Geochemical studies on Kashmir loess profiles

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Abstract. Major and trace element concentrations of a few representative loess profiles in Kashmir valley are studied using EDXRF spectroscopy. Principal component analysis for pattern recognition has been employed to study association between elemental concentration variations in various horizons. The present study reveals that elements related to clay illuviation (K, Rb, Fe, Ti, Mn) and plant activity (Cu, Zn) are generally higher in B horizon of the palaeosols whereas Ca and Sr have a high concentration in the loess layers. Such an elemental concentration variation provides us with an objective index for identification and confirmation of palaeosols. There is further a close association in the movement of (i) K, Rb, (ii) Fe, Ti, Mn, (iii) Cu, Zn and (iv) Ca, Sr. These clusters of elements are also present in modern soils, suggesting that the soil characteristics in palaeosols have been preserved. Concentration of iron and titanium is also observed to be higher in loess profiles on Pir Panjal mountain flank which is dominated by basic rocks, compared to profiles on Himalayan flank, suggesting that the loess in Kashmir might have been derived from the nearby rocks in a localized way.

Keywords. Loess; palaeosol; energy dispersive X-ray fluorescence; principal component analysis.

1. Introduction

The late cenozoic Karewa deposits in Kashmir are the products of glacio-fluvio-lacustrine conditions and are capped by a mantle of aeolian loess deposits (Pant *et al* 1978; Agrawal *et al* 1979). The average thickness of loess deposits is ~ 25 m. A variety of techniques have been used to date these loess deposits. The loess deposits in the valley are possibly younger than 200 KYrs and lie in the upper part of Brunes normal chron. Main loess palaeosol sequences have been dated using [14]C (Kusumgar *et al* 1980). The topmost palaeosol at Burazhom is dated at 18 KYr BP and the top soil at Khanchikhol I at 6 KYr BP. The ^{14}C dates lie in five main date clusters (table 1) (Kusumgar *et al* 1986).

We have used the energy dispersive X-ray fluorescence (EDXRF) technique to determine the concentration of major and trace elements in the loess palaeosol sequences of Kashmir valley. The technique has an advantage of multielement analysis of major and trace elements in a single run without any chemical treatment to the sample. We present the elemental data on loess profiles exposed at Burazhom, Wagahoma and Khanchikhol. The present study was undertaken with the following aims:

(i) To generate geochemical data which will aid in the investigation of the source of loess deposits in the Kashmir valley (Taylor *et al* 1983).

Table 1. Five main date clusters of ^{14}C dates of the Kashmir palaeosols.

C	$5,000 \pm 1000$ yrs.B.P.
C	$13,500 \pm 1500$ yrs.B.P.
C	$18,000 \pm 1500$ yrs.B.P.
C	$25,000 \pm 2000$ yrs.B.P.
$C > 31,000$ yrs.B.P.	

(ii) Once the sediments are deposited they are subjected to local weathering conditions. The weathering conditions depend to a great extent on the prevailing climate. Major and trace elements in the loess palaeosol sequence would provide a measure of the weathering intensity which in turn can be used to obtain some information on the past climate of the region (Retallack *et al* 1984).

(iii) Traditionally, a vertical repetition of morphological features such as colour, structure and compaction has been used to identify palaeosols buried in loess. We have instead attempted to use the major and trace elemental variation in a profile to distinguish various horizons. The elemental data approach for recognition of loess palaeosol horizons has earlier been used for loess in New Zealand (Childs and Searle 1975) and China (Qi-Zhong *et al* 1982).

(iv) Power spectrum analysis of geochemical data for loess has been carried out on Chinese loess (Qi-zhong *et al* 1984). We have used the principal component analysis (PCA) technique for statistical analysis of the multielement data. PCA is a good technique to describe the multidimensional data. The technique has helped us in identifying elements with similar collective behaviour and the identification of loess palaeosol horizons on the basis of collective behaviour has become more reliable compared to interpretation obtained on the basis of elemental concentrations seen in isolation.

2. Experimental technique

2.1 *Sample preparation*

The samples are dried in a hot air oven at $\sim 150°C$. The dried samples are ground in an agate mortar and pestle. The sample is pelletized into a 30 mm dia. pellet at 3·9 ton per square cm pressure using a hydraulic press. The weight of the pellet is kept around 20 to 30 mg/cm^2. As the samples contain large quantities of fine silt and clay, the pellets can be made without adding any binder. Standards for the analysis were synthesized by mixing pure element compounds in silicon dioxide matrix.

2.2 *EDXRF spectrometer*

The multielement analysis has been carried out on an EDXRF spectrometer (Bertin 1975) comprising a Si(Li) detector of resolution 155 eV at 5·9 keV. The excitation source used is a laboratory built transmission anode molybdenum X-ray

tube. The tube gives photon flux of MoK lines with very little continuum bremsstrahlung background. The multielement data are acquired on a pulse height analyzer (ECIL 4K). The data are analysed on the on-line data processing system consisting of a micro-computer (HCL MICRO-2200) with a floppy disk attachment.

2.3 *Quantitative estimation method*

We have used the Compton-scattered radiation standardization for quantitative estimation of analytes in the sample (Nielson 1979). The experimental Compton peak normalized excitation efficiencies were obtained using synthetic standards prepared in silicon dioxide matrix. For matrix absorption correction we have used the effective mass absorption cross-section (μ_{eff}) of the sample (Van Dyck and Van Grieken 1980). The (μ_{eff}) at various energies was obtained in an iterative loop using the tabulated mass absorption cross-sections (McMaster *et al* 1969). The initial estimate of (μ_{eff}) was obtained assuming the sediment matrix to be composed of SiO_2 and Al_2O_3 in the ratio of 80:20. Once the estimates of the major elements present in the sample are obtained the new (μ_{eff}) is computed. This procedure is repeated till a converging (μ_{eff}) is obtained. The final (μ_{eff}) is used to compute the absorption correction term for each analyte in the sample. This quantitative estimation procedure was tested for a large number of synthetic standards and accuracies better than 10% were obtained.

For the interpretation of multielement data at various sections, principal component analysis technique (Llinas and Ruiz 1986) was adopted. The reliability of the technique is apparent from its capability to characterize loess palaeosol sequences from the multielement data despite the fact that the sections have undergone post-depositional changes. The technique involves reduction of the elemental data set with a large number of variables (which are often correlated and sometimes redundant) to smaller number of independent variables. Furthermore, the analysis provides a graphical representation of objects and variables in a vector subspace with reduced number of dimensions. In our analysis we have used concentration values of K, Ca, Ti, Mn, Fe, Cu, Zn, Rb and Sr obtained from EDXRF analysis. The concentration of Ni and Br has not been included in the analysis due to high estimated errors in their concentration. The two major principal components account for 75% to 80% of the features in all the sections which is adequate for the interpretation of geochemical data on loess palaeosols.

3. Observations

We have studied the geochemical profiles of seven loess sections in Kashmir valley (figure 1 and table 2). However, here we present three representative loess sections namely, Burazhom, Wagahoma and Khanchikhol II. Burazhom and Wagahoma are plateau loess profiles on the Himalayan flank. The thickness of loess profiles on this flank varies from 6–20 m and they rest on upper Karewa laminated silt members. Khanchikhol II is a plateau loess section on the Pir Panjal mountain flank exposed by streams of recent origin (Khol is a Kashmiri term for stream). The loess sections on this flank are generally 20–25 m thick and rest on lower Karewa gravel
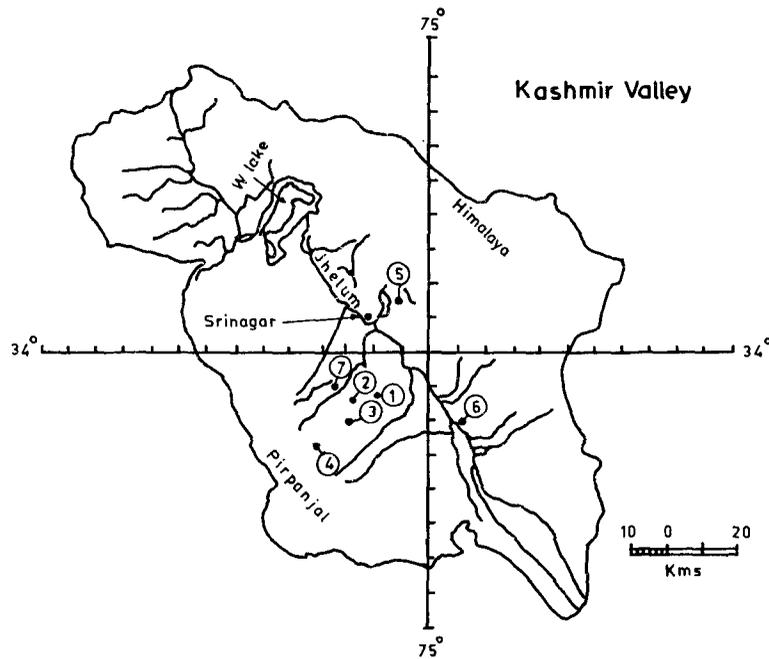
Figure 1. Map of Kashmir valley showing loess sections undertaken for geochemical studies using EDXRF spectrometer.

Table 2. Loess sections undertaken for geochemical studies.

Section	Location	Altitude (metres)	Thickness (metres)
Burzahom	E 74°53' N 34°30'	1620	6
Wagahoma	E 74°0'99'' N 33°46'	1700	21
Khanchikhol I (Karpura)	E 33°50' N 74°47'	2000	23
Khanchikhol II (Malpura)	E 33°54' N 74°49'	1740	22
Romu	E 33°53' N 74°50'	1850	22
Kanier	E 74°30'65'' N 33°45'94''	1800	20
Dilpur	E 74°57' N 34°30'	1800	19

beds. The stratigraphy of the main sections studied has been drawn according to our field observation. The various horizons have been marked on the basis of colour, structure, compaction and morphological features.
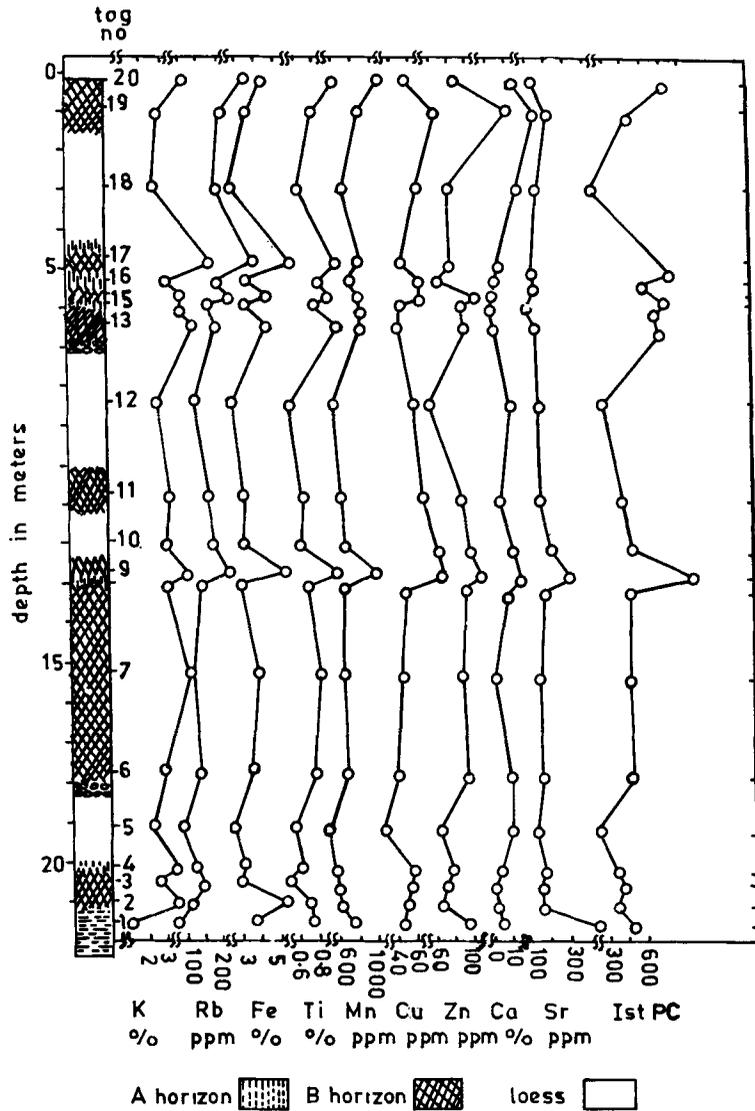
Figure 2. Wagahoma loess field stratigraphy, variation of various elemental concentrations and the first principal component.

3.1 *Wagahoma loess profile*

Wagahoma loess section near Brijbihara on Jammu Srinagar highway, is 21 m thick and located on the Himalayan mountain flank. Figure 2 shows the field stratigraphy, the variation of various elemental concentrations and the variation of the first principal component in the various horizons. The main results are summarized below:

(i) The concentrations of K, Rb, Fe, Ti and Mn are generally higher in B horizons of the palaeosols compared to the A horizon and the loess.

(ii) Palaeosols are observed to have generally low values of Ca and Sr. These elements accumulate below the B horizon of the palaeosol, forming a calcium carbonate horizon, or in the loess layer itself.

(iii) The loess layer between 10 and 11·25 m was marked as doubtful B horizon during our field observation as it appeared slightly darker in colour with low secondary calcium carbonate. However, the elemental concentration values as also the values of first principal component for this horizon are similar to the loess horizon above and below it. Thus elemental data help in identifying it correctly as part of the loess.

(iv) The average value of Fe is ∼ 3·8% and Ti is ∼ 0·8%.

(v) For this section the first principal component is high for B horizons of the palaeosol and low for the loess. The first and the second principal components account for 46% and 28% of the total variance respectively. The variation of concentration of K, Rb, Fe, Ti and Mn dominates in the first principal component while Ca and Sr variation dominates in the second principal component. Thus instead of seeing the variation of all the individual elemental concentrations in the horizons, the variation of the first and the second principal component with horizon gives their diagnostic characteristics.

(vi) The results for the association in movement among the elements in various horizons are shown in figure 3 by the variation in latent vector 1 (LV1) vs latent vector 2 (LV2). The clusters of elements with similar variability in concentration are (i) K, Rb, (ii) Fe, Ti, Mn, (iii) Cu, Zn and (iv) Ca, Sr.

(vii) These clusters show that the movement of elements within these groups follows a similar chemistry. The associated movement of the elements mentioned in the above groups occurs in the modern soils because of similar chemical changes they undergo under various stages of weathering. The principal component analysis brings out the above association for loess palaeosol sequences suggesting that the section has probably not undergone considerable post-depositional reworking.

3.2 *Burazhom loess profile*

This section is ∼ 20 km northeast of Srinagar on the Himalayan flank. The section has already been studied for stable isotope ratios of carbon to study the pleistocene climatic changes (Krishnamurthy *et al* 1982). The palaeosols at 3·5 m and 4·5 m
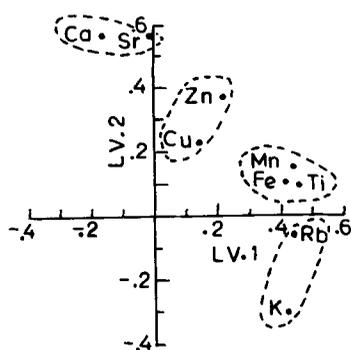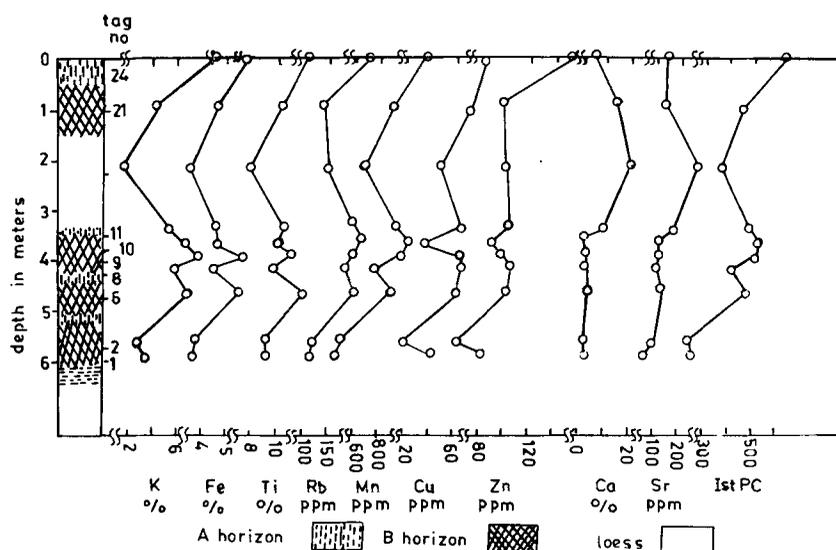

Figure 3. Two major latent vector plots for Wagahoma loess section.

Figure 4. Burazhom loess field stratigraphy, variation of various elemental concentrations and the first principal component.

have been dated at 18 KYr BP and 31 KYr BP respectively using ^{14}C technique. The field stratigraphy, the concentration profiles of various elements and the variation of first principal component are shown in figure 4. The main results are summarized below:

(i) The B horizons of the palaeosols are marked by generally high concentration of K, Rb, Fe and Ti compared to A horizons and the loess. The low concentration values of K, Rb, Fe and Ti in the bottom-most B horizon (tag no. 2) are probably due to the fact that this B horizon got mixed with laminated silt members, and some of these elements got removed in lacustrine environment.

(ii) Calcium is high in loess layers and low in palaeosols.

(iii) The average Fe concentration is $\sim 4.5\%$ and the average Ti concentration is $\sim 0.9\%$.

(iv) The first principal component accounts for 60% of the total variability in concentration of the elemental data set. It is high for palaeosols and low for loess. The maximum contribution in the variation of the first principal component for this section comes from the variation in concentration of K, Rb, Fe and Ti. Ca and Sr variations are dominated in the principal component 2.

(v) The clusters of elements with similar variability in concentration are (figure 5) (i) K, Rb, Fe, Ti, (ii) Mn, Cu, Zn and (iii) Ca, Sr.

(vi) The clustering of various elements is not so well as in the Wagahoma section because the number of variables is equal to the number of samples while for optimum class separation the number of samples should be much larger than the number of variables. This is probably the reason why Mn does not fall in the Fe, Ti cluster as seen for all other sections.
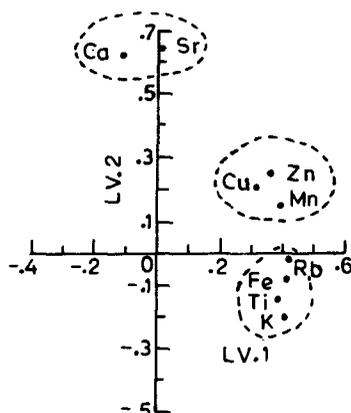
Figure 5. Two major latent vector plots for Burazhom loess section.

3.3 *Khanchikhol II loess profile*

This plateau loess section is $\sim$ 22 m thick and is located on the Pir Panjal mountain flank. The section is situated at Malpura which is $\sim$ 3 km north of Pakharpura and $\sim$ 4 km southwest of Pulwama. The field stratigraphy, concentration profile of various elements and the variation of first principal component are shown in figure 6. The main results are summarized below:

(i) The B horizons between 0·75 and 2·5 m, 6·25 and 6·75 m and 15·5 and 19·0 m are accumulation horizons for K, Rb, Fe, Ti and Mn. The horizon marked B at 13–14 m does not however act as the accumulation zone for these elements. Rather the accumulation takes place in the horizon marked loess at 14–15 m on the basis of field observation. It appears that the field stratigraphy for this horizon has to be modified with A horizon extending down to 14 m and the horizon between 14 and 15 m should be marked as B rather than a loess horizon. This inference drawn from the elemental data is further supported by mineral magnetic analysis (Agrawal *et al* 1986).

(ii) The horizon marked loess was observed in the field to be highly weathered. For this horizon, Ca, Sr, Fe, Ti and Mn are observed to be high. High Ca and Sr are due to a thick carbonate nodular horizon above this horizon but the high concentration of Fe, Ti and Mn suggests accumulation of the elements during secondary weathering process.

(iii) The average concentration of Fe is $\sim$ 5·5% and that of Ti is $\sim$ 1·2%.

(iv) The first and the second principal component account for 56% and 25% of the variance respectively.

(v) The principal component analysis for associations among elements show the following groupings (figure 7): (i) K, Rb, (ii) Fe, Ti, Mn, (iii) Cu, Zn and (iv) Ca, Sr.

4. Conclusions

The main conclusions drawn from the present study are:

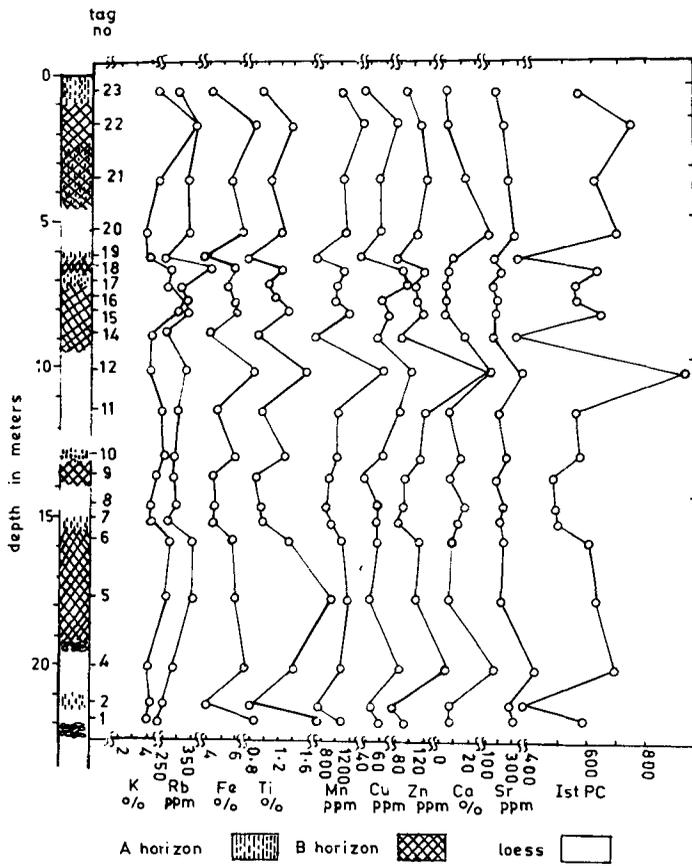(i) The elemental analysis of loess palaeosols reveals that elements related to clay

Figure 6. Khanchikhol II loess field stratigraphy, variation of various elemental concentrations and the first principal component.
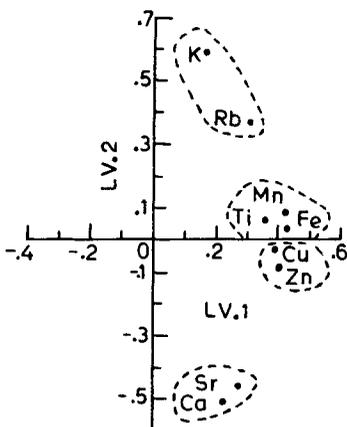
Figure 7. Two major latent vector plots for Khanchikhol II loess section.

illuviation (K, Rb, Fe, Ti and Mn) are generally higher in B horizons of the palaeosols whereas Ca and Sr are low in palaeosols compared to the loess layers. The concentration of these elements in palaeosols is closely related to the process of soil formation.

(ii) Palaeosol horizons which are rich in clay fraction (B horizons) are generally rich in K concentration. This is due to the fact that K gets fixed in the inter-layer space of the clay minerals. Likewise the behaviour of Rb in the soil-forming process is controlled to a large extent by its absorption in clay minerals. Illites and montomorillonites are common clay minerals that absorb K and Rb which explains the high concentration of K and Rb in B horizons of the palaeosols. The concentration of Fe, Ti, Mn and Cu, Zn in palaeosols is controlled by clay minerals and organic activity of plants. The mechanisms include surface adsorption and penetration to the interior of the crystals. Ca and Sr have a high leaching rate and get deposited below the B horizon of the palaeosol in the loess layers.

(iii) The principal component analysis for the associations among elements reveals that despite some post-depositional perturbations there is a close association in the movement of the elements such as (i) K, Rb, (ii) Fe, Ti, Mn, (iii) Cu, Zn and (iv) Ca, Sr. These associations are not obvious from the individual elemental concentration data seen in isolation. As these associations are also observed in modern soils due to their similar chemistry during various stages of weathering, the result suggests that the palaeosols have preserved the soil characteristics to a large extent.

(iv) The concentration of Fe and Ti is high in loess profiles on the Pir Panjal mountain flank compared to the Himalayan flank. The average Ti value for the Khanchikhol II loess section is $\sim 1 \cdot 2\%$ which is higher than that for the Wagahoma and Burzahom loess section on the Himalayan flank (Ti $\sim 0 \cdot 8\%$). Likewise, the average Fe value for loess profiles on the Pir Panjal flank (Fe $\sim 5 \cdot 5\%$) is higher than the value for the Himalayan flank (Fe $\sim 4 \cdot 5\%$). Further the movement of Fe and Ti is closely correlated in our data, suggesting the presence of ilmenite ($FeTiO_3$). The Pir Panjals are dominated by basic igneous rocks which usually have relatively high concentration of ilmenite. The Himalayan flank is made up of limestone which generally has lower concentration of Ti. Thus it appears that the source material for the loess deposits at various sections was derived from the nearby rocks.

Acknowledgements

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