Paleosols in Devonian red-beds from northwest China and their paleoclimatic characteristics

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A B S T R A C T
Paleosols have been discovered in the late Devonian (Famennian) Shaliushui Formation near Pingchuan City, Gansu province, China, and are recognized by evidence of root traces, soil horizons and soil structures. Root traces are remnants of substantial woody plants, reaching deeply within profiles as clayey inﬁlls and as drab-haled root traces. Soil horizons include thick layers of large calcareous nodules (Bk horizon), and subsurface accumulations of clay (Bt horizon), and slickensided claystone (vertic Bw horizon). Soil structures include blocky peds and calcareous nodules. The nodules and drab-haled root traces formed syndepositionally during the late Devonian, because they were also observed in clasts of paleosol and nodules in ﬂuvial conglomerates interbedded with the paleosols. Analyses for Rb/Sr and Ba/Sr ratios and magnetic susceptibility measurements conﬁrm that the more strongly developed paleosols with larger calcareous nodules and higher clay content are also more chemically differentiated and have higher magnetic susceptibility under semi-arid climates. This suite of paleosols is evidence of semi-arid to sub-humid, highly seasonal climate under dry woodlands and shrublands. Paleosols of the Shaliushui Formation are a potentially valuable archive of late Devonian palaeoclimates of northwest China.

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1. Introduction

Devonian paleosols have long been recognized from around the world, using the familiar criteria of root traces, soil horizons and soil structure (Allen, 1973, 1974; Boucot et al., 1982; Retallack, 2009; Narkiewicz and Retallack, 2014; Alekseeva et al., 2016; Genise et al., 2016; Xue et al., 2016). Late Devonian evolution of trees and tetrapods was a major transformation of ecosystems, landscapes and climates, including dramatic greenhouse spikes coincident with Frasnian-Famennian (Retallack, 1997; Retallack and Huang, 2011). A remarkably complete record of global change has been reconstructed from Devonian paleosols in the Old Red Continent of Euramerica (Retallack, 2011), but Devonian paleosol sequences from China remain little known (Boucot et al., 1982; Guo et al., 2016; Xue et al., 2016). This study introduces a newly discovered record of late Devonian paleosols from the Shaliushui Formation of Gansu (Fig. 1) and their paleoclimatic characteristics.

Preservation of Devonian paleosols was compromised by extensive greenish facies metamorphism, as well as burial decomposition of organic matter, burial gleization and iron oxyhydrate dehydration (Retallack, 2011; Retallack and Huang, 2011). These alterations to their appearance make them a gaudy green and red caricature of the original subtle colour of the profiles (Retallack, 1991). This paper details field characteristics of the paleosols and employs geochemical and environmental magnetic data to assess whether they are paleosols or not. One reason for failure to recognize paleosols until recently is that many red bed sequences may be lack of appreciation of the nature of soil development. Paleosols vary in predictable ways from thin and little altered with root traces (very weakly developed) to thick, nodular or massive clayey (moderate development) (Retallack, 2001). Our geochemical and susceptibility data are used here to examine the degree to which each field category of soil development correspond to environmental magnetic and geochemical differentiation during late Devonian soil formation.

2. Geological setting

Our three study sections are 14 km northeast and 24 km northwest of Pingchuan City, in Baiyin County, Gansu province, China (Fig. 1). Devonian rocks of the Northern Qilian Orogenic Belt include two formations: the early-middle Devonian Laojunshan Formation and the late Devonian Shaliushui Formation (Zhai, 1981). The early-middle Devonian Laojunshan Formation formed during the rapid uplift of the Northern Qilian Orogenic Belt. The orogeny of the Northern Qilian Orogenic Belt was diachronous in the trending direction, the eastern
sector had stronger tectonic intensity compared to the western sector, due to the oblique collision between the middle Qilian block and the Alxa block; the Laojunshan Formation was not present in our measured sections (Xu et al., 2010). The thickness of the Shaliushui Formation is ~250 m. The Shaliushui Formation in our sections overlies an angular unconformity with grey Silurian schists of the Hanxia Formation (Zhai, 1981). The uppermost Shaliushui Formation is conformably overlain by the Carboniferous Qianheishan Formation of grey-white gravelly sandstone and purple siltstone. In contrast, the Shaliushui Formation is composed of clastic rocks with red and green mottled claystones, with interbedded sandstone and conglomerate (Fig. 1B). According to the tempestite in sandstone in Shaliushui Formation, Du et al. (2001) suggested that the study region was located in a low latitude (5°–20°) zone, and Shaliushui Formation was mainly composed of fluvial and lacustrine deposits.

A late Devonian (Famennian) age of the Shaliushui Formation is evident from lycopsid stems of Leptophloeum rhombicum (Zhai, 1981; Xu et al., 2011). An earliest Carboniferous (earliest Tournaisian) ostracod Chamishiella lysei in the conformably overlying Qianheishan Formation confirms that this sequence includes the Devonian–Carboniferous boundary (Yao et al., 2016).

3. Materials and methods

Three paleosol sections from different sites including Ciyao section (CY), Dahongmen section 2 (DHM 2) and Dahongmen section 4 (DHM 4) were measured (Fig. 1B). CY section (N36.79085° E104.94379°) is 4.3 m thick, while DHM 2 (N36.9089° E104.6781°) and DHM 4 (N36.9077° E104.6821°) are 1 m and 4 m thick respectively. Powder samples were collected from DHM 2 and DHM 4 sections with 10 cm interval and from CY section with 50 cm interval. Totally 35 samples were obtained from three sections.

The samples were air-dried, then weighed and packed in a non-magnetic plastic box (2 × 2 × 2 cm). Magnetic susceptibility (χ, mass-specific) was measured using Bartington MS-2 meter (low frequency χ with 470 Hz). Hysteresis loop and thermomagnetic curves were measured using a Magnetic Measurements Variable Field Transition Balance (MMVFTB). The hysteresis parameters, including saturation magnetization (Ms), remanence saturation magnetization (Mrs), coercivity (Bc) and remanent coercivity (Bcr) of paleosols were determined on hysteresis loops.

4. Results and analyses

4.1. Paleosol field observations

4.1.1. Root traces

Root traces are the most diagnostic evidence of paleosols, and are common in the Shaliushui Formation. They have rootlets branching from a central tap root penetrating deeply into paleosol, with irregular striated surface like woody roots of progymnosperms such as Callixylon–Archaeopteris (Retallack and Huang, 2011). Some large cylindrical root traces (5 cm diameter, 60 cm deep, n = 3) show a central dark cylindrical woody streak after the root protostele and a carbonaceous epidermis separated by a zone filled with mud and calcite (Fig. 2A). In other many tubular root traces (1–3 cm diameter, 5–30 cm
deep), the tubular cavity from the rotted stele is filled with sparry calcite.

Especially common and conspicuous are drab-haloed root traces, with a central clayey thread surrounded by a diffuse halo of green-grey claystone (Fig. 2B–C). These are most common in surface horizons where they are truncated above by overlying sediments, and they reach deeply into the subsurface. They are not burrows filled with grey sand or silt from above, because they have a similar clayey texture as their matrix.

Features similar to drab-haloed root traces are formed in modern soils by surface water gleying above impermeable soil layers (Lindbo et al., 2010), but this is an unlikely explanation for drab-haloed root traces in the Shaliushui Formation for several reasons. First there are no clearly impermeable layers in the paleosols that would have deflected root penetration and ponded water (Fig. 3) nor are there rims of iron manganese or pyrite as evidence of gleization during soil formation (Retallack, 1983; Retallack et al., 2000). Deeply penetrating root traces and abundant carbonate nodules are evidence instead that
these paleosols were originally well drained and porous (Retallack, 2001). Drab mottles can form by burial gleization—the chemical reduction of iron hydroxides and oxides by anaerobic bacteria consuming organic matter buried with the soil below or near the water table (Retallack, 1991). Reduction haloes around buried organic matter can form in only a few thousand years (Allen, 1986). The drab-haloed root traces are formed from chemical reduction of matrix by microbes decomposing organic matter of roots buried in the paleosol as it subsided below water table, the drab-haloed root traces are thus evidence of burial gleization (Retallack, 1991; Retallack et al., 2000). Such early diagenetic drab-haloed root traces are widely known from Devonian paleosols (Retallack and Huang, 2011; Xue et al., 2016). Furthermore, there are also non-drab-haloed root traces in the same paleosols. The non-drab-haloed root traces are evidence of roots that had rotted in the soil prior to burial and filled with oxidized soil, like other Devonian root traces (Hillier et al., 2008).

4.1.2 Vertebrate burrows

Some paleosols and paleochannels have large (10–13 cm diameter and 25–30 cm deep) subvertical to oblique burrows filled with calcareous silt and sand (Fig. 2D–E). Indeterminate bone fragments were found within one of these.

Similar burrows are made by small vertebrates such as amphibians (Hembree et al., 2005), reptiles (Miller et al., 2001) and mammals (Hembree and Hasiotis, 2008), but no late Devonian quadrupedal fossorial vertebrates are known (Retallack et al., 2009). Burrows of the Shaliushui Formation are most like aestivation burrows of lungfish (Berman, 1976; Dubiel et al., 1987; Graham, 1997), including a lariat-like shape in some cases. In Africa today, lungfish burrow into soft soils and lake bottoms before the dry season, and pass the summer in torpor until rains return again (Janssens, 1964). All burrows of vertebrates require well drained, oxygenated soil, and lungfish burrows are indicators of a long hot dry season.

4.1.3 Soil horizons

Paleosols have recognizable soil horizons in the field, truncated sharply by overlying sandstone or siltstone horizon (Fig. 3C, D). Below sandstone or siltstone horizon, boundaries of different soil horizons and underlying parent material have diffuse contacts (Retallack, 1991). Normal and reverse graded bedding can also show similar gradational contacts, but lacks the slickensided clay skins (Fig. 2H) in both normal-below-reverse grading of an argillic horizon. Three kinds of soil horizon were recognized in paleosols of the Shaliushui Formation: horizon of calcareous nodules (calcic Bk) (Fig. 3D), horizons of subsurface clay enrichment (argillic Bt) and horizons of deformed and slickensided claystone (vertic Bw) (Fig. 3E). Paleosols with B horizons qualifying as calcic and argillic (Soil Survey Staff, 2014) are very weakly to moderately developed (Retallack, 1988).

Especially obvious are calcareous nodules of unusually thick calcic (Bk) horizons (Fig. 3D), like those found in Devonian red beds of Britain (Allen, 1973, 1974) and elsewhere in China (Boucot et al., 1982). Nodules in paleosols of the Shaliushui Formation are 1–5 cm in diameter, and form horizons 11–110 cm thick at depths to carbonate nodular horizon in soils of 0–72 cm. Some of these calcic horizons are truncated by sandstone (Fig. 3D), and many of the conglomerates contain calcareous nodules as clasts and proof of erosion of nodules that came from paleosols below the conglomerates (Fig. 3A). Calcic horizons of this thickness and depth are indications of an arid and highly seasonal palaeoclimate (Retallack, 2005).

The argillic and vertic horizons are dark red and slickensided claystone (Fig. 3E), unusual in this sequence of siltstone, sandstone and conglomerate (Fig. 2H). Large blocks of red claystone containing drab-haloed root traces are also found in paleochannel deposits (Fig. 3A) as evidence that these horizons formed during deposition and not as late diagenetic structures. The argillic and vertic horizons are weakly to non-calcareous above weakly calcareous parent material, and so are evidence of subhumid to humid palaeoclimates.
4.2. Petrographic observations

The argillic and vertic paleosols may reflect short episodes of global greenhouse palaeoclimate noted in other Devonian sequences of paleosols (Retallack, 1997).

4.1.4. Soil structures

Soil structures gradually form and replace the structures of parent materials such as bedding, crystal structure, and schistosity of parent materials, by the activity of plants and animals, wetting and drying and other soil-forming processes. Mud cracks from desiccation are an obvious structure of very weakly developed soils. Mud cracks from desiccation in the Shaliushui Formation are atop thin paleosols with coatings are common in slowly permeable parts of soils, and when thicker and more abundant than in the Shaliushui Formation are called argillans (Retallack, 1988; Caudill et al., 1996).

Comparable blocky peds and argillans are widely known in paleosols and E. (Retallack, 1988; Caudill et al., 1996). Purple to black Fe–Mn coatings (mangans) are another common cutan in claystones and around carbonate (Fig. 2D, E). These kinds of coatings are common in slowly permeable parts of soils, and when thicker and more abundant than in the Shaliushui Formation are called placic horizons (Retallack et al., 2000; Soil Survey Staff, 2014; Lindbo et al., 2010).

4.2. Petrographic observations

Observations in petrographic thin section confirm several field observations of paleosols in the Shaliushui Formation. The carbonate nodules that appear like pedogenic carbonate in the field also show both replacive (Fig. 4F) and displacive (Fig. 4A) structures diagnostic of soil carbonate. Soil carbonate is characteristically micritic replacing soil matrix which remains as isolated quartz grains with marginal texture (Wright, 1986; Searl, 1989). Displacive fabrics on the other hand are where angular pieces of nodule or matrix have fallen into voids later filled with sparry calcite, so are evidence of dilations formed in low pressure soil rather than deeply buried rocks (Braithwaite, 1989). Sparry calcite in veins, burrows and old root traces (Fig. 4A–F) also form in modern soils, but may also have been late diagenetic cements (Wright, 1986).

Clayey matrix to paleosols of the Shaliushui Formation also shows birefringence fabrics such as porphyroskellic insepic (Fig. 4C, D) in the terminology of Brewer (1964). The matrix-supported quartz and feldspar grains (porphyroskellic) were produced by weathering of matrix grains to clay, and the high birefringence oriented clay in random arrangement (insepic) produced by fine scale shrink-swell deformation by cracks, roots and burrows. These birefringence fabrics are unique to soils (Retallack, 1988) and can be contrasted with intertectic asepic fabrics (Fig. 2G).

Thin sections also reveal details of clay skins. The laminated interior of some clay skins mark them as illuviation argillans (Fig. 4C, D). Other cutans coating original voids filled with sparry calcite are hematite diffusion ferrans (Fig. 4E, F) and Fe–Mn diffusion mangans (Fig. 4F). This form of cutan is produced by diffusion of oxygen from the void into the matrix, abundant oxygen in the case of ferrans and limited oxygen in the case of mangans (Brewer, 1964). In both cases these are evidence of an oxygenated environment of soil formation which is a kind of early diagenesis, rather than the poorly oxygenated local environments of late diagenesis (Retallack, 1988).

4.3. Geochemical characteristics of paleosol sections

Our chemical analyses were designed to examine whether the degrees of paleosol development observed in the field (Fig. 3) corresponded with degree of chemical weathering. Two molar ratios in particular are useful indices of chemical weathering: Ba/Sr and Rb/Sr ratios (Retallack, 1988). Chemical index of alteration (CIA = Al2O3 / (A12O3 + CaO + K2O + Na2O) in which CaO is non carbonate: Nesbitt and Young, 1982) is a popular weathering proxy, but not appropriate for our paleosols because they have so much calcite. As would be expected for paleosols, the profiles showing greatest textural differentiation and homogenization due to soil formation also had the highest Ba/Sr, and Rb/Sr ratios (Fig. 5). None of these paleosols are deeply weathered chemically, as expected for their likely arid palaeoclimate and abundant pedogenic carbonate. The Ba/Sr and Rb/Sr ratios are based on relative solubilities of two chemically similar elements, and so are proxies for water/rock ratios of weathering.

![Fig. 4. The thin section characters of late Devonian; (A) spar filled root trace in micrite; (B) clay skin around micrite in clayey plasma matrix; (C) spar filled root trace with diffusion ferran in micrite; (D) diffusion ferran around micritic nodule; (E) intertectic silasepic parent siltstone; (F) calcite-filled tapering root trace in micrite. Red bars = 200 μm in A, B, D and F, 50 μm in C and E. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
The least chemically weathering paleosols have high Sr and CaCO₃, due to late dry season accumulation of low-magnesium carbonate in the paleosols (Retallack, 2005). The parent material reflected in weakly and very weakly developed paleosols also has high amounts of Sr and CaCO₃, derived from calcic soils of an arid upland.

Amounts of Ti and SiO₂ are also proxies for parent material and are uniform in clayey and silty parts of the measured profiles, but very different in sandstone paleochannels (Fig. 5). This is an indication, that as in many arid lands, the parent material of many of the paleosols was not alluvial sand but calcareous eolian dust (Guo et al., 2013; Retallack, 2013).

4.4. Magnetic characteristics

A thermomagnetic curve is generally preferred for determining composition of magnetic minerals in a sample (Evans and Heller, 2003). The thermomagnetic curves of CY-2 and DHM 2–4 samples are shown in Fig. 6A. The magnetizations have steep decrease at about 658 °C and gradually reduction from 658 to 700 °C on heating curves, suggesting that hematite is the major magnetic minerals of samples.

Hysteresis loop measurements also give information about the composition of magnetic mineral and particle size (Evans and Heller, 2003). No closure of loops in Fig. 6B at 300 mT and lack of saturation (which requires near zero slope of the loop at the highest fields) above 300 mT indicate mainly magnetic minerals are hard magnetic minerals such as hematite and/or goethite. Bcr >350 mT and the pot-bellied loops indicate that the high coercivity mineral is hematite in both samples (Dunlop and Özdemir, 1997). Taken together, both hysteresis loops and thermomagnetic curves show that the dominant magnetic mineral is hematite. Hematite is an indication of soil maturity and an arid climate, which is consistent with lungfish burrows (Fig. 2D–E).

Magnetic susceptibility (χ) is another indication of degree of soil development, as it increases with increasing pedogenic degree in aerobic soil with low and moderate rainfall. However, when the moisture is high, the susceptibility decreases (Maher and Thompson, 1994; Balsam et al., 2011). The susceptibility of DHM 2 and CY sections are higher and increase with decreasing depth (Fig. 5A, B), indicating that the pedogenic degree enhance. However, magnetic susceptibility of DHM 4 section is low with almost uniform value from bottom to top (Fig. 5C), which may be due to magnetic mineral transformation under high soil moisture content (Liu et al., 2012; Wang et al., 2013; Guo et al., 2018). Grimley and Vepraskas (2000) take \(20 \times 10^{-8} \text{ m}^{-3} \text{ kg}^{-1}\) as an upper threshold for soils, when fine-grained strongly magnetic minerals (mainly magnetite and/or maghemite) were converted into weakly magnetic minerals (mainly hematite) by pedogenesis, which resulted in a decline in magnetism and decreasing susceptibility (Guo et al., 2018). The low susceptibility may be due to burial gleization, as documented for magnetic susceptibility of other paleosols (Retallack et al., 2003).

5. Discussion

Studies show that the Shaliushui Formation was composed of clastic rocks with red and green mottled claystones, with interbedded sandstone and conglomerate (Zhai, 1981; Du et al., 2001; Xu et al., 2010). But we discover that the red and green mottled claystones show paleosol characteristics, so we assess whether or not they are paleosols by evidence of root traces, soil horizons and soil structures. Formerly woody root traces are ubiquitous in the red beds (Fig. 2A–C). Many of these show drab haloes due to burial gleization, but the non-drab-haloed root traces are evidence of roots that had rotted in the soil prior to burial and filling with oxidized soil, like other Devonian root traces (Hillier et al., 2008). Many red beds display diffuse changes down from a truncated top, similar to soil horizons of calcareous nodules (calcic Bk) or of illuviated clay (argillic Bt) or deformed clay (vertic Bw) (Fig. 3). The calcareous nodules have both replacive and displaceable textures of pedogenic carbonate (Fig. 3). Soil structures such as blocky peds are outlined by clay skins, and thin section study
reveals these to be illuviation argillans (Fig. 4). Other planar features in the soil are diffusion ferrans and diffusion mangans created during soil formation and exposure to air rather than deep burial diagenesis. A variety of field observations and thin sections analyses confirm that the Shaliushui Formation has a long sequence of clayey and calcareous red paleosols.

Paleosols of the Shaliushui Formation are a potentially valuable archive of late Devonian palaeoclimates, life and palaeogeography of northwest China. The dominant hard magnetic hematite in red beds (Fig. 6) and abundant carbonate nodules at shallow depth in the profiles (Fig. 3D) are evidence of arid climates, but the spread of nodules within the profiles are indications of strongly seasonal, monsoonal climates (Retallack, 2005). Devonian tropical climate potentially exhibited an even more intense monsoonal circulation (Streel et al., 2000), characterized by seasonally wet-and-dry climates (Cecil, 1990).

The Ba/Sr values show that paleosol weathering intensity of the DHM 4 section was stronger than DHM 2 and CY sections (Fig. 5). However, the magnetic susceptibility as an indication of degree of soil development is lower within the DHM 4 profile than DHM 2 and CY profiles (Fig. 5), and hematite is the dominant magnetic mineral in red beds. The argillic (Bt) and vertic (Bw) paleosols reflect short episodes of global greenhouse palaeoclimate (Fig. 3E). Orgeira et al. (2011) proposed that soil water balance is the most important factor that controls magnetic enhancement because it dominates the annual soil ‘wetting’ and ‘drying’ cycle. When the moisture is high and over an upper threshold (Grimley and Vepraskas, 2000), the parts of the fine-grained strongly magnetic minerals (mainly magnetite and/or maghemite) were converted into weakly magnetic hematite by pedogenesis, which resulted in a decline in magnetism and a significant decreasing in susceptibility of DHM 4 section (Liu et al., 2012; Wang et al., 2013; Guo et al., 2018). Scattered through the sequence are argillic and vertic paleosols with little carbonate (Fig. 3E) also reflect the brief episodes of humid climates attributed to global greenhouse spikes in other Devonian paleosol sequences (Retallack, 1997, 2011). Overall, the soil horizons and magnetic susceptibility reflect semi-arid to sub-humid, highly seasonal palaeoclimate in the late Devonian in northwest China. This is compatible with the study of Zhao et al. (1986), who speculated that the climate of the late Devonian Zhongning Formation in the southern Ningxia Autonomous Region, northwest China, might be a warmer and humid interval after a long dry period, according to the lithological variations and fossil flora. The dramatic greenhouse spikes commonly occur in other late Devonian strata (Vleeschouwer et al., 2013).

These vertic and argillic paleosols have deeply reaching stout root traces of woodlands (Fig. 2A–C), but the root traces of calcic paleosols also are deeply reaching and with nodules so shallow (Fig. 3D) that their vegetation would have been an arid shrubland, by comparison...
with other Devonian paleosols (Retallack and Huang, 2011). Such highly seasonal monsoonal palaeoclimates also imply a large North Qilian Mountain range near at hand (Retallack, 2005), as a source for the course conglomeratic paleochannel sandstones.

6. Conclusions
A variety of field observations and laboratory analyses confirm that the red beds of Shalishui Formation has a long sequence of clayey and calcareous red paleosols. Weathering ratios and magnetic susceptibility confirm that the more strongly developed paleosols with larger calcareous nodules, more clay and higher susceptibility under low and moderate soil moisture. Some large woody root traces and abundant carbonate nodules at shallow depth in the profiles indicate dry woodlands and shrublands in a coastal plain to a range of high mountains.

Argillic and vertic paleosols with little carbonate reflect the brief episodes of humid climates, and abundant carbonate nodules at shallow depth reflect arid climates, this suite of paleosols reflect semi-arid to sub-humid, highly seasonal climate in the late Devonian in northwest China.

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