

SCANNING ELECTRON MICROSCOPY OF AUTHIGENIC SULPHATE MINERALS IN SOILS

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I. Introduction

Both highly soluble and practically insoluble authigenic sulphate minerals may be present in soils under different climatological and geomorphological conditions. Their crystallization is a reflection of specific micro and macro environmental conditions.

The normal environment of the soluble sulphate minerals is where evapotranspiration exceeds precipitation during most of the year as in an aridic soil moisture regime (SCS, 1975). The supply of the cations and anions for the crystallization of the salt is generally from the ground water table. Soluble salts may also be present in a wetter moisture regime as in udic soil moisture regime. This is seen in acid sulphate soils where gypsum and jarosite crystallize in the subsoil.

The actual type of salt that is present depends essentially on the concentration and types of cations and anions present in the soil solution and the temperature. The type of salt may be predicted from thermodynamic considerations or by the use of mineral stability diagrams. Though a large number of salts are theoretically possible, the number encountered in soils is much less.

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Although many micromorphological studies are reported on saline soils, descriptions of authigenic soluble sulphate minerals are few, partly because these salts were not encountered in thin sections. One of the reasons for this is that salts, especially when finely dispersed in soils, are dissolved in the impregnating mixture. In cases where there is only a small amount of salt in the soil, these tend to crystallize on ped or prism faces. Petrographic-size thin sections of the interior of the larger peds do not pick out the salts. Consequently, it is necessary to study ped faces on all soils where soluble salts are suspected.

Scanning electron microscopic (SEM) studies of sulphate salts in soils are up to now, few. Micrographs of soluble sulphate minerals were published by DRIESSEN (1970) and DRIESSEN and SCHOORL (1973) (thenardite, bloedite), CHEVERRY et al. (1972) (gypsum, jarosite) and ESWARAN and BARZANJI (1974) (Gypsum). In addition, few pictures were published in more general papers. Fewer studies exist in the less soluble or insoluble anhydrous sulphate minerals (anhydrite, barite, celestite) as authigenic soil constituents and no SEM-micrographs of them are yet published.

The objective of this study is to report on the morphologies of some authigenic sulphate minerals encountered by us during the routine SEM examination of salt affected soils. As, in many cases, it is the first time that such micrographs are presented, we are uncertain if they are the common habits of the respective minerals. It is however necessary to develop a bank of such micrographs prior to further investigations, as for example on the influence of soil micro-environmental conditions on the crystal form. For reasons of completeness a review of published SEM-data is given for each mineral.

II. MATERIAL AND METHODS.

Soils in the collections of the authors were employed for the study. Thin sections were made of undisturbed samples. Fracture surfaces of peds were first examined with an incident light microscope to locate the efflorescences. Small pieces of the soil material were then mounted into aluminum stubs and coated with gold for the SEM-study. The efflorescences on other peds of similar material were scraped off, ground and analysed with X-ray diffraction for identification of the minerals. In some cases additional chemical tests were performed.

III. MINERAL DESCRIPTION

Thenardite (Na_2SO_4).

This mineral is rather common in salt lakes and playas where it can be formed directly from the salt solution, or as a dehydration product of mirabellite ($\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$).

DRIESSEN (1970) and DRIESSEN and SCHOORL (1973) published a few SEM micrographs of efflorescences of prismatic thenardite crystals in salt crusts with a rather loose structure from the Konya basin (Turkey). Crystal forms could not be recognized on these pictures. A micrograph of a rosette-like aggregate of thenardite was published by STOOPS (1973).

Plate I a, b, c, shows thenardite efflorescences on ped-surfaces in the C-horizon of a saline alluvial soil from Peru. The crystals have clearly a prismatic habit, sometimes with a tendency to lath-shaped individuals. From their optical behaviour it can be deduced that the prisms are elongated according to $[100]$.

Anhydrite (CaSO_4).

Although the presence of anhydrite in gypsiferous

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soils has been indicated, no published micromorphological descriptions are available.

The conditions of its formation, directly from the salt brine or by dehydration of gypsum are still under discussion in geology. In general, the soil environment does not present the thermodynamic conditions necessary for its crystallisation. MOIOLA and GLOVER (1965) were the first to describe the alteration of gypsum to anhydrite in (rather extreme) soil conditions, namely in the Clayton Playa, Nevada. The large gypsum crystals show an epitaxial replacement by anhydrite with an intermediate zone of hemihydrate, both minerals being fibrous.

Plate I, d, e, f shows fibrous anhydrite crystals on gypsum in a soil from Peru. The fibers have in general a well developed parallel orientation but neither their crystallographic form nor their crystallographic relation to the gypsum crystals could be determined. In thin sections, the transformation is clearly shown by an increase of the birefringence colours and the fibrous character of the newly formed product.

Barite (BaSO_4)

The presence of authigenic barite microlites in soils is reported by LYNN et al. (1971) in some poorly drained Alfisols and Ultisols of the southern part of the USA. The crystals, covering ped surfaces or occurring in pockets, have prismatic or tabular habits, dominated by following forms: $\{00\bar{1}\}$, $\{100\}$, $\{010\}$ and $\{210\}$.

Barite was also found in the B-horizon of a Haplustalf from Peru (STOOPS and ZAVALETA, in preparation) with a rather high electrical conductivity. Here they occur as crystal chambers. The crystals in the center have a tabular habit, the peripheric ones are prismatic and clearly length slow (due to their elongation according to $[100]$).

SEM micrographs (plate II a, b,) show that the tabular crystals are composed of following forms : $\{001\}$, $\{011\}$ and probably $\{101\}$. The prismatic crystals seem to have partially the same combination of forms, but others show essentially the $\{011\}$ form, which makes them very similar to the celestite microlites observed in gypsiferous soils.

Celestite (SrSO_4).

Authigenic celestite in soils was reported by BARZANJI and STOOPS, 1974 in gypsic and petrogypsic horizons from Euphrate and Tigris terraces soils from Iraq. Meanwhile the senior author observed it as a common feature in many gypsiferous soils, e. g. from Algeria, Iran and Iraq. In thin sections the microlites appear as length-slow pointed prisms with a square cross-section. They practically always occur as clusters in the clayey matrix, or in packing voids of sandy materials. In SEM (plate II, c, d, e, f) they appear as long square prisms elongated according to $\{100\}$ and with a well developed $\{011\}$ form. The indices of the terminal faces could not be determined on the pictures. Upon weathering, the prism-surfaces develop grooves according to $\{100\}$, although this is not a cleavage direction in this mineral. These grooves, though not very evident are shown in plate III, a, b, c.

Gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

Gypsum is a very frequent mineral in arid soils where it can even be a characteristic or dominant constituent, e. g. in the gypsic or petrogypsic horizons of gypsiorthids. In these soils it practically invariably occurs as coarse or fine lenticular or discoid crystals, developing essentially within pores as idiomorphic individuals. By the process of pedoturbation however they may become embodied in the soil matrix. Continuous growing of closely packed crystals leads to the formation of compact gypsum layers

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with an allotriomorphic granular fabric (BARZANJI & STOOPS, 1974).

Different habits of gypsum have been recognized in other soils, e. g. short prismatic in acid sulphate soils (MIEDEMA et al. 1973), fibrous in a Calciorthid from Egypt (LABIB, 1970), or elongated prismatic in polder soils from Tchad (CHEVERRY et al., 1972), Plate III, d, e, f shows the typical shape of the lenticular gypsum crystals with SEM. This form is developed normal to the cleavages, as can be seen clearly in thin sections. Weathering of such crystals therefore give rise to a comb like shape corresponding to the cleavage planes, as shown in plate IV, a, b, c.

Plate IV, d, e, f represents short prismatic gypsum crystals from a Torriorthent from Peru. Basing purely on the forms in the micrographs, some of the crystals seem to be elongated according to $[00\bar{1}]$, with well developed (010) and (100) prism faces. In thin sections and in the X-ray diffractogram the presence of anhydrite was clear in this sample.

Plate V, a, b, c shows rosette like aggregates of gypsum prisms in a cat-clay from Nigeria (MOORMAN et al., 1977, in preparation).

The individual crystals are elongated according to $[00\bar{1}]$ and the prism zone is commonly striated. It is most probably the combination of $\{110\}$ and $\{0\bar{1}0\}$ which is responsible for the hexagonal cross-section of the prisms.

Hexahydrate ($MgSO_4 \cdot 6H_2O$)

This is a rather un common mineral, found in the deposits of some salt lakes and as efflorescences. With respect to soils it was recorded by DRIESSEN (1970) in salt crusts, probably as an intermediate dehydration product between epsomite ($MgSO_4 \cdot 7H_2O$) and leonhardite ($MgSO_4$).

$4\text{H}_2\text{O}$). The habit of these crystals was not discussed, nor were micrographs presented by DRIESSEN (1970).

In a salic Gypsiorthid from Iran, hexahydrate crystals were found covering ped surfaces, intermingled with lenticular gypsum crystals. In thin sections only the gypsum was noticed, although hexahydrate should be easily recognizable because of its higher birefringence. This suggests that it is soluble in the resin. Plate V, d, e, f shows the SEM-micrographs of these crystals. Although the mineral belongs to the monoclinic system, crystals show a pseudo-hexagonal shape, which can be explained as a thick tabular habit composed of following forms: $\{100\}$, $\{110\}$ and $\{001\}$.

Bloedite $(\text{MgNa}_2(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O})$.

This mineral was reported by DRIESSEN (1970) and DRIESSEN and SCHOORL (1973) in the surface crust of flooded solonchak in the Konya basin (Turkey). It forms rather pure (up to 90%) glass-like crusts which seal the underlying soil, because of the overlapping of the welded crystals, and their ability to close all pores by a growth from the edges towards the centre. Some SEM pictures are shown but crystal-forms are not analysed.

Jarosite $(\text{K} \cdot \text{Fe}_3(\text{SO}_4)_2 \cdot (\text{OH})_6)$.

This sulphate mineral was reported already in several publications as reaction product of pyrite weathering in soils. Micromorphological studies discussing it and providing SEM pictures are for instance CHEVERRY et al. (1972), VAN DAM et al. (1972), MIEDEMA et al. (1973), ESWARAN et al. (1974). Crystal forms of the microlites were not yet analysed. It is a common constituent of acid sulphate soils (Sulfaquepts).

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LEGENDE OF PLATES

- Plate I, a, b, c : SEM micrograph showing efflorescences of thenardite on ped surfaces. Prismatic habit elongated according to $[100]$.
Magn. : 460, 3750 and 15, 000 x resp.
- d, e, f : SEM micrograph of anhydrite fibres on gypsum. Magn. : 5000 and 10, 000 resp.
- Plate II, a, b, : SEM micrograph showing tabular and prismatic barite microlites on a pore-wall.
Magn. : 2250 and 5600 x resp.
- c, d, : SEM micrograph of prismatic celestite
e, f, microlites elongated according to $[100]$.
Magn. : 320, 124, 310 and 820 x resp.
- Plate III, a,b,c : SEM micrograph of partially weathered celestite microlites. Note the grooves (arrow) normal to the prism-faces.
Magn. : 125, 575 and 1150 x resp.
- d, e, f : SEM micrograph of lenticular gypsum crystals in a pore.
Magn. : 52, 525 and 2100 x resp.
- Plate IV, a,b,c : SEM micrograph of comb-structure as a result of the weathering of lenticular gypsum crystals along cleavaques.
Magn. : 200, 1000 and 1000 x resp.
- d, e, f : SEM micrograph of prismatic gypsum microlites with well developed $\{100\}$ and $\{010\}$ form.
Magn. : 1900, 4750 and 9500 x resp.

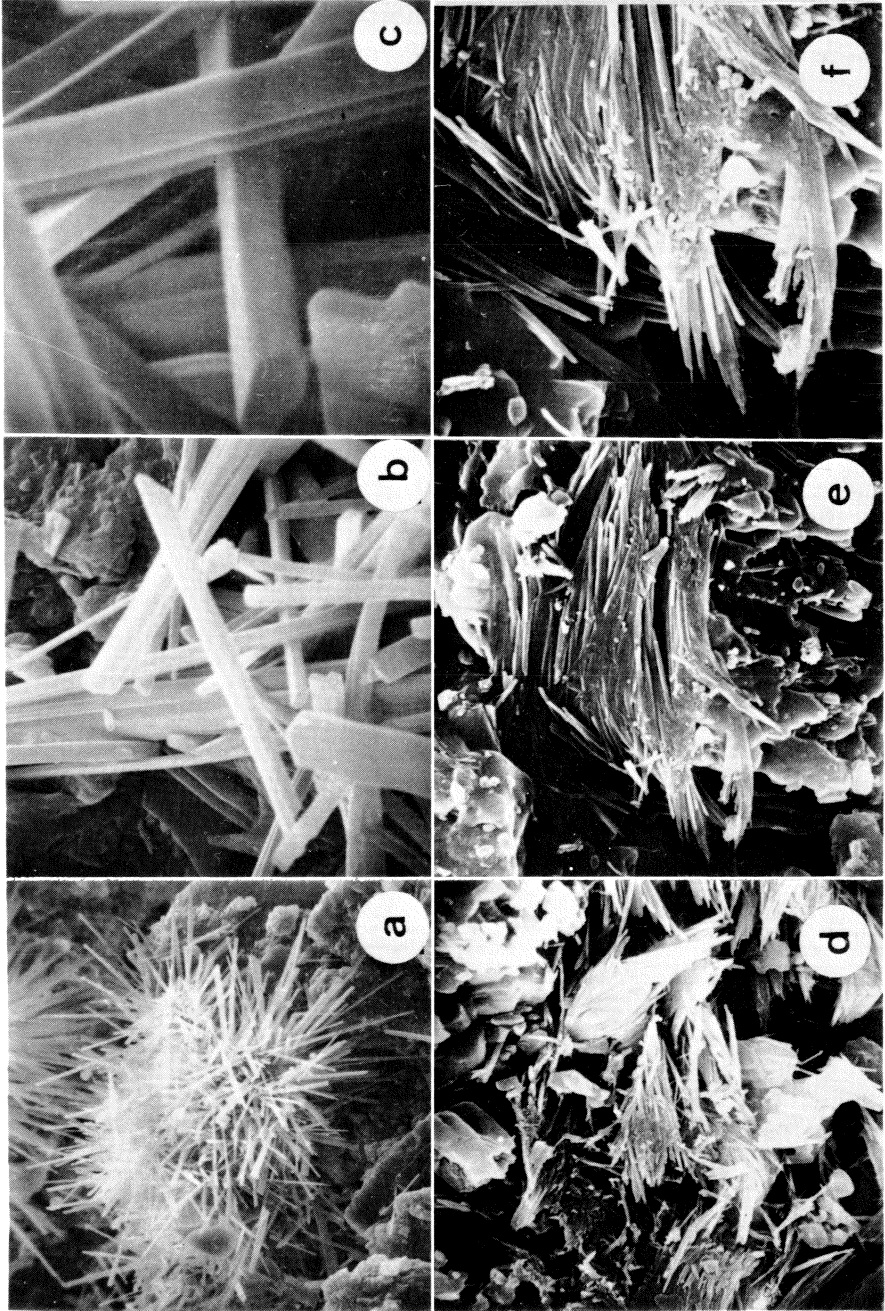


Plate I

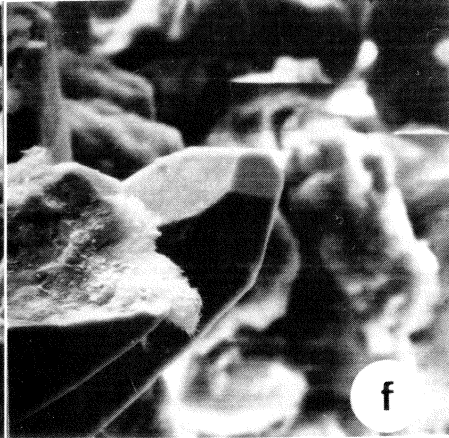
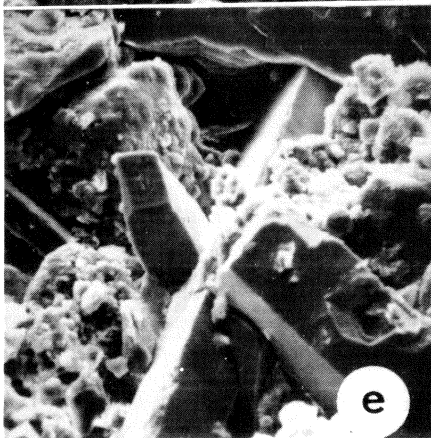
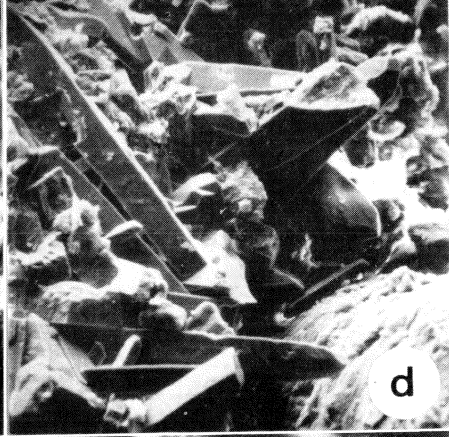
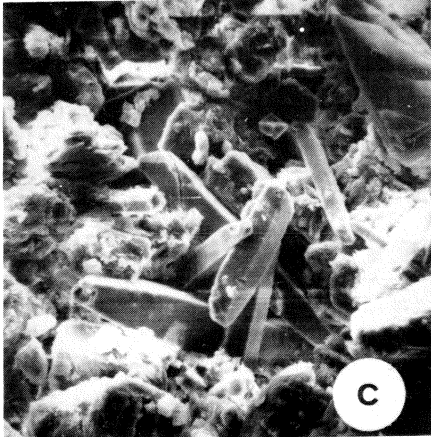
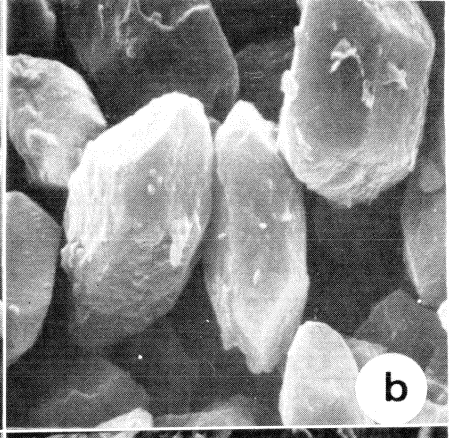
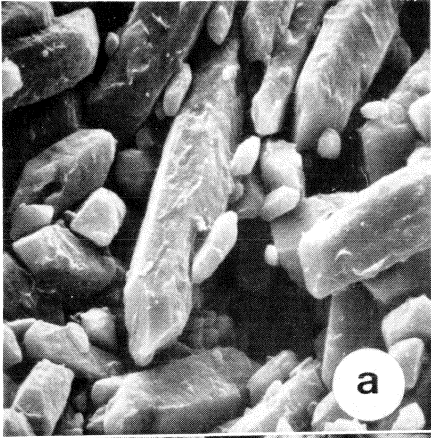


Plate II

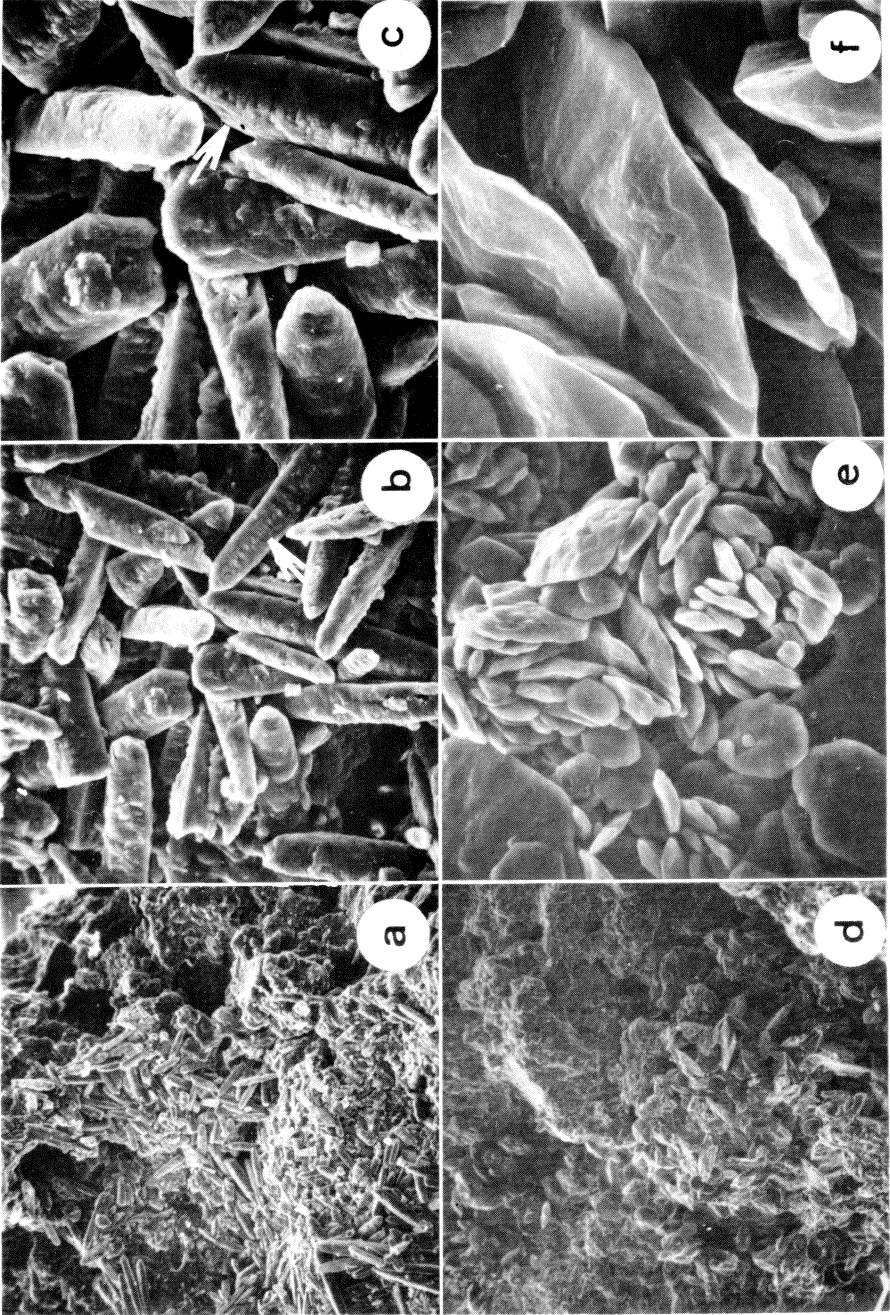
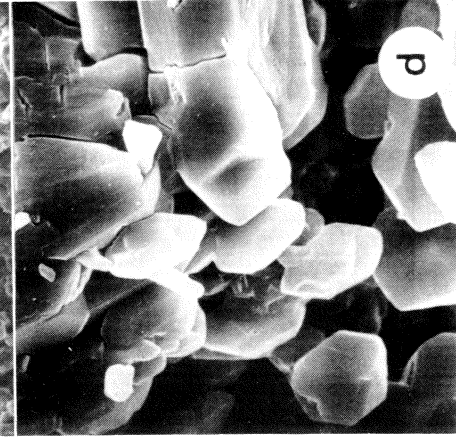
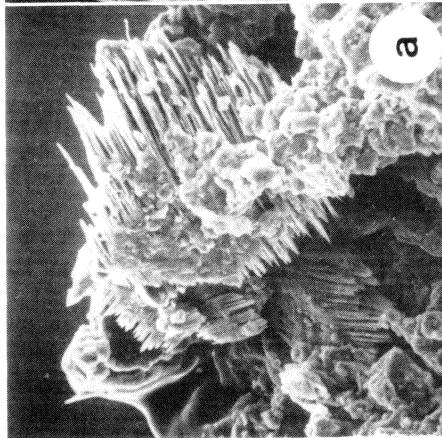
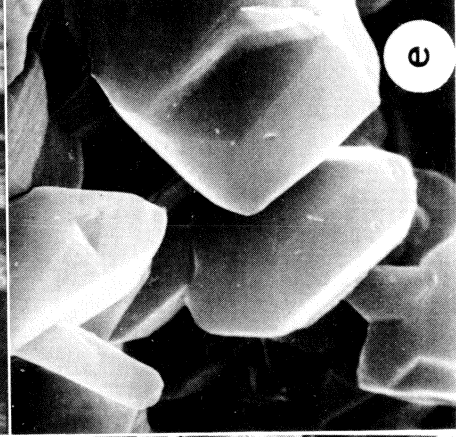
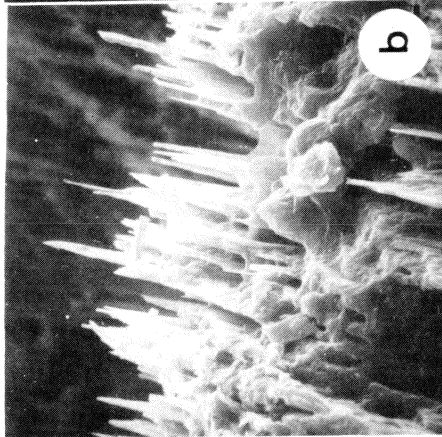
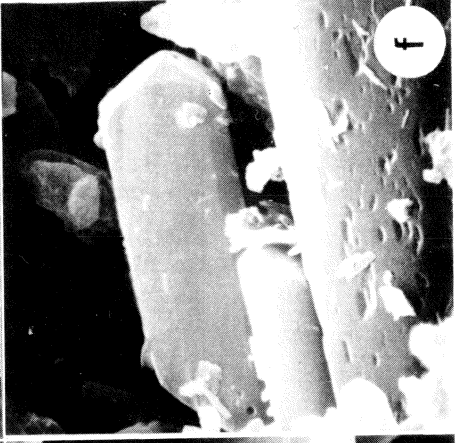
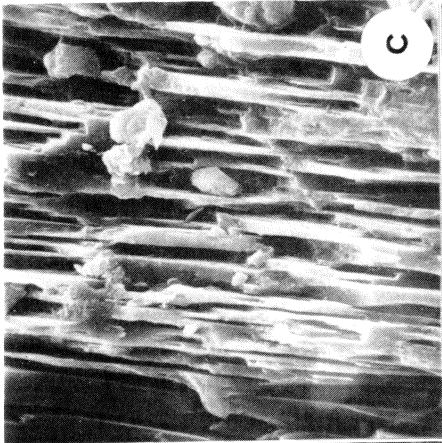


Plate III



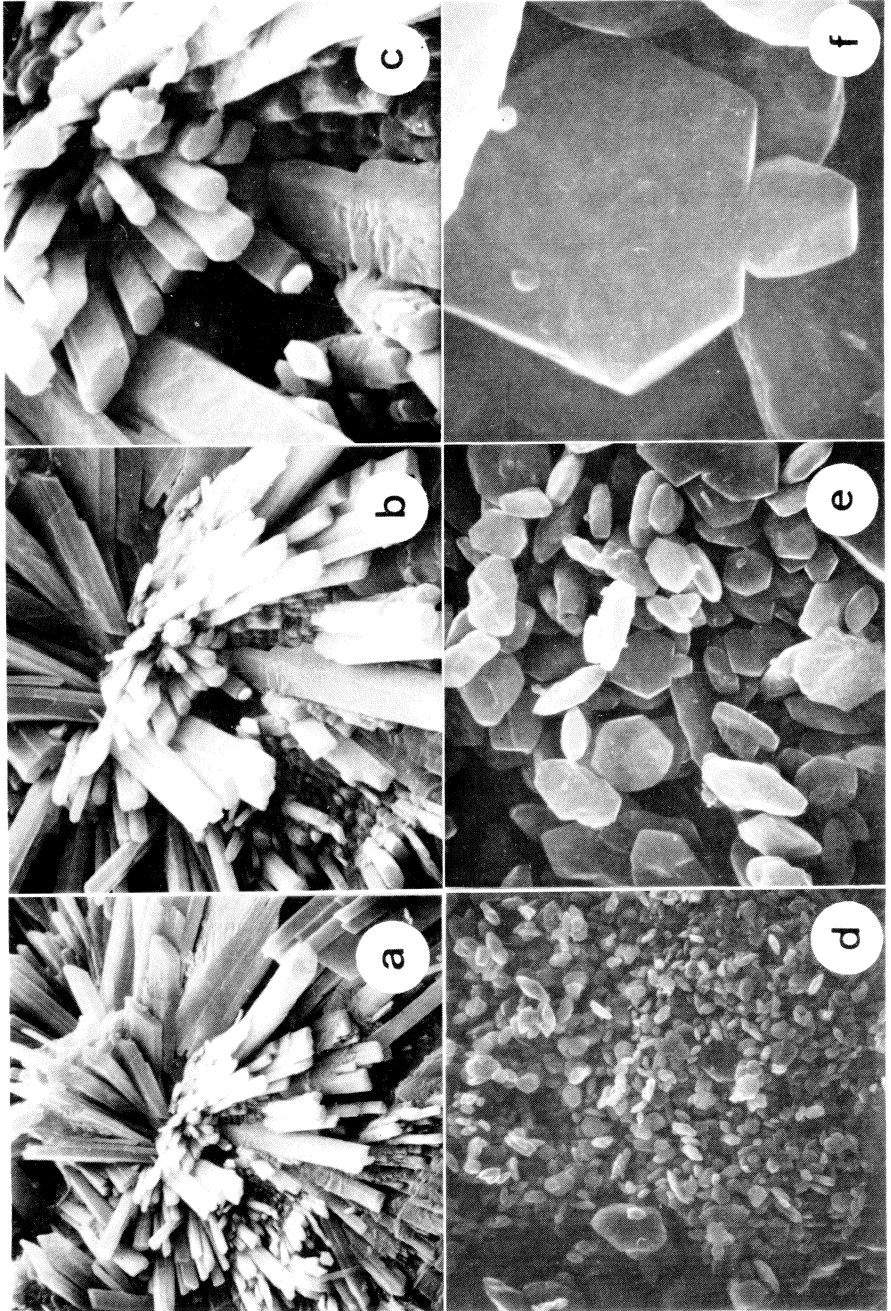


Plate V

Plate V. a, b, c : SEM micrograph of a rosette-like aggregate of prismatic gypsum crystals elongated according to $[001]$. Note the striations on the prism faces.

Magn. : 1300, 2600 and 6500 x resp.

d, e, f : SEM micrograph of pseudo-hexagonal he-xahydrate crystals on a ped surface.

Magn. : 600, 2400 and 12,000 x resp.

SUMMARY

SEM micrographs of some authigenic sulphate minerals in salt affected soils are presented. They include thenardite, anhydrite, barite, celestite, gypsum and hexahydrate. A brief discussion is included on two other, more frequently occurring sulfate minerals - bloedite and jarosite - and published work on these minerals is referred to.

Changes in soil environment may result in conditions unfavourable to the presence of some of these minerals. They begin to show dissolution features and examples of these are given. The dissolution may or may not follow crystal symmetry pattern.

Finally the same salt may exhibit several crystal habits and some of these are illustrated. The reasons for different habit are complex and not dwelled upon.

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