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**TITLE** APPLICATIONS OF SCANNING ELECTRON MICROSCOPY TO THE STUDY OF MINERAL MATTER IN PEAT

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# APPLICATIONS OF SCANNING ELECTRON MICROSCOPY TO THE STUDY OF MINERAL MATTER IN PEAT

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## ABSTRACT

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) have been used for *in situ* analysis of minerals in peats by combining methods for producing oriented microtome sections of peat with methods for critical point drying. The combined technique allows SEM analysis of the inorganic components and their associated botanical constituents, along with petrographic identification of the botanical constituents. In peat deposits with abundant fluvial- or marine-derived minerals, one may use the above technique and/or medium- or low-temperature ashing followed by x-ray diffraction to readily identify the various mineral components. However, in some freshwater environments the scarcity of non-silica minerals makes the above techniques impractical. By separating the inorganic residues from the peat, one can isolate the non-silica mineral matter in the SEM for analysis by EDS. Furthermore, such separation allows SEM analysis of features and textures of both silica and non-silica mineral particles that might otherwise be unidentifiable. Results indicate the occurrence of detritial minerals in both Okefenokee and Snuggedy Swamp peats, the presence of authigenic or diagenetic minerals growing within peats, and dissolution features on freshwater sponge spicules that may account for the absence of spicules in Tertiary lignites.

# INTRODUCTION

Peat, the precursor of coal, is composed predominantly of partially decomposed plant debris and secondarily of varying amounts of inorganic material. This inorganic material consists of a mixture of distinct mineral species and ionically-bound or complexed inorganic compounds. The composition of this inorganic fraction is controlled by various botanical and depositional environments and processes specific to particular areas of peat accumulation (COHEN and SPACKMAN, 1977).

Analysis of mineralogic components of peats has always been hindered by the inability to identify with scanning electron microscopy (SEM) the botanical constituents containing or associated with the minerals being studied. Both freeze-drying and critical point drying techniques are capable of producing non-dessicated peat specimens suitable for SEM analysis. However, neither of these methods allows one to identify the altered, decomposed plant materials which make up the bulk of most peats. The combination of methods for producing oriented microtome sections of peat with those for critical point drying has resulted in an in situ technique that allows one not only to carry out SEM analyses, but also to identify the botanical affinities of the associated plant materials. Observations of these relationships can be an important first step in understanding the distribution, genesis and diagenesis of mineral matter in peat.

Another problem of major consequence in studying mineral matter in peat is that some components of the inorganic fractions may be so scarce that they will not be readily observable either in thin sections or in the x-ray diffraction pattern of a low- or medium-temperature ash. For example, in the peats of the Okefenokee Swamp the dominant mineral matter is authigenic, biologically-derived, silica particles (ANDREJKO et al., 1982). However, the peats contain some non-biogenic mineral particles of both siliceous and non-siliceous compositions that can be separated from the organic peat material for SEM analysis by ashing and acid bath techniques. Although the specific relationships between minerals and botanical constituents are lost using this technique, very minor mineralogic constituents that otherwise would be ignored are observable.

In this paper we discuss the sample preparation for the *in situ* mineralogic analysis and concentrated mineral analysis techniques. This will be followed by a discussion of a few preliminary results that shows the significance of the techniques to peat studies.

## SAMPLE PREPARATION

### In Situ Mineralogic Analysis

The method for preparation of oriented, microtome peat sections for petrographic analysis is from COHEN (in press). In brief, an oriented sample of peat is sealed in a two cubic centimeter box made from 100 mesh (150 micron opening) copper screen. The sample is then "fixed" for a maximum of 48 hrs. in a solution of ethanol, water, formaldehyde, and acetic acid. Next, the sample is gradually dehydrated in a series of ethanol and tertiary butyl alcohol solutions. Using a vacuum oven, the dehydrated sample is impregnated with molten paraffin and later removed from the oven and allowed to cool. After the paraffin hardens, the copper box is removed and the impregnated cube is mounted with specific orientation on a wooden block such that microtoming will produce sections that parallel ths original vertical plane of the peat. A 15 micron thick slice is cut with a sliding microtome and mounted on a 25x75mm glass slide with Haupt's adhesive. Xylene is used to dissolve the paraffin from the mounted peat thin section, and before the xylene can evaporate, the slide is made permanent by securing a cover slip to the slide with Canada balsam.

The preparation of peat thin sections for SEM analysis is similar to that above except that a 25 micron thick section is cut, and after dissolution of paraffin with xylene, the wet slide is immediately placed in a critical point dryer and immersed in liquid $CO_2$. The 25 micron section of peat allows minerals greater than 15 microns in diameter (e.g. large pyrite framboids) to remain in the peat section following microtoming. Placing the xylene-saturated sample in the critical point dryer helps avoid dessication features from forming as a result of the evaporation of xylene. We follow critical point drying procedures as suggested by LADD (1982), the manufacturer of our instrument. After critical point drying, the samples are immediately sputter-coated with approximately 200 angstroms of gold or gold-palladium.

Petrographic and SEM sections can be made independently of each other. However, in order to improve correlation between the two, it is preferable to cut serial sections of 15 and 25 micron thicknesses from the paraffin-embedded block, and mount the thinner section for light microscopy and the thicker adjacent section for SEM.

## Concentrated Mineral Analysis

The peats used as examples in the analysis of concentrated minerals are from the Grand Prairie and Minnie's Lake areas of the low-sulfur, exclusively freshwater, Okefenokee Swamp of southeastern Georgia. Unlike other peat deposits, the inorganic fraction of the Okefenokee peats is primarily composed of silica, most of which consists of biologically-derived, authigenic particles. However, a very sparse population of nonbiogenic mineral particles of both silica and non-silica composition are present.

In order to concentrate the minerals, a combination of ashing and acid bath techniques are employed. Normally the concentration can be performed during analysis of the peat sample for moisture and medium-temperature ash weight percent. Note that the concentration method is primarily suited for silicates; many sulfates and carbonates will not survive the rigor of the method. Peat samples are placed in glazed porcelain crucibles (which were pre-fired and pre-weighed) and oven-dried at 105°C for 16 hours. After moisture content is determined, the crucibles are placed in a temperature-regulated muffle furnace and ashed at 550°C for 16 hours to determine total ash content. The ashed material is digested in dilute HCl (1.2 N) to remove any artifacts that might have developed as a result of the ashing, and is then filtered through ashless filter paper. Each filter paper is placed into the corresponding original crucible and ashed again at 550°C for 1 hour. The resultant residue is dispersed on an aluminum stub, sputter coated with gold or gold-palladium, and examined with the SEM. Qualitative elemental composition of the mineral particles within the inorganic residue is determined by use of energy dispersive spectrometry (EDS). Identification of mineral forms in the residue is based on observed elemental ratios and grain morphologies.

## ANALYTICAL RESULTS

### In Situ Mineralogic Analysis

The sample used as an example for the *in situ* technique came from the Snuggedy Swamp, which is located in the southeastern corner of South Carolina. The Snuggedy Swamp contains a freshwater peat surrounded by an encroaching brackish water, salt marsh (CORVINUS and COHEN, in press). Fluvial input and fluctuating brackish conditions resulted in abundant detrital and authigenic mineral matter in the peat sample.

Figure 1a is a SEM photomicrograph showing a transverse section across a plant root. Approximately the same area of the adjacent serial section is seen in the petrographic photomicrograph shown in Figure 1b. The open area around the root may be an artifact of the sampling or petrographic thin-sectioning technique. In both images note the occurrence of cell-filling in the upper right hand corner of the root. This feature along with those shown in Figures 2a and 2b indicate the success of the serial sectioning. Portions of Figure 2a are enlarged in Figures 3 and 4 to illustrate the ease of studying minerals incorporated in the organic material of the peat. Energy dispersive x-ray analysis indicates these minerals to be potassium-aluminum-silicates (possibly feldspar) and titanium-iron-oxide (possibly illmenite). Other minerals present in Figure 4 are small pieces of silica, one of which is a fragment of a sponge spicule. In Figure 5 the SEM photomicrograph reveals detailed relationships of single crystals of pyrite, framboids of pyrite, pyritic conglomerations and plant materials. In Figure 6 a well-preserved cross section of a root demonstrates that the critical point drying technique allows hollow cells to be preserved with a minimum of shriveling or collapse. Any mineral matter present as infillings of the cells would have been easily observable. In Figure 7 a potassium-aluminum-silicate (probably a clay mineral) is observable as it begins to infill cellular material. Pyrite and a potassium-aluminum-silicate mineral are jointly encroaching on plant material in Figure 8.

## Concentrated Mineral Analysis

The large grain exhibiting frosted texture in Figure 9 is composed of silica, probably in the form of quartz or chert. The majority of background particles are biogenically-derived, siliceous sponge spicules. Though silicates, exclusive of pure silica minerals, formed an extremely small portion of the mineral matter within the peat, it was possible to determine with EDS the elemental compositions of those that were observed. Crystal structure and elemental ratios (as measured with the EDS system) suggest that the grain in Figure 10 is an amphibole. An example of a non-siliceous mineral is the sub-rounded titanium-oxide mineral, possibly rutile or leucoxene, that can be seen in Figure 11.

Textural and surface features are readily observable on the mineral matter concentrates. As well as being able to note the frosting and rounded nature of the inorganic, detrital grains seen in Figures 9 and 11, higher magnification has revealed possible areas of bioerosion on biologically-derived, authigenic particles. The large grains in Figure 12 are a siliceous sponge spicule and a siliceous diatom frustule. The grid of 0.1 micron holes is normal for the diatom frustule. The holes in the spicule are not normal. In Figure 13, higher magnification resolves that the edges of the holes are very sharp and that an area is present where small chips have been removed in what appears to be the beginning of the formation of another hole. Various stages in the degradation of sponge spicules as seen with peat depth are shown in Figures 14a - 14d. Note that Figure 14b represents the same stage of degradation a shown in Figure 13.

## DISCUSSION

There has long been a controversy regarding the origin of mineral matter in coals. Some researchers, such as CECIL et al. (1981), have advocated an authigenic origin for most minerals. Others, such as FINKELMAN (1981), felt that although some minerals might have been authigenic in nature, there was strong evidience for substantial detrital input into the original coal-forming environment. FINKELMAN also felt that some minerals which might be considered by some as authigenic, were actually diagenetic alterations of detrital minerals. Such views however are somewhat premature without detailed examination of the original minerals that occur within a modern coal-forming environment.

Some of the mineral particles shown earlier exhibited weathered textures resulting from their transportation into the swamps (Figs. 9 and 11). Other particles had elemental compositions and crystal forms not compatible with an authigenic origin (Figs. 3, 4, and 10). As a result of using the techniques presented herein, there can be little doubt that detrital minerals occur within modern peat-forming environments. Such data supports the conclusions of FINKELMAN (1981), and substantiates earlier claims by STAUB and COHEN (1979) that sands, silts, and clay minerals derived from nearby streams are common in coastal peats and by COHEN (1974) that small quantities of fine grained sand and silt of probable aeolian origin are present in Okefenokee peats. A complete understanding of the forms in which detrital minerals occur and the abundances in which they may be found in certain depositional environments is achievable with further application of the techniques.

The occurrence of authigenic or diagenetic minerals forming within the peat can also be documented with these techniques. Some peat-producing plants in the Everglades and Okefenokee are known to be silicon-accumulators, such as grasses and sedges (ANDREJKO, 1983), and produce a variety of silicophytoliths. Following the concentration technique these silicophytoliths can be classified with the SEM to a degree heretofore unachievable (ANDREJKO, et al., 1983). The occurrence of sponge spicules and diatom frustules within peats can likewise be documented. Furthermore, we can investigate the occurrence of authigenic pyrite and and authigenic or diagenetic clay minerals occurring within organic frameworks using the *in situ* technique (Figs. 5, 7 and 8). In addition, in other studies of macrophytes from the Okefenokee swamp (BARDIN and BISH, in press) the *in situ* technique showed that although calcium oxalate minerals occur most commonly within living plants, calcium oxalate is also present to a limited degree in upper peat layers. The capability of identifying and locating various authigenic and diagenetic minerals within peats, and noting their specific relationships to plant components, aids interpolation of where silica and metal accumulations may exist in older coals.

Resolving the occurrence of holes in sponge spicules that lead to the various stages of degradation shown in Figure 14 may further aid our understanding of silica accumulations in coals. Originally it was presumed that holes in spicules as seen in Figures 12, 13, and 14 were common to a particular sponge taxon, and the presence or absence of perforated spicules was dependent on which sponge taxa were present in the peat depositional environment. Furthermore, the observed degradation was initially believed to be a function of artificial factors such as field sampling or microtome thin-sectioning and natural phenomena such as peat compaction or possibly the feeding activities of invertebrate organisms (RESH, 1976). However, comparative research in carbonates (e.g. PERKINS and HALSEY, 1972) has led us to believe the perforation might be a bioerosional product of microscopic organisms (ANDREJKO, et al., 1982). Such bioerosional activities would play a significant role in silica dissolution and mobility in a peat-forming environment. The appararent lack of observed spicules and the occurrence of chert lenses in Tertiary lignite deposited under similar conditions to the Okefenokee peats might be a function of such bioerosional activities (ANDREJKO and RAYMOND, in press).

## CONCLUSIONS

The method for making oriented microtome sections of peats for light microscopic observations has previously been described by COHEN (in press). The technique of critical point drying of botanical specimens for SEM analysis is a common biological procedure, as are the procedures for removal of organic matter by ashing and acids baths. Thus, the techniques we are suggesting for the study of mineral matter in peats are not new developments in specimen analysis for botanical materials. Rather, we have made minor adjustments of biologic procedures so that they are more applicable to specific problems of mineral matter in peat research. As a result, effective procedures are available for determining the geochemistry and possible mineralogy of minute individual particles in peat, both of material still _in situ_ and of mineral fractions that otherwise would be unobservable.

Great insight is necessary for the development and conceptualization of realistic depositional and geochemical models regarding the origin of mineral matter in coal. The correlation of mineral matter with different peat types will provide the needed data with which to support or modify such models. The procedures we have described for SEM analysis of mineral matter in peats should make such data available.

## ACKNOWLEDGEMENTS

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the Los Alamos National Laboratory on Mineral Matter in Peat: Occurrence, Form and Distribution, Sept. 26-30, 1983.

## REFERENCES

ANDREJKO, M.J. (1983) Distribution of siliceous mineral matter in Okefenokee peats. Ph.D. Dissertation, Univ. of South Carolina, 146 p.

ANDREJKO, M.J., RAYMOND, R.,Jr., and COHEN, A.D. (1982) SEM observation of dissolution features on freshwater sponge spicules. Scan. Elect. Micros./ 1982, v. 2, p. 629-638.

ANDREJKO, M.J. and RAYMOND, R.,Jr., (1983) Occurrence of detrital mineral matter in Okefenokee peats. in *Microbeam Analysis, 1983*, R. Gooley (ed.), San Francisco Press, p. 19-21.

ANDREJKO, M.J. and RAYMOND, R., Jr., (in press) Biogenic silica in peats: Possible source for chertification in lignites. in *Mineral Matter in Peat: Occurrence, Form, and Distribution*, R. Raymond, Jr. and M.J. Andrejko (eds.), Los Alamos National Laboratory.

ANDREJKO, M.J., Ehrlich, R., BOYLAN, D.C., RAYMOND, R., Jr., and COHEN, A.D. (1983) Grain-shape analysis: A new tool for phytolith classification. (abst.) AAAS Annual Mtg, Detroit, Mich.

BARDIN, S.W. and BISH, D.L. (in press) The occurrence of calcium oxalate minerals within aquatic macrophytes from Okefenokee swamp. in *Mineral Matter in Peat: Occurrence, Form and Distribution*, R. Raymond, Jr. and M.J. Andrejko (eds.), Los Alamos National Laboratory.

CECIL, C.B., STANTON, R.W., DULONG, F.T., and RUPPERT, L.F. (1981) A geochemical model for the origin of mineral matter in coal. (abst.) Geol. Soc. of Amer., *13*, no. 7, p. 424.

COHEN, A.D. (1974) Petrography and paleoecology of Holocene peats from the Okefenokee Swamp-Marsh complex of Georgia. J. of Sed. Pet. *44(3)*, 716-726.

COHEN, A.D. (in press) Obtaining more precise descriptions of peats by use of oriented microtome sections. Testing of Peats and Organic Soils, ASTM STP 820, P.M. Jarrett, Ed., American Society for Testing and Materials.

COHEN, A.D. and SPACKMAN, W. (1977) Phytogenic organic sediments and sedimentary environments in the Everglades/Mangrove Complex, Part II, Origin, description, and classification of the peats of S. Florida. Palaeontographica *172(B)*, 61 p.

CORVINUS, D.A. and COHEN, A.D. (in press) Petrographic characterisitcs of carbonaceous sediments from the Snuggedy Swamp of South Carolina. *Compte Rendu*, IX Int. Conf. Carboniferous Stratigraphy and Geology, May 1979, Urbana, Illinois.

FINKELMAN, R.B. (1981) Recognition of authigenic and detrital minerals is coal. (abst.) Geol. Soc. of Amer., 13, no. 7, p. 451.

LADD INSTRUMENTS (1982) Operational manual for Ladd critical point dryer, Cat. no. 28000, 23 pgs.

PERKINS, J.T. and HALSEY, S.D. (1972) Geologic significance of microboring fungi and algae in Carolina shelf sediments. Jour. Sed. Pet. 42, 843-853.

RAYMOND, R., Jr. and BARDIN, S.W. (1983) *In situ* elemental and mineralogic analysis of peat using SEM and petrographic techniques. in *Microbeam Analysis, 1983*, R. Gooley (ed.), San Francisco Press, p.15-18.

RESH, V.H. (1976) Life cycles of invertebrate predators of freshwater sponges. in *Aspects of Sponge Biology*, F.W. Harrison and R.R. Cowden (eds.), Academic Press, N.Y., pg. 299-314.

STAUB, J.R. and COHEN, A.D. (1979) Snuggedy Swamp of South Carolina: A back-barrier, estuarine coal-forming environment. J. of Sed. Pet. 49, 133-143.

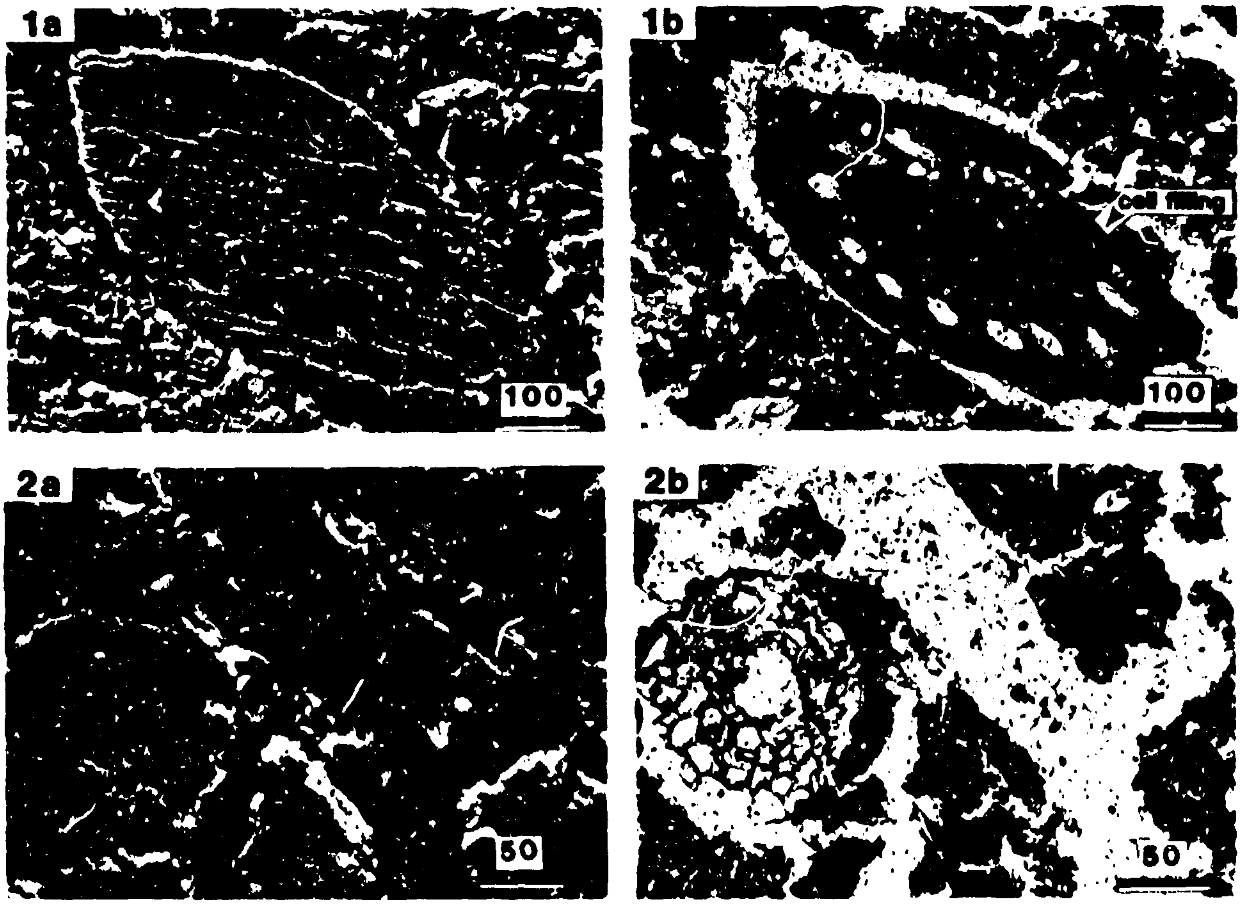
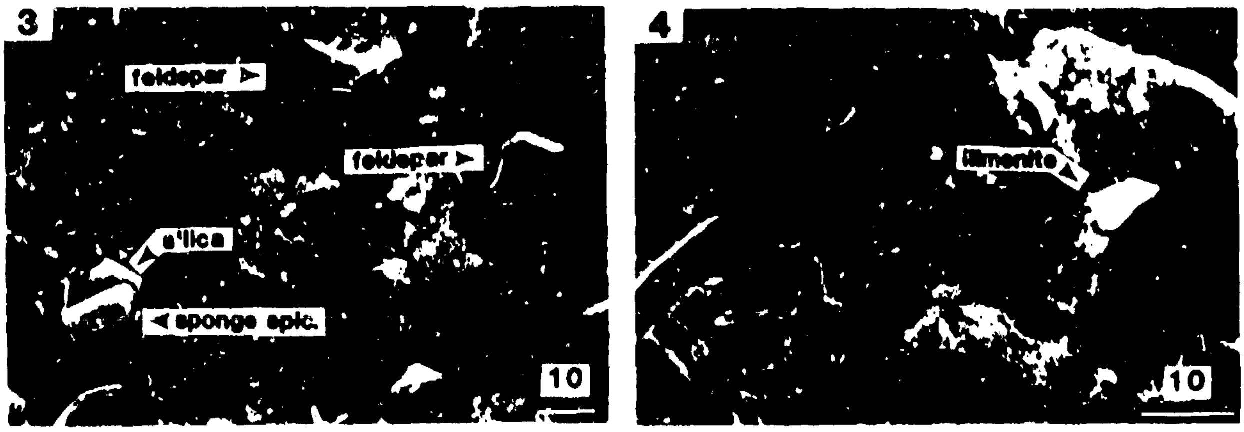
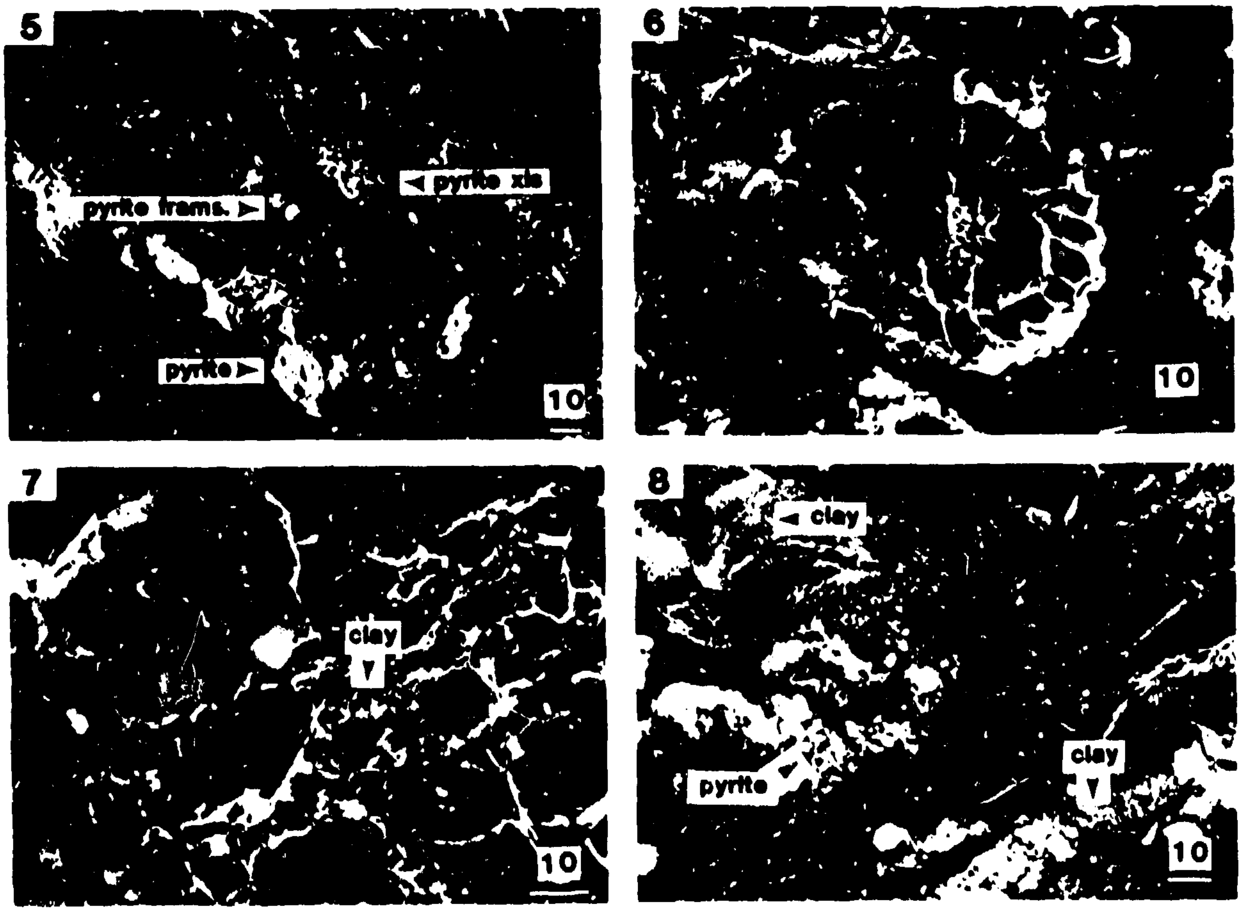


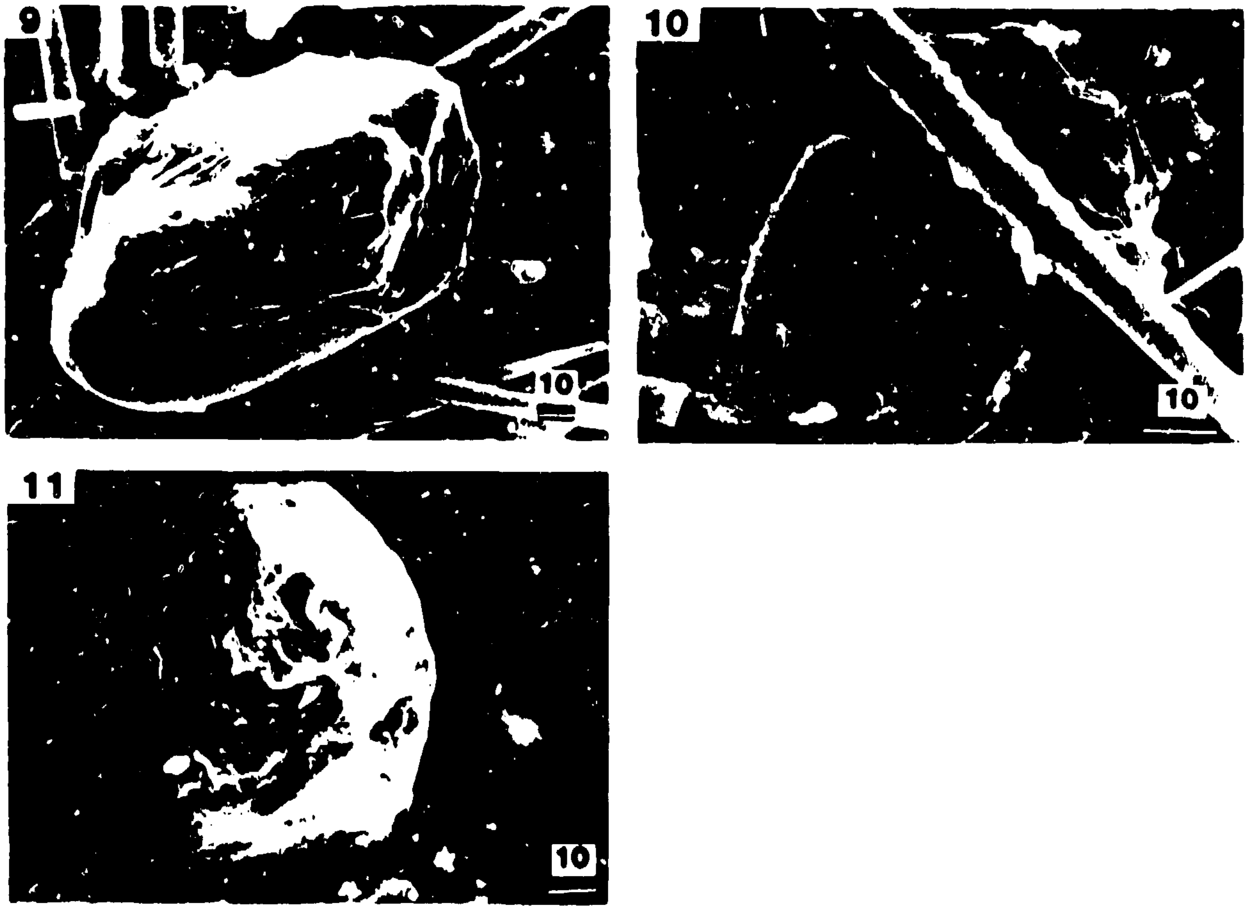
Fig. 1 and 2: Backscattered electron photomicrographs (figs. 1a and 2a) and transmitted light, petrographic photomicrographs (figs. 1b and 2b) of adjacent serial sections of peat samples cut with a sliding microtome. (scale bars in microns)(from RAYMOND and BARDIN, 1983)



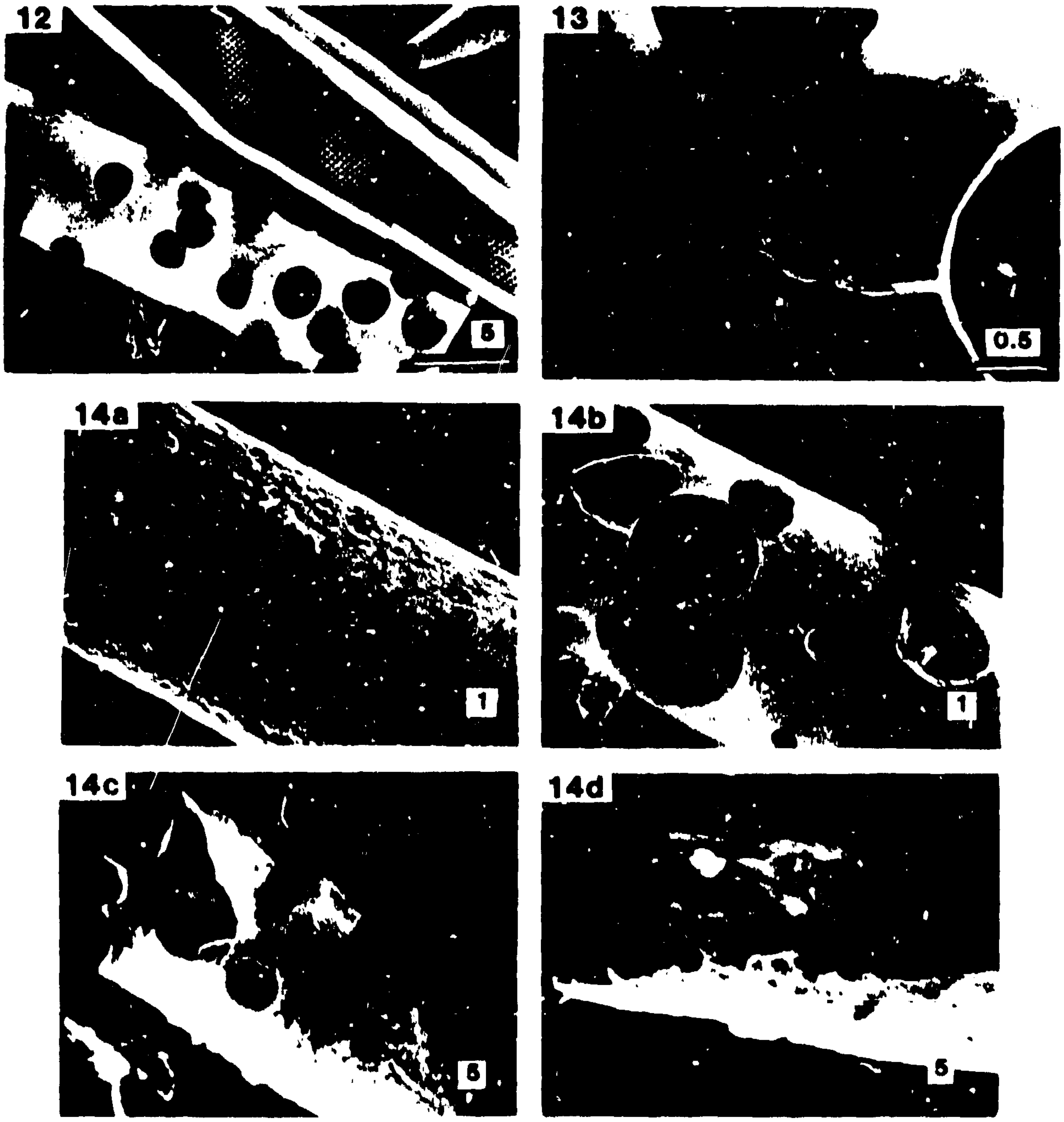
Figs. 3 and 4: Backscattered electron photomicrographs showing portions of Figure 2a at higher magnification including feldspar and illmenite grains. (scale bars in microns)(from RAYMOND and BARDIN, 1983)



Figs. 5,6,7 and 8: Backscattered electron photomicrographs of peat samples showing occurrence of authigenic mineral matter and structural integrity of samples after microtome sectioning. (scale bars in microns)(Figs. 5 and 7 from RAYMOND and BARDIN, 1983)



Figs. 9,10, and 11: Backscattered electron photomicrographs of detrital mineral grains from the Okefenokee Swamp including a quartz or chert grain (fig. 9), an amphibole grain (fig. 10), a rutile or leucoxene grain (fig. 11). (scale bars in microns)(from ANDREJKO and RAYMOND, 1983)



Figs. 12,13, and 14: Backscattered electron photomicrographs of authigenic siliceous mineral grains from the Okefenokee Swamp including a bored siliceous sponge spicule and diatom frustule (fig. 12), a close-up of the spicule borings (fig. 13), and the four stages of spicule degradation seen in peats with depth (fig. 14). (scale bars in microns)(Fig. 14 from ANDREJKO, 1983)