

Isotopic signature of Tian-Shan mountain soils as a record of climatic changes of the Late Pleistocene and Holocene

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Abstract Specific features of the polygenetic mountain soils of the Tian-Shan (Kyrgystan) are due to the action of present-day and relict soil processes that vary in age and intensity under the influence of glacier movements and climatic fluctuations. These properties can be used as indicators of paleoclimatic changes. The diagnosis of ancient pedogenesis was based on criteria with the longest response time, namely, soil morphology, characteristics of organic matter, ^{13}C -NMR spectra of soil humic acids, isotope composition of humus and carbonates, and the soil age. The results indicate a glacial climate of the Late Pleistocene, a dry and cold climate during the Early Holocene, warm and dry conditions of soil formation in the Middle Holocene, and humidity climate of the Late Holocene.

1. Introduction

Global warming and impending sea-level rise have attracted an increasing interest in regional climate changes and in the methods of their investigation. The soil cover of the extensive territories of the Tian-Shan is represented by polygenetic soils along with soils buried by the Late Pleistocene and Holocene loess. Specific features of these soils are due to the action of elementary modern and relict soil processes, whose age and intensity varied under the influence of glacier movements and climatic fluctuations. These properties could help to elucidate conditions of soil formation during the Late Pleistocene and Holocene. This paper presents records of $^{13}\text{C}/^{12}\text{C}$ ratios of soil organic matter and carbonates, combined with chemical properties of humus and radiocarbon dating, to reconstruct changes in climate and paleoenvironments during the Pleistocene and Holocene in the high mountains of Asia, focusing on the Kirgizskiy Range of the Tian-Shan (Kyrgystan).

2. Materials and methods

A soil chronosequence was studied in the central part of Kirgizskiy Range (at the longitude of the city Bishkek, $74^{\circ} 42' \text{ E}$) at elevations between 1800 and 3400 m above sea level on interfluvium of the Alamedin and Ala-Archa Rivers. The interfluvium is the highest part of Kirgizskiy Range that was glaciated by the Shopokov Glacier.

The studied valley contains typical glacial features including U-shaped cross-sections, cirques, moraines, and glaciofluvial sediments. Bedrock is comprised of limestone, diorite, porphyrite and metamorphic rocks.

This study examined 40 soil profiles, representing the change of soil types from the foothills to the top slope of the Taty, Chon-Kurchak, Kurchak-Tor valleys.

The older members of the chronosequence developed on the lowest frontal moraines of the Last Glacial Maximum (LGM) at altitudes of 1900-2100 m. These soils are mountain Chernozem (Chernozems Haplic) profiles with the following horization: A-AB-B-BC1-C1-Bb₁-C2-C3-Bb₂-C4-



Bb₃. Vegetation cover is herbage-estragon (*Festuca valesiaca*, *Artemisia dracunculus*, *Poa relaxa*, *Stipa capillata*, *Phlomis oreophila*, *Elytrigia repens*) meadow-steppe.

Upvalley, moraines are present at 2100, 2350, 2450 and 2600 m above sea level. These moraines characterize Late Glacial ice advances in Holocene [3]. These soils are polygenetic soils that have buried A and B horizons. These soils can be classified as Chernozem-like soils (Leptosols Mollic) with A-Ab-AB-B-Bt-C1-B_{b1}-C2-B_{b2}-C3 horizonation. Vegetation is a prairie-grass-herbage meadow steppe (*Brachypodium pinnatum*, *Helictotrichon schellianum*, *Phleum phleoides*, *Campanula glomerata*, *Galium septentrionale*, *Ranunculus polyanthemus*) and dry subalpine meadows (*Phlomis oreophila*, *Aegopodium alpestre*, *Alchemilla retropilosa*, *Dichodon cerastoides*, *Ligularia thomsonii*, *Brachypodium pinnatum*, *Poa angustifolia*, *Dactylis glomerata*, *Geranium regelii*, *Alopecurus pratensis*).

Incomplete soils developed on the frontal moraines with large porphyrite and granite-diorite boulders occur at altitudes of 3100 m. These soils are in the initial stages of their formation and are classified as alpine-meadow soil-rankers (Leptosols Umbric), with A-AC-C horizonation. Vegetation is kobresia meadow from *Kobresia humulis*, *Alchemilla retropilosa*, *Allium atosanguineum*, *Astragalus alpinus*, *Potentilla nivea*, *Carex stenocarpa*.

All samples taken from soil pits were air dried, sieved (<2mm), and ground prior to chemical analysis. In addition, macro-, meso- and micromorphological [1] descriptions were made for all studied profiles. Total C and N, as well as organic C (C_{org}) were analyzed by dry combustion with a Carlo Erba ANA 1500 C/N/S Analyzer. Group and fractional composition of humus was analyzed by the Tyurin method [5]. The optical properties of humic and fulvic acids were measured in the alkaline extract by the spectrophotometer "CF-18" and the coefficient of extinction, color coefficient were determined. These analyses are defined as follows: (1) coefficient of extinction, E, is the optical density of the solution when the $\lambda = 465$ nm, the concentration of humic acids is 0.001 %, and the cuvette length is 1 cm; (2) color coefficient $Q = D_{465}/D_{650}$, where D is the optical density at 465 and 620 nm wavelength; (3) Cha/Cfa, where ha – humic acid, fa – fulvic acid.

Radiocarbon analyses of extractable humic acids were carried out at the geochemical laboratory of the Institute of Geography, Russian Academy of Sciences. We also used radiocarbon data, obtained by Maksimov and Pomortsev [6] for soils studied at Leningrad University.

¹³C NMR spectra were recorded for HA preparations. The preparations were isolated from the studied soils, including iron–manganese nodules, by triple extraction with a 0.1 M NaOH + 0.4 M NaF mixture from the samples decalcified with 0.05 N H₂SO₄. After the separation from colloids by centrifugation (Beckman Model J-6 centrifuge, 2500 g, 15 min), the HA preparations were purified from mineral salts by electrodialysis (MWCO 12000–14 000) [6]. The dialyzed and frozen-out HA preparations (50 mg) were dissolved in 0.6 mL of 0.3 M NaOD/D₂O. Spectra were recorded on a Bruker Avance DRX 500 NMR spectrometer at 25.18 MHz and 290 K.

The ¹³C/¹²C ($\delta^{13}\text{C}$) ratio was measured for all samples on a Finnigan MAT 251 mass spectrometer with PDB as reference and average precision less than 0.1 ‰ at Soil Science Institute of Bayreuth University (BRD). The isotope composition of carbon is expressed by the ¹³C/¹²C ratio or the relative density: $\delta^{13}\text{C}, \text{‰} = 1000[(R_{\text{sample}}/R_{\text{standard}} - 1)]$, where $R = ^{13}\text{C}/^{12}\text{C}$. For the PDB standard, ¹³C/¹²C = 0.01125, and $\delta^{13}\text{C} = 0$.

3. Results and discussion

The ¹³C/¹²C ratio in carbonates and humus has been under examination for loess and soils in order to clarify the type of vegetation and conditions promoting carbonates formation. Based on the radiocarbon chronology, soil morphology, chemical properties and $\delta^{13}\text{C}$ data of the recent and buried soils the following major climatic events can be reconstructed.

Mountain Chernozems are not clearly differentiated in terms of humus properties (table 1). Their profile can only be subdivided into upper and lower parts, which are assessed as recent and early Holocene, respectively. The criteria to subdivide the profile are the values of the color coefficient ($Q > 4$ and $3 < Q < 4$), the coefficient of extinction (0.08 and 0.19). This subdivision is in agreement with

the climate of the modern meadow-steppe and the effect of the early and middle Holocene xerothermic period in the formation of ancient Chernozems. Soil texture is strongly affected by aeolian silt additions. Loesslike loam contains buried Pleistocene soils (Bb) transitioning to the highly weathered and rubefied metamorphic bedrock. According to Zech et al. [9], the radiocarbon age of such buried soils (Bb₂ and Bb₃ horizons) in loess of North-Western Tian-Shan is 15930±460 and 24300±1160 years BP. Authors assume that the latter paleosol developed during a warmer interstadial which is postulated for oxygen isotope stage 3, between the Sartan (Late Valdai, isotope stage 2) and Zyryanka (Early Valdai, isotope stage 4) ice advances. Beginning with the Sartan glaciation about 24 000 years BP, solifluction debris and Shopocov till began to cover the paleosol. $\delta^{13}\text{C}$ values of -4 to -5‰ from carbonate in the C3 horizons of the mountain Chernozem (on the LGM moraine) characterized the glacial climate too.

Based on the $\delta^{13}\text{C}$ data, -8 to -10‰ in the C1 and C2 horizons the cold and dry climatic period with little alpine desert vegetation and slightly weathered interstadial soils can be reconstructed. A similar horizon is described by Zech in Western Tian-Shan [9] (24300±1160 years BP), as well as by Yan et al. in Tibet (25910±400 years BP) [8]. According to $\delta^{13}\text{C}$ in the B_{1b} horizon (-24.41 ‰), the warm period is reconstructed at about 14030±880 years BP [6] in Chon-Kurchak valley with C-3 type of vegetation. The peak areas of aromatic and aliphatic fragments of the buried soils humic acid molecules are similar - about 28 % in NMR spectra (figure 1).

Cold and dry climate with, probably, CAM-type of photosynthesis ($\delta^{13}\text{C}$ in the C1 horizon -7 to -10 ‰) (table 1) predominated, in the Early Holocene at about 10100±564 and 9130±640 years BP [6]. At the 8-6 kyr BP, the warm and dry period can be reconstructed, when peats spread out in the piedmonts and lowlands due to glacial melting. Meadows with C-3 type of plants developed, based on $\delta^{13}\text{C}$ values ranging from -19 to -29 ‰. The age of B horizon at the altitude 2350 and 2450 m in studied valley is 7130 and 6440 years BP respectively [6].

1. The profiles of the Chernozem-like soils, which were formed on the moraines of the Shopocov glacier during the last 10000-13000 years, are clearly differentiated in terms of the morphology and organic matter properties. The upper A horizons have dark-brown color and crumbly structure, as well as the values of the color coefficient $Q>4$. Moreover, the humus type is humic-fulvic in the A horizon. The radiocarbon age of these horizons is 3010±90 years BP (IGAS-1028).

2. Very high values of the humification index, high values of the coefficient of extinction, and the spectral curve slope with the color coefficient $3<Q<4$ are intrinsic to the Ab and AB horizons (table 1). The latter being indicative of a more complex structure of humic acids is rich in benzoid compounds typical of mountain Chernozem profiles. Black buried horizon of the humus profile of a previous stage of soil formation has a residual granular structure and provides evidence for a warmer and wetter period than at present, with high plant biomass production. The radiocarbon age of it is 5560±120 years BP (IGAS-1027).

The data in figure 1 and table 1 show that in the buried horizons Ab the peak areas of aromatic part of the humic acid molecules are larger than their halos for humic acids of the surfaces horizons by 1.5 times (30 and 46 % respectively)

Besides that, the Ab horizon has the following relict characteristics: high values of the Cha/Cfa ratio, humic humus with the predominance of humic acids bound to Ca, along with a darker color, the well pronounced granular structure (as distinct from A horizon). Thus, humus composition in the horizons below the A is identical to that of the mountain Chernozems, reflecting the previous stage of Chernozem pattern of the development. This all indicates that dry conditions of soil formation existed in the area of Chernozem before the climatic changes that occurred between the Middle and Late Holocene. The Holocene optimum events with a warm and dry climate, air temperatures higher than at the present, a C-3 type of vegetation on the Chernozem soils in the valleys can be reconstructed at 6-4 kyr BP.

At the same time, A horizons forming under modern bioclimatic conditions differ appreciably from the underlying horizons with respect to the condensation of aromatic nucleus which are closer to typical

alpine soils. The peak areas of aromatic part of the mountain meadow alpine soils humic acid molecules are about 26 % (figure 1).

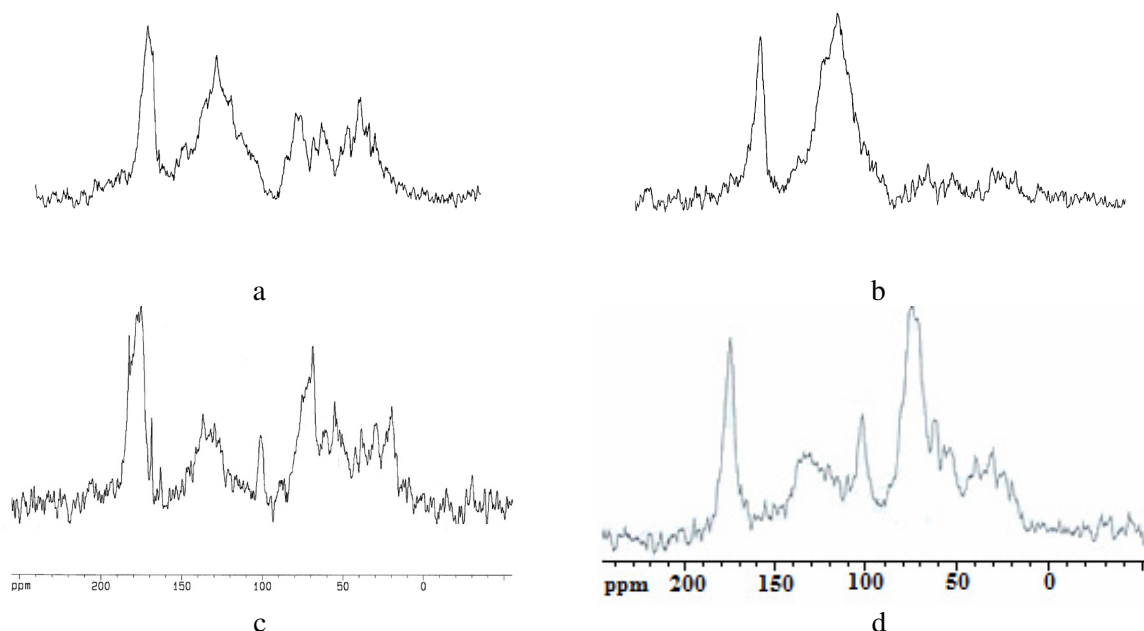


Figure 1. ^{13}C NMR spectra of humic acid from (a) the surface (3010 ± 90 years BP) and (b) buried horizons (5560 ± 120 years BP) of chernozem-like soils, c – from A horizon of mountain-meadow soils (109 ± 1.47 years BP), d – from Bb horizon (14030 ± 880 years BP).

Thus, the Late Holocene climatic changes toward cooling and wet caused the formation of a new subalpine soil type on the profile of mountain Chernozem in the zone from the lower boundary of the LGM (2100 m) to the alpine belt (3000 m). Favorable and relatively stable climatic conditions of Middle Holocene gradually changed to the Late Holocene. Decreasing of $\delta^{13}\text{C}$ values in humus, the traces of trees phenolic compounds in soil humus [5], optical properties of humus acids detect wetter conditions than in Middle Holocene.

Soil in initial stages of formation at the altitude above 3100 m are characterized by the high humus content (up to 15 %), humate-fulvate type of humus, low value of the extinction coefficient (0.06), the considerable green humic acids content, all of which indicate a humid and cold climate of the alpine zone during, at least, the last 100-200 years. The radiocarbon date of the A horizon in the alpine soil is 109 ± 1.47 years BP (IGAS-1029). These soils correspond with glacial advances during the so-called “Little Ice Age” with a maximum advance at about 1850 in the Alpine [9]. Modern subalpine and alpine vegetation and Chernozem-like soils below the 3000 m, and subalpine soils at the altitude above 3000 m began to develop at 4-3 kyr BP, and a trend towards increasing humidity has taken place ever since ($\delta^{13}\text{C} = -28$ ‰).

Thus, Late Holocene climatic changes toward cooling and wet caused the formation of a new soil type on the profile of mountain Chernozem. A horizons forming under modern bioclimatic conditions in the subalpine zone of mountains studied differ appreciably from the underlying horizons with respect to the condensation of aromatic nucleus which are closer to typical alpine soils (aromaticity of humic acids is 34 and 27% respectively)

Thus, climatic changes in the Late Pleistocene and Holocene in the mountain regions of the Tian-Shan (Kyrgyzstan) seem to coincide with Tibet and Eastern Europe [7] and correspond to the global climate changes [2, 3, 4, 8, 9]. But, these changes in Central Asia were probably less intensive than those in the other regions.

Table 1. Isotope composition of carbonate and humus carbon and some chemical properties of soils.

Soil, Altitude above sea level, m	Article I. Horizo n, depth, cm	Cha Cfk	E	Q	Radiocarbo n age, years B.P.	$\delta^{13}\text{C}$ humus , ‰	$\delta^{13}\text{C}$ carbonates, ‰
	Article II.						
Chernozem	A 12-18	2.2	0.09	4.61	-	- 25.50	-
Haplic	38-44	3.1	0.08	4.20	-	- 25.22	-
1800 m	B 56-76	2.1	0.14	4.15	-	-25.03	-
	76-83	1.4	0.19	3.16	-	-14.91	-
	BC1 83-101	1.6	0.12	3.33	-	-12.30	-10.07
	C1 101-114	1.2	0.15	3.64	-	- 9.00	-7.68
	C2 114-126				-	- 9.59	-8.53
	Bb ₁ 126-157				-	-9.41	-8.01
	C3 157-187				-	-5.09	-4.36
	Bb ₂ 187-200				> 24000	-5.59	-4.65
Article III.	A 0-12	1.5	0.08	4.08	-	-25.34	-
eptosols	A _b 37-50	0.4	0.11	4.47	-	-25.39	-
Mollic	B 80-95	1.8	0.17	4.00	-	-19.37	-
2100 m	C ₁ 100-110	2.1	0.24	3.36	-	-8.32	-7.84
	Bb ₁ 110-125	1.5	0.23	3.40	14030±880	-24.41	-19.55
	C2 125-135	1.1	0.14	3.34	-	-8.53	-7.80
	C3 135-165	0.4	0.05	3.31	-	-8.62	-7.54
	Bb ₂ 165-200					-9.11	-8.04
Article IV.	A 4-35	1.0	0.14	4.41	3010±90	-24.91	-
eptosols	A _b 35-50	2.5	0.17	4.87	5560±120	-25.25	-
Mollic	B 87-97	1.7	0.07	3.57	7130± 610	-28.80	-11.94
2350 m	C 97-110	1.2	0.06	3.63	-	-10.58	-8.00
	B _b 110-120	1.3	0.08	3.55	10100±564	-10.36	-9.30
Leptosols	A 0-14	1.6	0.09	4.41	-	-26.01	-
Mollic	23-37	1.3	0.13	4.87	-	-25.43	-
2450 m	A _b 37-50	1.7	0.13	4.07	6440±180	-25.32	-
	BC 73-83	2.8	0.18	3.42	-	-21.01	-11.52
	Bb ₁ 83-100	0.5	0.01	3.33	9130±640	-11.12	-10.09
	C ₁ 100-130	0.3	0.03	3.50	-	-10.19	-9.11
	Bb ₂ 130-150	0.8	0.01	1.50	-	-10.62	-9.27
Leptosols	A 3-10	1.3	0.06	5.03	109±47	-24.18	-
Umbric	AC 10-35	0.9	0.06	5.13	-	-24.21	-
3100 m	C 35-50	0.9	0.09	4.59	-	-23.89	-
		0.8	0.05	5.11	-		

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