, all samples were taken at the same weight and measured under identical conditions. The magnetic susceptibility was measured in the State Key Laboratory of Loess and Quaternary Geology in Xi'an, with a Bartington MS2 meter.

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RESULTS AND DISCUSSION

1. Mössbauer effect

Selected Mössbauer spectra for loess-palaeosol from the Luochuan section shown in Figure.1 demonstrate a mixed-pattern of Fe^{2+} and Fe^{3+}. Most of these spectra can be fitted in a composition of three doublets (D1, D2 and D3), and a few spectra (for 93L130, 93l480, 93L560, 93L839) have to be added in a small amount (~1%) of the D4 doublet. Identified Mössbauer parameters for each doublet in all samples of the sequence indicate the same components of iron sites in loess-palaeosol, while

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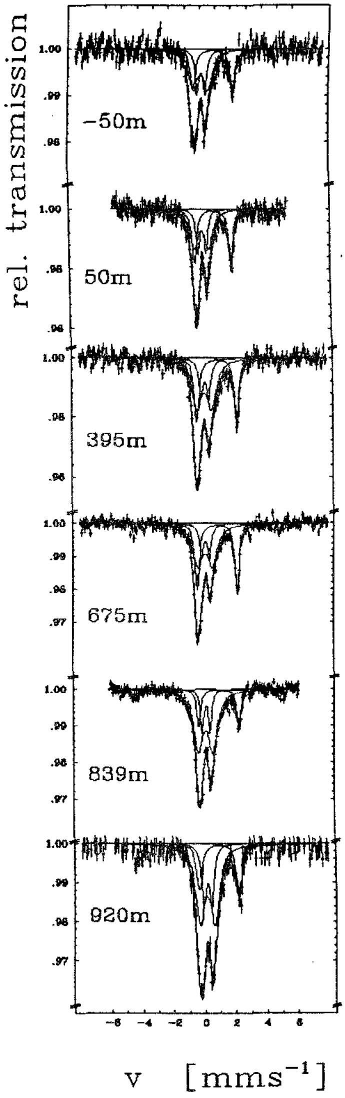

Figure 1. Selected Mössbauer spectra for loess-palaeosol from Luochuan sequence.

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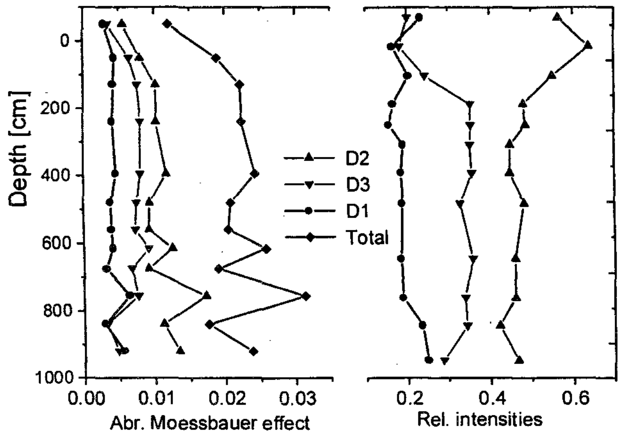

Figure 2. The profiles of Mössbauer effects and relative intensity for each doublet vs. Depth for the loess-palaeosol sequence.

TABLE 1
Mössbauer parameters for samples from Luochuan Loess-palaeosol section

Sample/doublet	D1	D2	D3	D4
Q.S.	0.51	0.95	2.60	2.27
I.S.	0.19	0.16	0.93	0.13

intensities of each doublet vary with the depth of sample collected (Figure 2). Typical parameters are listed in Table 1. According to a classification of iron valence from isomer shifts, D3 with larger I.S.~0.93 mm/s is easily refined from a ferrous iron site in a high spin state, while D1, D2 and D4 (I.S.<0.20mm/s) are attributed to ferric iron sites significantly.

In the study of x-ray diffraction data for the Luochuan sequence samples, a substantial amount of chlorite was found in the loess-palaeosol, and about 15% FeO consisted in chlorite from the estimation of diffraction data. So it is reasonable to attribute D3 species to the silicate iron sites in the layers of clay minerals, for example in that of chlorite, where the ferrous ion with octahedral configuration is in a high spin state. Similar Mössbauer parameters for Fe^{2+} in chlorite was also reported by Graham et al., although a minor quantity (~2%) of this component was shown in the spectrum at room temperature.[14]

The unique D4 species with I.S.~0.13mm/s is assigned to iron(III) but with the Q.S.~2.27mm/s it deviates from standard value of Fe(III), so much so that the usual octahedral or tetrahedral configurations cannot be applied for this iron site. It is possible from a defect iron site, where one or more neighbor oxygen positions of iron are vanishing, to construct a strong asymmetric structure with a large electronic gradient field in the iron nucleus. The very low intensity of this species is not important for our discussion of loess-palaeosol, but in extent defects of this site imply the influence on loess-palaeosol from a palaeoclimate. This point is proved by using a process with HCl solution on loess-palaeosol samples, in which a high of 10% of this species was found as a result of oxygen loss after boiling the material in 10% hydrochloric acid.

In order to observe iron contents versus depth from the Mössbauer effect, areas of each subspectrum and their area sum, determined by dividing the baseline value, were calculated and plotted together with relative intensities of each species in Figure.2. It exhibits low iron content of Holocene (S0) palaeosol in the surface materials, nearly constant iron content of the Malan (L1) loess (200-600cm), and unstable iron content of S1 palaeosol (>750cm), indicating influences of palaeoclimate.

2. Ultrafine particles and amorphous particles

Unlike other Mössbauer studies for Chinese loess-palaeosol sequences shown with

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some obvious hyperfine magnetic sextets from magnetite or maghemite,[15-19] all Mössbauer spectra in this sequence have no notable hyperfine magnetic species at room temperature. However, this Mössbauer pattern does not mean there is no existence of such ferrimagnetic particles in our Loess-palaeosol section since ultrafine grain magnetic particles often exhibit superparamagnetic behavior and contribute only a doublet in the Mössbauer effect at high temperatures. It is well known that superparamagnetic behavior for ultrafine superparamagnetic particles depends upon temperature because of relaxation rate decreasing by temperature decreasing.

Either for inspection of superparamagnetism or for characterization of D1 and D2 in these samples, Mössbauer spectra were recorded for samples 93L839 and 93L615 at various particle sizes. Results are shown in Figure 3 and Table 2, an obvious size effect was found. Intensities of each doublet varying with particle size reflect the relative portion changes of iron compounds versus particle size. The disappearance of the ferrous doublet D3 as the particle size becomes smaller than 0.1μm agrees with the outcome of ferrous in silicon clay minerals of loess-palaeosol. In contrast, the intensity of the D1 doublet decreases significantly as particle size increases; particularly when there is no D1 doublet for sample 93L839 for particle sizes larger than 45μm. Therefore, the D1 doublet might be from ultrafine particles, and shows superparamagnetic behavior at room temperature. The appearance of the D1 doublet for samples between 0.1μm-45μm particle size may be explained as two major factors: (1) the separation for particles with different size in our sample preparation is not perfect, so some ultrafine particles are still mixed in with the larger size samples. (2) Ultrafine grain particles are not free in the soil and might be absorbed into the layers of silicate compounds.

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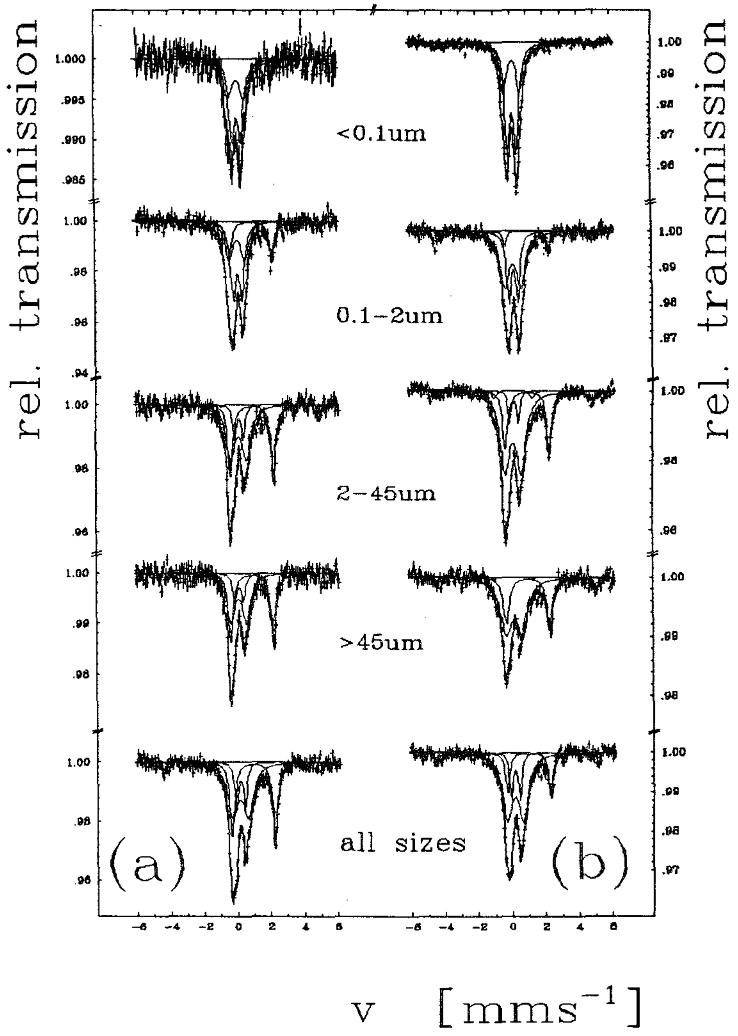

Figure 3. Mössbauer spectra for loess-palaeosol at various grain sizes.
(a) for location 93L839
(b) for location 93L615

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TABLE 2
Relative intensities (%) for each subspectrum from sample 93L839 and 93L615

Sample	**931839**				**931615**			
Size/doublet	**D1**	**D2**	**D3**	**D4**	**D1**	**D2**	**D3**	**D4**
<0.1μm	**62.8**	**37.2**	**0**	**0**	**58.1**	**41.9**	**0**	**0**
0.1-2μm	**36.6**	**57.2**	**6.2**	**0**	**53.5**	**37.0**	**9.5**	**0**
2-45μm	**8.7**	**62.4**	**25.9**	**3.0**	**13.1**	**48.7**	**37.2**	**1.0**
>45μm	**0**	**66.0**	**33.0**	**1.0**	**13.6**	**45.1**	**41.3**	**0**
All size	**16.6**	**63.9**	**18.5**	**1.0**	**15.8**	**48.7**	**35.5**	**0**

In analysis of doublet D2 with Q.S.=0.95mm/s and I.S.=0.16mm/s, its relative intensity is the strongest, somewhat independent upon the size of particles, and the doublet with quite large width of 0.5mm/s demonstrates an uncertain environment for this species. However, powdered x-ray diffraction does not show any peak for such a crystallized iron compound. Consequently, the D2 species is attributed to amorphous iron oxides or iron compounds low in crystalline iron complexes in loess-palaeosol, such amorphous complexes are possible ferrihydrite compounds which exhibit similar Mössbauer parameters.

3. Correlation with magnetic susceptibility and palaeoclimate

A high value over $200\bullet10^{-8}m^3kg^{-1}$ of magnetic susceptibility was found for samples with low iron content (<5% in weight) taken from the Luochuan section, so that the source of magnetism in samples is not from paramagnetic or antiferromagnetic iron-bearing minerals ($\chi<100\bullet10^{-8}m^3kg^{-1}$), but should be from some amount of ferrimagnetic maghemite (χ $\sim26000\bullet10^{-8}m^3kg^{-1}$) or magnetite ($\chi\sim 56500\bullet10^{-8}m^3kg^{-1}$) at room temperature.[20] The semi-quantitative analysis from Mössbauer studies is based upon the Debye-Waller factors for each, and with the

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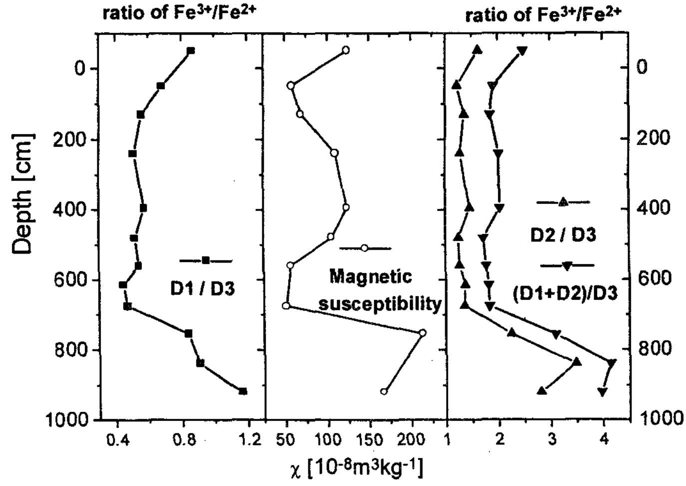

Figure 4.Comparisons of profiles between magnetic susceptibility and intensity ratios from D1/D3 (armophous iron compounds/ Ferros iron silicon compounds), D2/D3 (ultrapartile iron compounds/ Ferros iron silicon compounds), and (D1+D2)/D3 (sum of armophous and ultraparticles iron compounds/ Ferros iron silicon compounds).

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fundamental relative intensities of doublets meaningful for comparing each other. Ratios of Fe^{3+}/Fe^{2+} were calculated and plotted in Figure 4 where a high correlation with magnetic susceptibility was established by the study of Mössbauer spectroscopy.

It is not suprising that the profile for variation of ratios of D1 and D3 intensities has a good linear relationship with magnetic susceptibility. This occurs since ultrafine grain ferrimagnetic particles (D1) contribute most of the magnetic susceptibility, rather than other paramagnetic particles or even amophous particles in evidence. The interesting result is that profiles of D2/D3 have very high correlation with magnetic susceptibility. The least-square factor R as the correlation parameter is derived by linear fiting as shown in in Figure 5, all R values of approximately 0.8 were

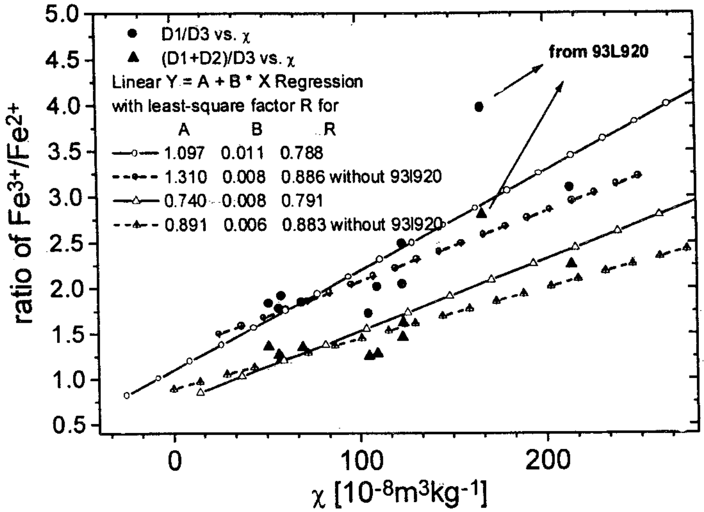

Figure 5. Linear regression for correlation of magnetic susceptibility data with ratios of D1/D3 and D2/D3.

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demonstrated. The point from 93L920 (S1) in Figure 5 diverges from the group of data, eliminating this point will derive a better R (~0.89) value. This strong deviation of the parameters for this palaeosol (S1) layer implies different conditions occurred over the time scale of S1.

4 Mechanism of links between magnetic susceptibility and palaeoclimate

The linkages of so many different parameters are certain to be caused from the palaeoclimate, but details of each process are found in varied mechanisms. The relationship between ferrous/ferric ratios and mica/chlorite ratios will be emphasized and focused on. From Mössbauer studies, three major iron sites: ferrous in chlorite, amorphous iron oxides, and ultrafine grain iron oxides, were found and their varying constitutions dominate the magnetic behavior of samples. The ferric irons were dissolved from chlorite during the developing of loess-palaeosol, oxidized in the geochemical process, and constructed in large particles or even crystallized over time. But the effect from chemical weathering made iron oxide particles into a small grain size, stronger weathering produces higher amounts of ultrafine grain, thus contributing increased strength of magnetic susceptibility. The mica/chlorite ratio in loess-palaeosol is an indicator of chemical weathering. High ratios indicate strong weathering; additional weathering of chlorite creates more free iron from the silicate layers, and more ferric iron complexes in the loess-palaeosol. Therefore the relative Fe^{3+} intensity vs. Fe^{2+} in clay analyzed using Mössbauer spectra can reflect the capacity of chemical weathering and demonstrates a similar profile with magnetic susceptibility. The geochemical process for amorphous iron sites resembles ultrafine grain iron compounds.

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SUMMARY AND CONCLUSIONS

Presentation of Mössbauer studies for a sequence of loess-palaeosol from Louchuan reveals:

(1) Loess-palaeosol samples contain at least four species of iron compounds including: a ferrous site in chlorite, two sets of grains in the forms of iron oxides and related compounds, and a small amount (~1%) of an iron site from other iron positions.

(2) The Mössbauer effects or relative intensity for each species, relating to the iron content in loess-palaeosol, depends upon the depth and indicates the degree of weathering of the ancient environments studied.

(3) Particle size effect play an important role in studies of magnetic susceptibility, one set of grain iron oxides is ultrafine, showing superparamagnetic behavior at room temperature, and contributes the most to the strength of magnetic susceptibility.

(4) The ratio of Fe^{2+}/Fe^{3+}, having a similar profile to that from magnetic susceptibility and other parameters, also reflects palaeoclimatic changes and becomes a new indictor for the study of palaeoclimate.

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