MICROMORPHOLOGICAL (SEM) AND MICROCHEMICAL (SEM/EDXRA) STUDY OF THE CLINOPYROXENE SAND GRAINS FROM THE SOIL ENVIRONMENT OF PAKISTAN

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The micromorphological and microchemical investigations of the clinopyroxene grains collected from the fine sand fraction in the surface horizon of the Khurrianwala Soil Series revealed the microtextural features: 1) irregular and elongated grains, 2) needle and lenticular shaped overgrowths, 3) parallelism of striations to C direction, 4) dissolution pattern, 5) etching pattern, 6) Si-coatings, 7) cellular humps, and 8) oriented dish shaped pattern. The presence of clinopyroxenes in the heavy fraction of the fine sand suggests that mafic igneous rocks have contributed to the soil parent material. Submicroscopic investigations of the clinopyroxene grains revealed the solution, precipitation/overgrowth and etching as the main shaping mechanisms of minerals. It is also concluded that mineral shape under SEM could provide information about the sedimentary history.

INTRODUCTION

Micromorphological (SEM) features of the heavy minerals (S.G.> 2.95 g cm^{-3}) in the fine sand fraction give considerable insight into the sedimentary history of the deposit from which the grain has come as well as or indication of some of the processes which have taken place in the soil environment. The results of the physical and chemical environments may be preserved on the sand grains surfaces e.g. solution and precipitation features which are the most important.

Weathering is visibly evident in the progressive etching of the sand grains; it is most obvious in pyroxenes. Pyroxene is one of the important group of rock-forming minerals belonging to inosilicates. In the pyorxene or Si_2O_6 structure, the silica tetrahedra are arranged into single chains which parallel the c-crystallographic axis (Loughman, 1969).

Agencies like glacial, fluvial, aeolian and chemical in nature impose their recognizable characteristic features and etch patterns on grain surfaces (Krinsley and Doornkamp, 1973). A set of distinctive sand grain microtextures has been recognised by Krinsley and Margolis (1969) providing a means for distinguishing grains which have been acted upon by chemical and mechanical processes in varying environments. Micromorphology of the heavy minerals also allows estimation of the relative age of the soil (White, 1981) and soil parentage (Shahid *et al.*, 1990).

Not much has been published on the heavy mineralogy of the soils of Pakistan only in one paper such an investigation has been emphasized (Shahid *et al.*, 1990). This preliminary study is based on one soil profile of the Khurrianwala Soil Series.

The objectives of the present investigation were to study micromorphological features of the mineral species "clinopyroxene" which is considered to be highly susceptible to such changes. Such information may be quite useful to gain an insight into the environmental history of the soil concerned and the parent material and to elucidate the shaping mechanisms of soil particles.

MATERIALS AND METHODS

A surface soil sample collected from 0-5 cm of the Khurrianwala Soil Series (*Natric Camborthids*) was air-dried and sieved through 2 mm sieve. The physical and chemical measurements suggest that the soil is saline-sodic. The texture is silt loam.

The separated heavy minerals from the fine sand fraction of the surface sample of the Khurrianwala Soil Series (Shahid *et al.*, 1990) were used for microtextural study under a Scanning Electron Microscope (SEM). In order to identify the minerals and to study their surfaces morphology, obscuring soil clay was removed ultrasonically. The cleaned heavy minerals were immersed in methyl salicylate (Refractive Index = 1.54) and the constituent mineral species were identified under the polarizing microscope. The individual clinopyroxene species (10 grains) was then separated from the other minerals by suction up a fine capillary. These were washed with acetone and hand-picked under a binocular microscope (Wild M3Z Heerbrugg, Switzerland).

Adhesive material and mounting of grains on SEM stub: The adhesive material from a 10 cm long (1 cm wide) cellutape was dissolved in 10 ml of trichloroethane and a drop of the solution was placed on carbon stub, and 10 mineral grains mounted on it. Later, the whole surface of the sample was coated with carbon (in an evaporator), a few nanometer thick.

Studies by SEM/EDXRA and microphotography: The mounted grains were thoroughly studied at varying magnifications. The SEM was operated at an accelerating voltage of 15-25 kv. The magnification was progressively stepped up as this helps in the selection of sub-areas for more detailed observations. As the application of SEM to the identification of soil minerals from the morphology alone is still in its infancy, further confirmation of identity was obtained by using the Energy Dispersive X-Ray Analyser (EDXRA) facilities. EDXRA examined the surface chemistry of minerals both in terms of peak heights which reflect the relative amount of each element and peak positions which reflect relative binding energies. By coupling the morphological information (SEM) with microchemical (EDXRA) studies, it may be possible to elucidate various mechanisms responsible for shaping the sand grains as well as for the creation of microtextural features.

Micrographs of entire grains were taken first at x 100, and finally at higher magnifications depending upon the features under observation. Micrographs were taken for topographical details. The model of SEM used was S-520 (Hitachi, Japan).

RESULTS AND DISCUSSION

The study of various clinopyroxene species under the SEM revealed variation in their shapes, but homogeneity of the micromorphological features also existed. In this section the microtextural features observed under the SEM and their microchemical analysis by EDXRA will be described.

A number of micromorphological features occur on clinopyroxene grains surfaces. Often, two or more types of surface textures were apparent on the same grain. The main features are illustrated in the following figures. Briefly, these are:

1. irregular and elongated shaped grains;
2. needle shaped and lenticular crystals overgrowth;
3. parallelism of striations to C direction;
4. dissolution and etching pattern;
5. Si-coating;
6. cellular humps; and
7. oriented dish shaped pattern etc.

The morphological (SEM) and microchemical analysis (EDXRA) of the four cleaned grains revealed different shapes and composition. Two of them as shown in Figures 1 a and 1 d, show similar composition. The EDXRA of one of them (Fig. 1 a) show the presence of Mg, Si, Ca, Fe (EDXRA spectra-Fig. 3 a). Whilst the third grain (Fig. 2 a) gives a composition of Si, Al, K, Ti and Fe (EDXRA spactra-Fig. 3 b). The comparison of these elemental composition confirmed that the first two grains (Fig. 1 a, 1 d) are of pigeonite species $[(Fe, Ca, Mg)_2Si_2O_6]$, where as the third grain is titanaugite $[Ca (Mg, Fe, Al, Ti)(SiAl)_2O_6]$. Chemical composition of the third grain (Fig. 2 a) reflects only the species titanaugit, along with K as an impurity or K is present as an ionic substitution. Dear *et al.* (1983) have stated that a wide range of ionic substitution is possible in the monoclinic pyroxenes. As far as the mineral purity is concerned, it was assured by handpicking and chemical removal of traces of accompanying phases ultrasonically. The fourth grain of clinopyroxene (Fig. 2 c) consists of Si, Ca and Fe (EDXRA spectra Fig. 3 c). The species is suggested to be hedenbergite (Ca, Fe, Si_2O_6).

The composition of the overgrowth features (bladed and stellate) as shown in Figures 2 a and 2 b, revealed the presence of Al, Si, K, Ca and Fe (EDXRA spectra, Fig. 3 d). This suggests the overgrowth features are either of augite or ferroaugite, the observation of the EDXRA spectra revealed that Fe is present in sufficient amount and, therefore, it is possibly ferroaugite. Such a growth of ferroaugite on titanaugite may be possible at high pH (Schott and Berner, 1984). This might help to explain the present observation. Similar overgrowth has also been suggested by Luce *et al.* (1972). The effect of such overgrowth seemed to be protective in the sense that diffusion of dissolved species to and from the unaltered primary mineral surface is inhibited by the surface layer.

All the four grains show parallelism of striations of the crystal and the pattern of dissolution being controlled by the chain structure of silicates (Fig. 1 a, b; 2 a). The grain in Figure 1 a clearly illustrates etching on the upper and front part alongwith Si-coating (Fig. 1 c) which covers the original features and perhaps restricts further weathering of the grain. The selective dissolution of the grain relate to difference in chemical resistance within the grain (Krinsley and Doornkamp, 1973) or this may be the application of the principle of Riecke (1895) whereby a mineral grain under stress has an increased solubility. If a grain is stressed inhomogeneously it will be dissolved at stressed points and precipitation may occur on the surface of lower stress. For the Si coating on the clinopyroxene grain (Fig. 1 c), it is suggested that in hot environment like in Pakistan, during the day/night cycles the pH of the soil water rises due to the presence of dissolved evaporites in the evening which may lead to the removal of small amounts of Si and other nutrients/elements depending on the nature of the mineral under stress. This removed Si is redeposited on the grain surfaces as an irregular layer of opal or silicic acid (Kuenen and Pedrok, 1962) which subdues the grain surface (Margolis and Krinsley, 1971).

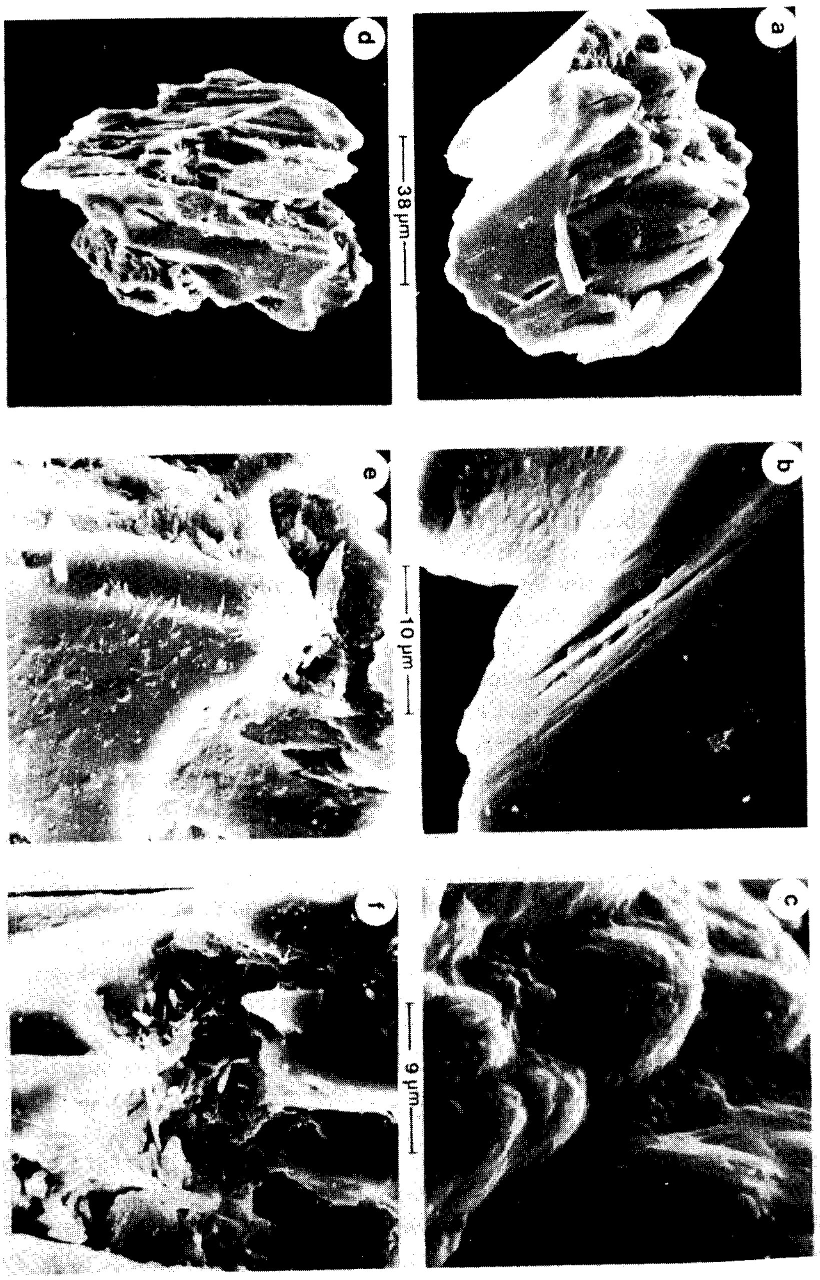

Fig. 1. a) Etched clinopyroxene grain. b) Details from "a" showing the parallelism of striations to c. c) The top of the clinopyroxene grain coated with Si. d) Etched clinopyroxene grain. e) Details from "d" showing (a) overgrowth of acicular crystals (b) "humps". f) Infilling of a highly weathered part of the clinopyroxene grain with acicular crystals.

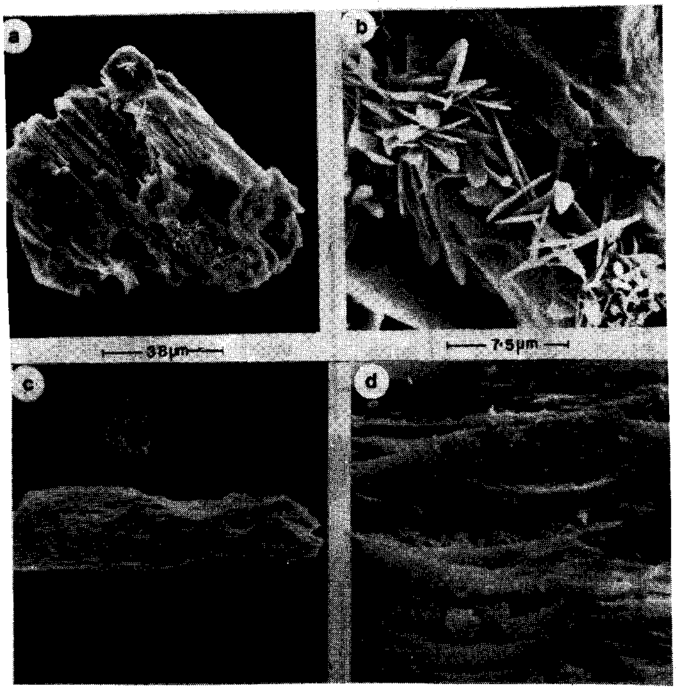

Fig. 2. a. Etched clinopyroxene grain.
b. Overgrowth of bladed crystals.
c & d. Clinopyroxene grain showing oriented lenticular etch pits (c), infilled with acicular crystals (d).

The clinopyroxen grain (Fig. 1 d) also shows overgrowth features (Fig. 1 e) this shows cellular humps, lenticular crystals and the signs of chemical weathering. The deposition of the lenticular crystals in the highly weathered part of the grain (Fig. 1 f) and within the oriented dish shaped pattern can be seen in Figures 2 c and d. This suggests that etching and filling has taken place simultaneously. The presence of oriented pits with their longer axes parallel to one another suggests that these grains undergo dissolution etch pits parallel to the c axis of the crystal. Thus allow to determine the orientation of otherwise lacking cleavaged grains. Observations of coexisting grains show that clinopyroxene becomes extensively pitted and thus weathered more rapidly than others. These pits then serve as a source of chemical reactions at the interface of the mineral and the soil water, this results in the release of ions into the solution.

The comparison of the shapes of the clinopyroxene sand grains from Pakistan with those from Hofuf, Saudi Arabia (Jenkins, 1976) revealed that, the grain from Hofuf are rounded without edges or elongated but still rounded. By contrast the grains from Pakistan as presented in this paper are irregular in shape. The difference in their shapes reflecting the rounding of grains from Saudi Arabia under aeolian (wind deposited) conditions. The preservation of the sharp edges of the clinopyroxene

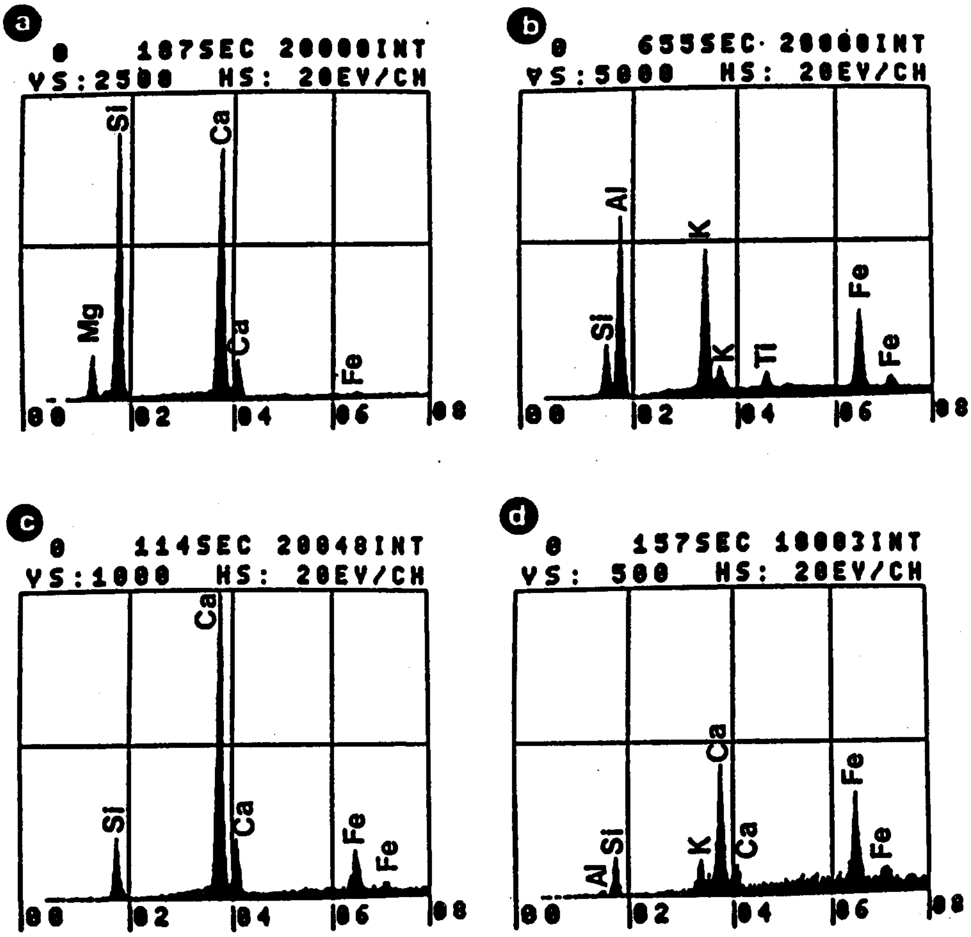

Fig. 3. a. EDXRA spectra of the grain as showin in Fig. 1 a.
b. EDXRA spectra of the grain as shown in Fig. 2 a.
c. EDXRA spectra of the grain as shown in Fig. 2 c.
d. EDXRA spectra of the overgrowth features as showin in Fig. 2 a and b.

is due to the cushioning effect of water during transportation before deposition as the soils of Pakistan are derived from the alluvium.

It is, therefore, concluded that apart from microtextural features, the shape of the mineral as seen under the SEM in particular can provide useful information about their sedimentary history.

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