

CONF-820807-4

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APPLICATION OF SCANNING ELECTRON MICROSCOPY AND ULTRAVIOLET FLUORESCENCE TO A STUDY OF CHATTANOOGA SHALE

CONF-820807--4

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Pyrite ( $\text{FeS}_2$ ) is a common mineral in organic-rich sedimentary rocks.<sup>1,2</sup> Numerous studies have been performed to determine the relationship between pyrite and organic matter in these rocks. Most investigators agree on certain aspects of pyrite formation, namely, that sulfate-reducing bacteria were necessary to produce the dissolved sulfur for subsequent reactions with iron in minerals or solution.<sup>3</sup> However, the thesis that pyrite framboids were formed as replacements within the microorganisms either during their lifetime or upon their death has not received the same broad acceptance.

We recently had the opportunity to study a set of samples from the Dowellton and Gassaway members of the Chattanooga shale, one of the better known organic-rich formations of North America. Most of the previous studies relating pyrite to organic matter relied heavily on chemical analysis, x-ray diffraction, and optical microscopy. Of these analytical methods, only microscopy permitted a study of phase relationships; however, the fine-grained nature of shales precludes reliable optical

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microstructural analyses. We have used ultraviolet light fluorescence and scanning electron microscopy to investigate the interrelationships of the phases in the shale specimens. Backscattered-electron imaging, energy-dispersive x-ray analysis, and electron-beam microprobe analysis served as complementary techniques for identifying minerals and enhancing the contrast between phases.

### Sample Preparation

Samples were obtained from large blocks of shale by cutting sections both normal and parallel to the bedding. The samples were set in epoxy mounts and polished by standard metallographic techniques. Care was taken to avoid backfilling the samples with epoxy to eliminate any fluorescence contribution from the epoxy. Samples viewed in the electron microscope were coated with carbon only.

### Presentation and Discussion of Observations

A qualitative optical examination of polished surfaces of several Chattanooga shale specimens clearly showed a positive correlation between the mineral pyrite and organic constituents. Ultraviolet light fluorescence microscopy of these same specimens revealed intense fluorescent emissions from the irradiated organic constituents (Fig. 1). This technique permitted us to distinguish more clearly between organic and inorganic constituents within the shale microstructure. Pyrite framboids enclosed within organic entities appeared to be a common feature in these specimens.

The fluorescent intensities observed for the above organic constituents appeared to be much stronger than fluorescence emissions

obtained from exinite macerals in high-volatile bituminous coals, which are younger than the Chattanooga shale. Differences in the fluorescent character of the organic constituents in shales and coals may be due to at least two factors: first, the source of the organic matter (i.e., whether marine or terrestrial), and second, the packing of the organic constituents in relatively impermeable sediments such as shales, which might impede the structural and chemical changes that organic constituents normally undergo during coalification.

Backscattered-electron imaging of identical shale specimens showed pyrite framboids surrounded by organic constituents such as shown in Fig. 2. X-ray microanalyses of selected regions of the above microstructure revealed only iron and sulfur in the framboids [Fig. 3(a)], whereas the minerals surrounding the organic solid [Fig. 3(b)] consisted primarily of elements associated with clay minerals. Weak peaks recorded for titanium and calcium could indicate the presence of rutile ( $\text{TiO}_2$ ) and calcite ( $\text{CaCO}_3$ ), respectively, or these elements could have substituted for elements within the clay structure. This may be especially true of titanium, which is known to substitute for aluminum in clay minerals.<sup>4</sup>

The x-ray spectrum presented in Fig. 3(c) is typical of the energy spectra obtained from several locations within the organic constituent. In addition to the peaks associated with the elements found in clay minerals, a sulfur peak was recorded. The presence of the x-ray spectrum for clay minerals from the organic material is attributed to the penetration of the electron beam through the organic body and its subsequent exciting of the minerals below the surface. However, the strong sulfur peak without any comparable iron peak (from the organic

material) suggests the presence of organic sulfur in the maceral. These findings were corroborated by additional analyses of other organic constituents throughout the specimens. In each of the subsequent x-ray analyses, sulfur peaks were associated with the organic entities and iron was not detected.

The observed positive correlation between pyrite and organic constituents is undoubtedly not fortuitous. However, we obtained no direct evidence that corroborated the thesis that pyrite framboids are due to replacements in microorganisms. Indeed, if that premise were correct we would have expected to observe organic structures within the framboids. Since no organic materials were observed within the framboid structures, the growth mechanism of pyrite framboids was not a replacement process. Suggestions that the internal organic structure of framboids has been removed by wear or dissolution are not consistent with observations of the organic constituent in coal, where they are found to be relatively tough and resistant to wear.<sup>5</sup>

In addition to the syngenetic pyrite framboids that were found to be associated with the organic constituents, several occurrences of epigenetic sphalerite (zinc sulfide) were observed. One such example of epigenetic sphalerite growth is shown in Fig. 4. Iron and zinc x-ray maps shown in Figs. 5 and 6, respectively, distinguish between the two minerals. The sphalerite was apparently formed (at a more recent geological time than the pyrite) by the reaction of zinc, carried in percolating ground waters, with the preexisting pyrite.<sup>6</sup> Note that even though the organic constituents surrounding the sulfides contained sulfur, no sphalerite crystallization appears other than that observed on

the pyrite surface. This observation suggests that organically bound sulfur does not react readily with zinc carried in groundwater. This behavior may be due to a considerable physicochemical change from the early stages of diagenesis, in which anaerobic conditions prevailed, to the more recent oxidizing conditions in groundwater.

Finally, shales are typically a potpourri of minerals. Figure 7 illustrates this observation. For example the pyrite framboid is adjacent to a titanium-rich mineral (probably rutile), but slightly further along the central section of the organic body a quartz fragment is located. The location of a variety of minerals within a collapsed exinite in the shale is similar to observations made of sporinite in coal. It is worth noting that the quartz and rutile are considered as detrital minerals washed into the sedimentary basin, whereas pyrite framboids are believed to be grown in situ during early diagenesis.

### Conclusions

Microanalytical techniques such as scanning electron microscopy, energy-dispersive x-ray analysis, and electron-beam microprobe analysis have been shown to be ideal for determining the host phases of the minor and trace elements in the Chattanooga shale. Positive correlations were found between pyrite and organic constituents. However, these observations provided no evidence that microorganisms acted as hosts for pyrite framboids. Interestingly, appreciable organic sulfur is still present, suggesting that the sulfur used for the formation of pyrite must have been derived mostly from other sources. It may be that the sulfate-reducing bacteria had an affinity for organic matter and that the organic fragments acted as substrates for pyrite growth.

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### Figure Captions

FIG. 1.--Ultraviolet light fluorescence microscopy of Chattanooga shale shows emission from irradiated organic constituents.

FIG. 2.--Pyrite framboids surrounded by organic material.

Backscattered-electron image. (a) Pyrite. (b) Material surrounding organic solid. (c) Organic solid.

FIG. 3.--Energy-dispersive x-ray spectra of selected areas shown in Fig. 2. (a) Framboid, showing only S and Fe. (b) Material around organic solid, showing primarily elements of clay. (c) Organic solid, showing S peak with mineral elements excited by penetrating electron beam.

FIG. 4.--Backscattered-electron image of pyrite framboid surrounded by sphalerite.

FIG. 5.--X-ray map of iron from field in Fig. 4.

FIG. 6.--X-ray map of zinc from field in Fig. 4.

FIG. 7.--Backscattered electron image showing the variety of constituents in a Chattanooga shale specimen. QZ, quartz; PY, pyrite framboid; R, titanium-rich mineral.

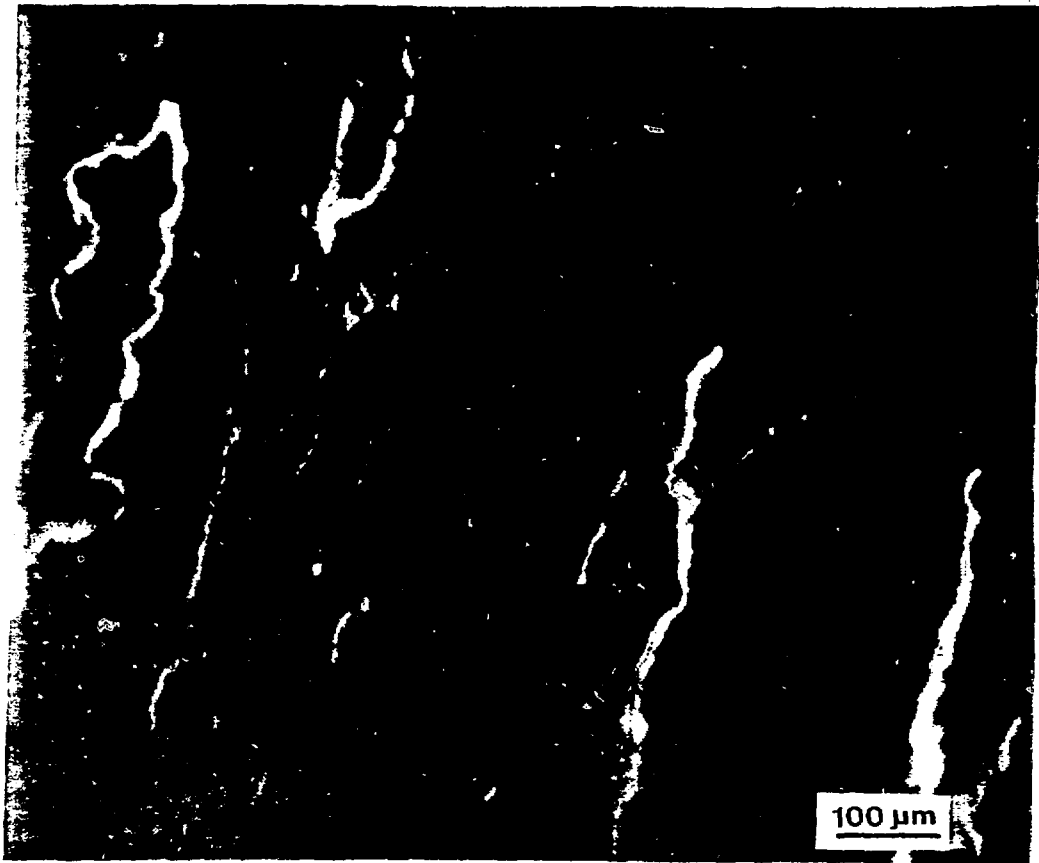


Fig. 1 Ultraviolet Light Fluorescence Microscopy of Chattanooga Shale shows Emission from Irradiated Organic Constituents



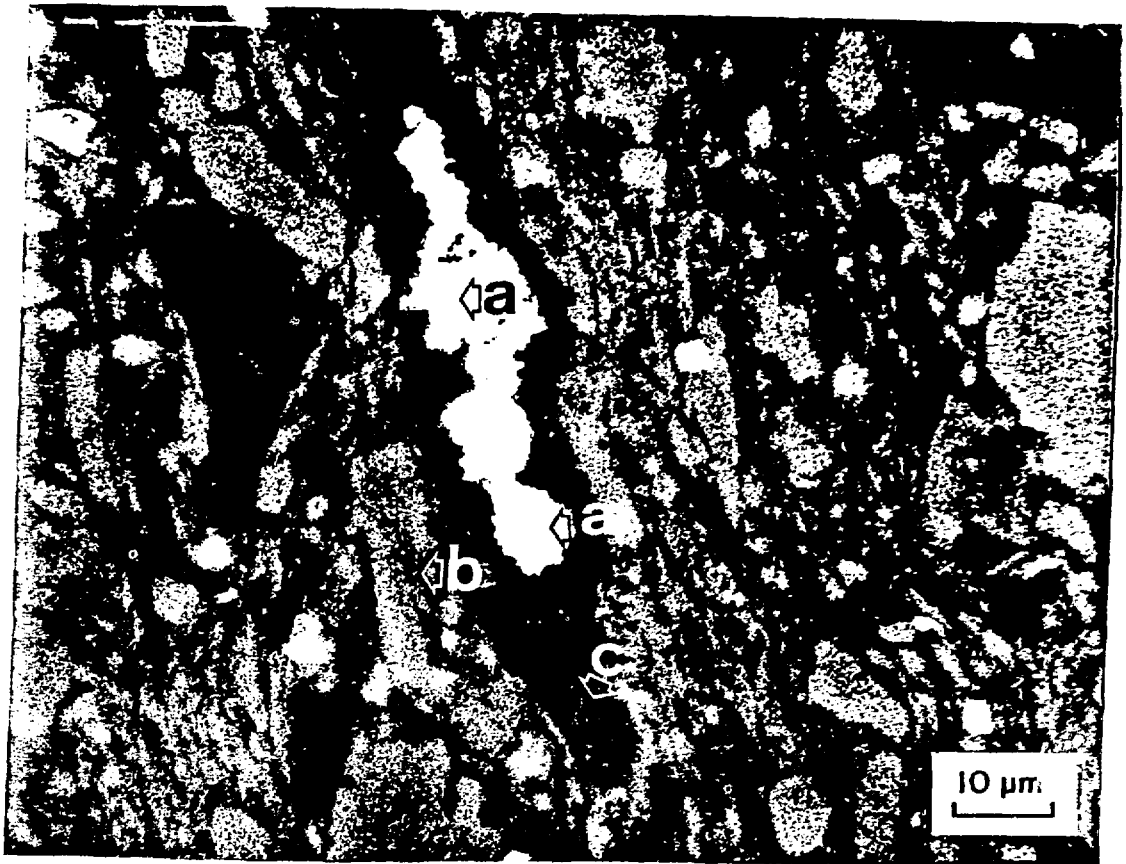


FIG. 2. Pyrite Framboids surrounded by Organic Material. Back-scattered electron image. The areas designated a, b and c correspond to the (a), (b) and (c) analyses of FIG. 3.

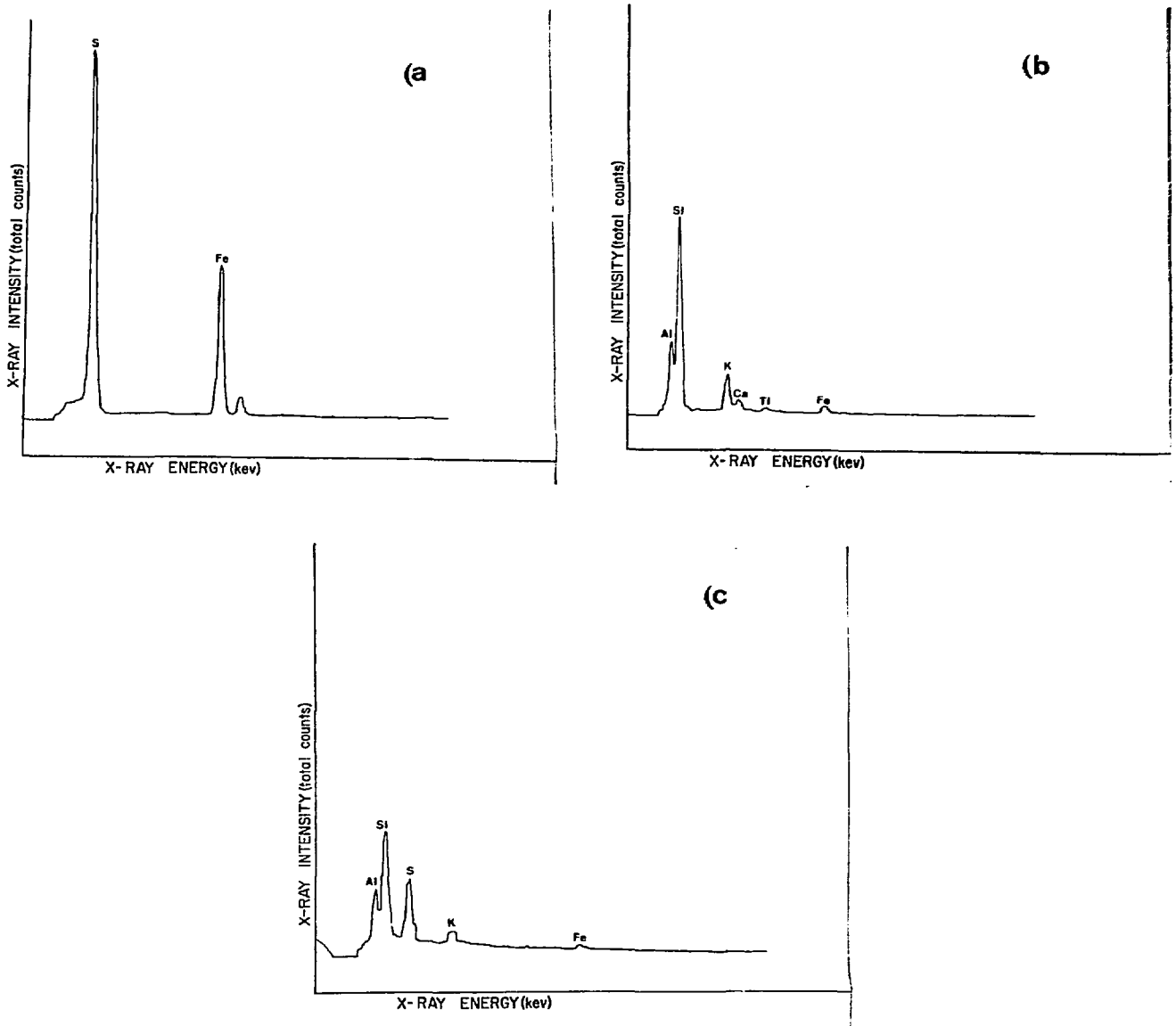


FIG. 3. Energy Dispersive Spectra of Selected Areas shown in FIG. 2. a) taken from Framboid shows only S and Fe; b) from material around Organic Solid, Primarily Elements of Clay Mineral; and c) from Organic Solid showing S Peak with Mineral Elements excited by Penetrating Electron Beam

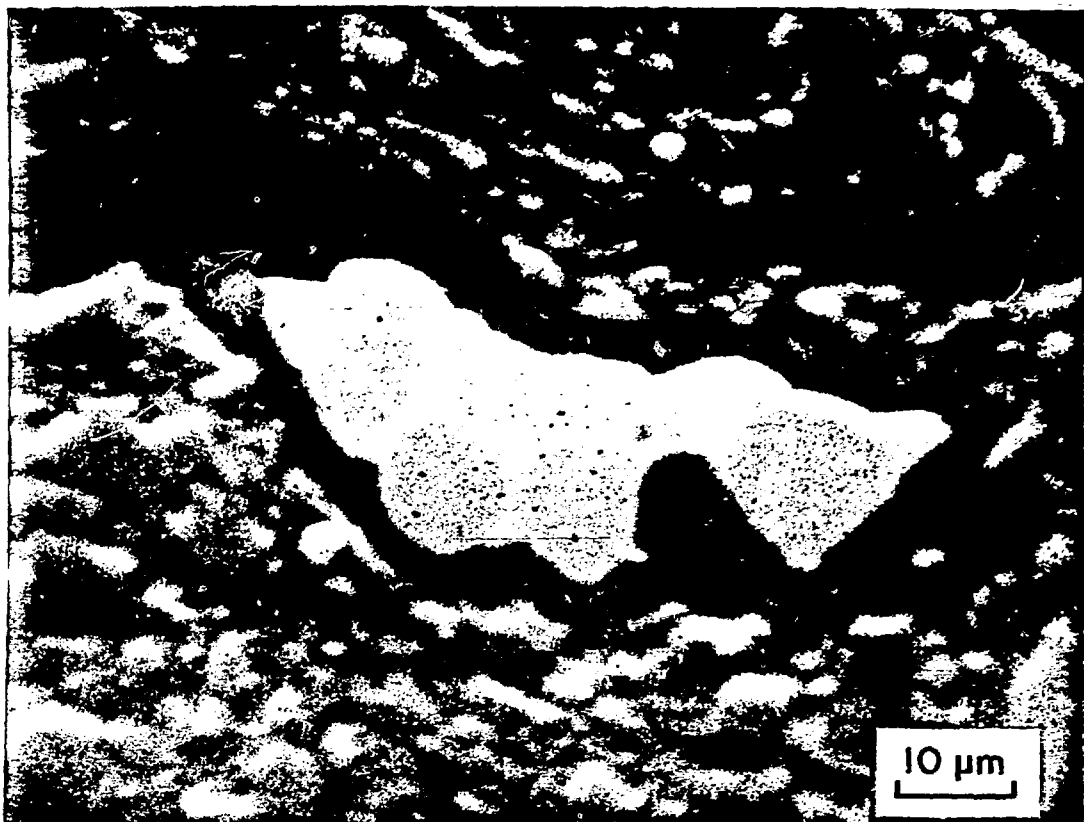


FIG. 4. Backscattered Electron Image of Pyrite Framboid surrounded Sphalerite.

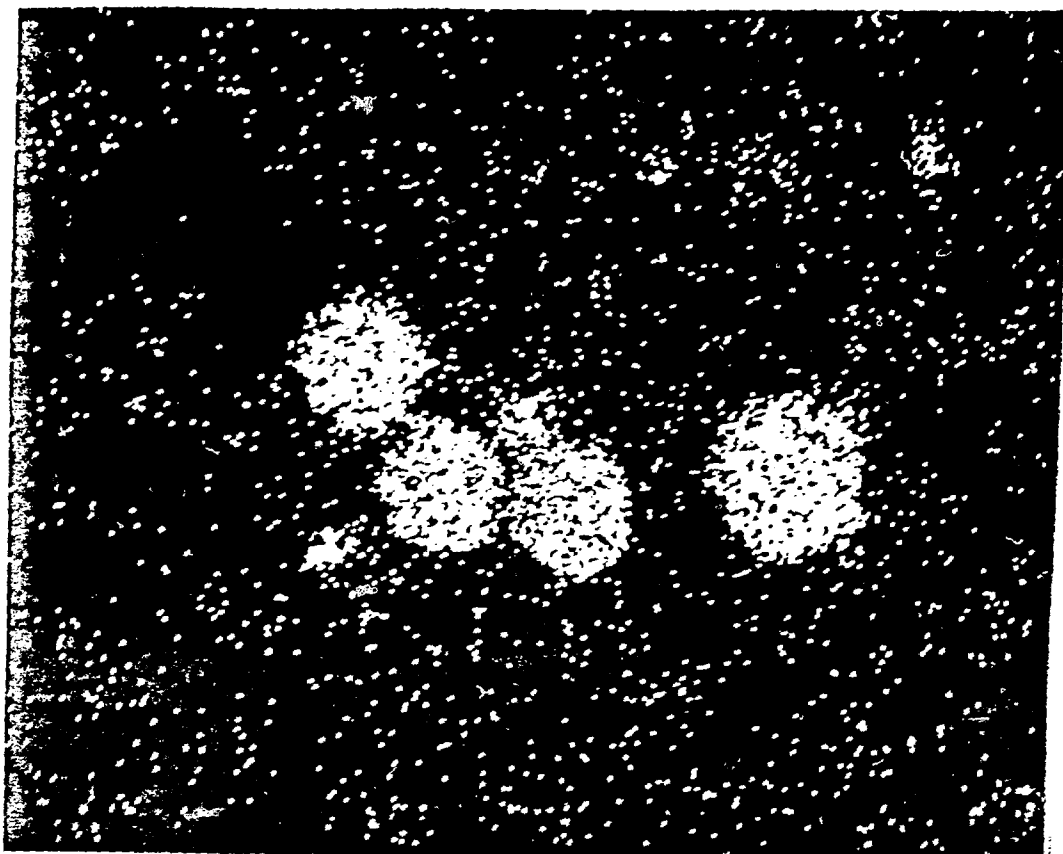


FIG. 5. X-ray Dot Map of Fe from Field in FIG. 4.



FIG. 6. X-ray Dot Map of Zn from Field in FIG. 4.

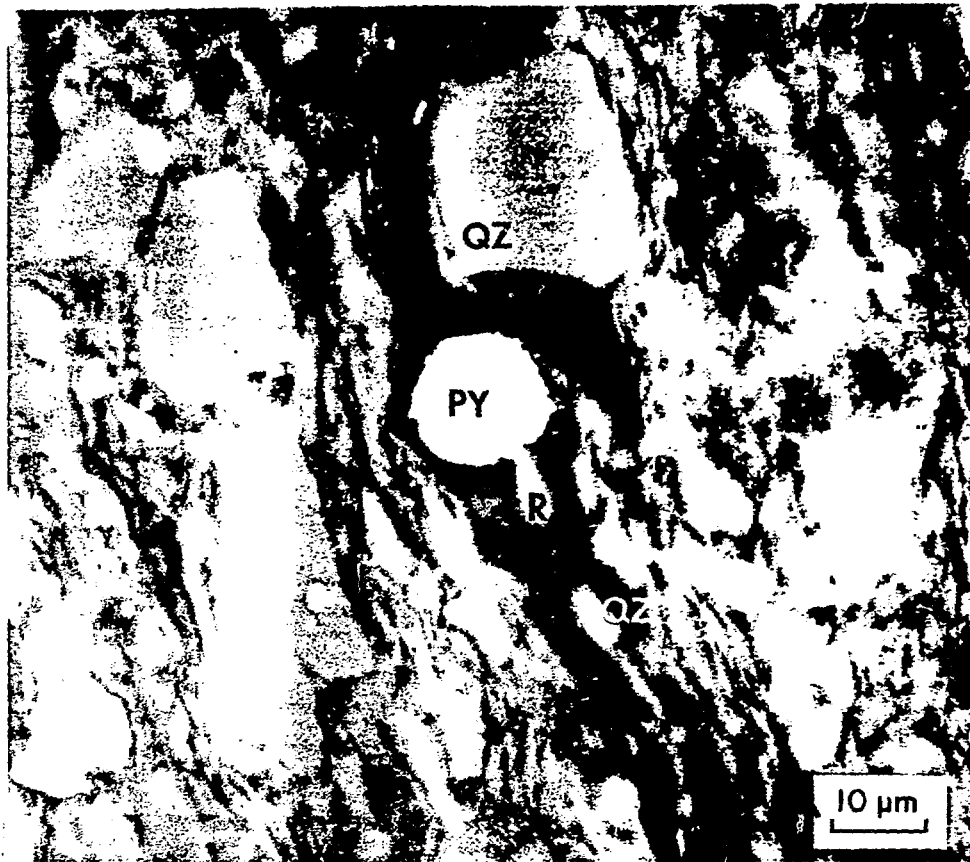


FIG. 7. Backscattered Electron Image showing the Variety of Constituents in a Chattanooga Shale Specimen.