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Surficial Alteration at the Cathedral of Learning in Pittsburgh, Pennsylvania

by

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ABSTRACT

Surfaces of the Cathedral of Learning are either light, black, or red-brown. The light surfaces are limestone with no significant surficial alteration; they are typical of washed surfaces on carbonate stone buildings. Black crusts are the dominant surficial alteration feature at the building, and they are similar to black surficial alteration that commonly develops on sheltered areas of carbonate stone buildings in urban environments. The crusts are composed of gypsum with abundant fly ash particles. The gypsum varies in morphology and habit, but generally occurs as blocky, elongate crystals with rounded edges. Fly ash particles, which are trapped between the gypsum crystals, are variable in composition but they are usually either dominantly Fe-rich or Si- Al- rich. There appears to be no distinct characteristics of the black crusts, either in the gypsum habit or in the particulates trapped on the sample, that correlate with the position of the sample on the building. There is as much variation in characteristics within a single sample of the black crust as there is between samples. Red-brown discolorations at the Cathedral of Learning are localized in occurrence and they are not directly associated with the environmental exposure of the building. The red-brown discolorations appear to be rust that has developed around small iron spheres that are lodged in the surface of the limestone. The spheres are probably a remnant of the grinding mix used to finish the limestone surface. In general the limestone at the Cathedral of Learning has maintained its integrity; even where the black alteration crusts have accumulated, the crusts are tightly adhered and the stone underneath appears to be intact.

INTRODUCTION

The Cathedral of Learning in Pittsburgh, Pennsylvania is being studied to learn about airborne pollutant delivery and deposition on a high-rise stone building. The Cathedral of Learning is a 42-story limestone building, located at the University of Pittsburgh. Built between 1929 and 1937, the building is a well known landmark in Pittsburgh. The building has distinctive patterns of surficial discoloration (Fig. 1A). The dark surficial accumulation is concentrated on the lower areas of the building, but dark discoloration can be seen extending up as high as the 30 story level. The dark surficial crusts are not evenly distributed around the building. Viewed as a whole and from a distance, two sides (facing northwest along Fifth Avenue and facing southwest along Bigelow Boulevard) are lighter and appear to have less accumulation of crusts than the other two sides. On a large scale, there appears to be a typical

"V" or "W" shape to the pattern of the dark and light areas (Fig. 1B) that may reflect the way water flows on the building when it rains.

A group of researchers from Carnegie Mellon University, led by Cliff Davidson, are using the Cathedral of Learning as a field laboratory to study air pollution damage to buildings. Some of the project components include: assessing the distribution of deterioration, monitoring meteorological conditions and pollutant deposition at the building, and modeling the pollutant delivery and deposition on the building. In order to link the pollutant monitoring and modeling with the visible black surficial deterioration on the building, the surficial deposits must be examined and identified.

This study focuses on characterizing the surficial alteration crusts that disfigure the Cathedral of Learning, in order to understand what the alteration crusts reveal about the environmental exposure and deterioration of the building. Four goals have guided the collection and examination of samples from the Cathedral of Learning; they are to:

1) characterize the alteration crusts that occur on the building,
2) identify pollutant particles in the crusts,
3) determine if there are differences in the crusts that correspond with their position around the building,
4) determine if there is a link between the alteration crusts and deterioration of the limestone.

BACKGROUND

The Cathedral of Learning is constructed from Indiana Limestone (written communication, Jack Donahue) which is quarried from the Middle Mississippian Salem Limestone in south-central Indiana. The Salem limestone is a homogeneous, fossiliferous limestone and it is nearly pure calcite (McGee, 1989). The Indiana limestone has been widely used as a building stone throughout the United States because of its homogenous composition and texture.

In typical urban settings, calcite in carbonate building stone reacts with moisture and air pollution to form gypsum ($CaSO_4 \cdot H_2O$). Gypsum is soluble in water, so even though it may form on all surfaces of the building, it tends to accumulate in areas that are sheltered from rain. Although gypsum is a light colored mineral, the interlocking network of gypsum crystals that accumulate on the stone surface act as a trap for dirt and air pollutants and cause the alteration crust to appear dark in color. On marble, black surficial alteration crusts can be deleterious as well as disfiguring; the marble under thick alteration crusts may disaggregate, so that if the black crusts are removed the underlying stone is no longer intact (Amoroso and Fassina, 1983; McGee, 1992). A similar deleterious effect of the black crusts on limestone is not yet well documented.

At close range, there are three types of surface features at the Cathedral of Learning: dull black crusts that cover broad areas of the building, light areas where features of the limestone are visible, and patches of red-brown surficial crusts that cover from one square centimeter up to nearly all of the surface of a block of limestone. For this study, all three types of surface features were examined in situ, and typical samples of each were collected for further examination. Black, light, and red-brown samples were collected by scraping or prying small amounts of material that could be examined using optical and scanning electron microscopes. Details of the sampling procedure are given in an earlier report (McGee, 1995).

THE SAMPLES

A total of 37 samples were collected. Thirty of the samples represent common or typical features of the surficial accumulations that are distributed around the building. Black crusts were the most common type of alteration crust sampled; red brown crusts and light areas were also sampled in several places. Some of the samples represent examples of the varied occurrences of each type of crust, while others were collected because of their position on the building. Pairs of black and light samples were collected from adjacent locations, and black samples were collected from similarly configured areas on several sides of the building to determine if any characteristics of the crusts vary with the orientation of the building (McGee, 1995).

CHARACTERIZATION

The three types of surface areas, black, light, and red-brown, were examined in situ on the building to see how the crust occurs and to determine characteristics, such as whether the alteration adheres tightly to the underlying stone. Samples were examined visually and optically and some were selected for examination with the Scanning Electron Microscope (SEM). The samples were selected for analysis based on their appearance, the type of sample, and the location from which it was collected.

BLACK SAMPLES

On the building, the surface texture of the blackened encrusted areas varies from nearly smooth to irregular and rough. Where the black crusts are smooth they adhere tightly to the limestone. Samples of the smooth black crust were removed with difficulty by scraping with a knife blade; the resulting sample tends to be a fine powder and where the sample was taken, the stone surface remains obscured by the crust. In contrast, in some places the surface of the black crust is very irregular and thin pieces of surficial material can be pulled or pried off fairly easily. Where the black crusts are rough, pieces of the crust come off more easily, but a base layer of black crust still remains on the stone surface after the sample is removed. Although the black areas are generally opaque, in some places, where the surface is uneven and broken, an orange to red-brown layer is visible under the black outer surface. Two forms of black samples were examined in this study: powders that were scraped from the building surface, and pieces that were spalling off of the building or that could be pried off easily where the building surface was rough.

Optically, the powder samples appear to be very fine gray to black grains. Some of the larger (~ 1 mm) grains have a white center, visible on one side, that appears to form a core around which the fine black grains have accumulated. The spall pieces are thin (approximately 1-2 mm) pieces with an irregular outer surface that is covered by small black bumps and a thin layer of fine black material. The SEM and energy dispersive X-ray analysis, show that the black samples are predominantly composed of gypsum. Typically the black samples consist of clusters of blocky to slightly elongate gypsum crystals with slightly rounded edges (Fig. 2). Sitting among and on the gypsum crystals there are a large number and variety of 1-10 micron spheres that have compositions and appearances typical of fly-ash particles (Fig. 3). Irregularly shaped, fine particles that look like broken mineral fragments are also common on these samples. Knobs and bumps in the black samples are large clusters of gypsum crystals that have grown together (Fig. 4). White cores, seen optically in some of the larger fragments of the black powder samples, are calcite or a mixture of calcite plus gypsum. However, calcite is not a significant constituent of the black samples. The macroscopic and microscopic characteristics of the black samples are comparable to features of gypsum alteration crusts that typically accumulate in areas on marble and limestone buildings that are sheltered from rain and washing (Amoroso and Fassina, 1983; McGee, 1992).

LIGHT SAMPLES

The light colored areas on the building are limestone with no visible surficial accumulation. Generally the light areas have a slightly rough texture and in some places small fossils and fossil fragments are visible. The grains and fossil fragments in the stone are tightly cemented, so the light samples are mostly fine powders that were scraped with difficulty from the wall surfaces.

Optically the light samples appear to consist of grains and fragments of limestone; in rare instances a fragment has some structure and appears to be a small fossil piece. The SEM shows that most of the fragments in the light samples are angular pieces of calcite; many of the grains have stepped edges that are typical of calcite cleavage surfaces (Fig. 4). Unlike with the black samples, fly ash particles are rarely present in the light samples. Calcite is the predominant phase in the light samples, but minor amounts of silica and aluminum are present, suggesting that there are small traces of dirt fragments on the grains. The silica and alumina might be traces of clay or silicate minerals, but the traces found in these samples do not resemble the rare inclusions of clay or silicate minerals that are typically found in the Salem Limestone (McGee, 1989). A minor amount of gypsum is present in some samples. In one sample, small clusters of gypsum that look similar to the gypsum knobs in the black sample are attached to a calcite grain (Fig. 5). The macroscopic and microscopic characteristics of the light samples are similar to samples of Indiana limestone that have had minimal to no surficial accumulation (McGee, 1989). The features of the light samples are typical of limestone buildings that are regularly washed either by rain or by routine cleaning.

RED-BROWN SAMPLES

An unusual red-brown surficial encrustation also occurs on the Cathedral of Learning. The red-brown stains occur in small concentrated discolored areas, of approximately one square centimeter, or they may cover up to nearly one third of the surface of a block of limestone (Fig. 6). The red-brown accumulations resemble rust, but they are widely and randomly distributed over the building and they are not associated with any obvious metal features that might be a source for rust. The red-brown discolorations occur mostly right on the outer surface of the limestone. Thus, samples of the red-brown spots were generally easy to remove when pried off gently with a knife blade. Where the red-brown accumulations came off easily in a thin piece, the white limestone surface underneath showed only a trace of red-brown discoloration. However, in some areas the red brown stain seems to be incorporated into the grains of the limestone, particularly where it is covered by the general black surficial alteration.

Two forms of red-brown samples were examined in this study: powders that were scraped from the building surface, and pieces that were pried off easily in rough areas or where the outer surficial crust was spalling off of the building. For comparison, an area stained red-brown adjacent to a metal bar was sampled to see whether features of the stain near the bar resemble features of the unknown randomly distributed red-brown samples. Small, approximately 2-4 mm, black spheres with a dull metallic luster found in some of the red-brown discoloration areas were also collected to determine if they might explain the presence of the red-brown discoloration.

Optically the red-brown samples, especially the powders, appear lighter orange than they appeared on the building. Powder samples of the red-brown material consist of fine, friable, almost fluffy grains. Small pieces of the red-brown encrustations are a mixture of grains. The base of the sample is composed of angular grains that look like calcite covered with a layer of very fine red-orange particles. Small black grains, some of which are magnetic, are mixed with small (0.8mm), rounded, clear white grains on the outer surfaces of the piece samples of red-brown discoloration. On the SEM, the red-brown samples have a very fine, indistinct appearance and some appear spongy. Pieces of red-brown alteration have grains of gypsum, calcite, and quartz. Energy dispersive X-ray analysis (EDAX) on the SEM shows that iron is a major component of the red-brown samples. Minor amounts of calcium, sulfur, and silica in the spectra suggest that the iron may be covering gypsum crystals and quartz grains in some areas. The EDAX spectra of the rust sample collected adjacent to the iron bar shows a similar Fe-rich pattern with minor peaks for calcium, silica, and sulfur. The texture of the known rust sample is variable, but similar in some places to some of the textures found on the randomly distributed red-brown samples. The black metallic spheres, that were collected in conjunction with the red-brown samples, are magnetic, they have smooth surfaces and they contain only iron. The small black grains on some of the red-brown samples are similar to the larger metallic spheres. The rounded clear white grains on the outer surfaces of the samples are quartz. Although the predominant feature of the red-brown sample is the iron rich coating, fly ash spheres are present on the samples, and they are particularly abundant on the darker samples.

It appears that the red-brown discoloration is a localized phenomenon not directly associated with the environmental exposure of the building. The red-brown discoloration resembles rust on the limestone surface. The spots are distributed randomly on the building and do not appear to be associated with any metal features on the building. It is highly unlikely that the rust spots come from an iron phase that is part of the limestone. Salem Limestone does not typically contain many mineral phases in addition to calcite (McGee, 1989), and any inclusions of hematite or magnetite that it might contain would not be abundant enough to cause as much widespread discoloration as there is on the building. Because the red-brown discoloration is primarily a surficial feature, it is likely that the source of the rust comes from outside the stone. The fine iron particles and surface appearance of the red-brown samples, particularly in the vicinity of the metal spheres, are similar in composition and in appearance to the fine iron particles trapped on the limestone surface where an iron bar was in contact with the stone. So it seems likely that the small black metallic spheres are rusting on the stone surface. Although the metallic spheres are not an expected component of the limestone, they are associated with rounded quartz grains, like those that might be used as an abrasive to finish a stone surface. The metal spheres may have been used as a component of the grinding mix used to provide the surface finish of the limestone (oral communication; Jim Strickland, Maryland Stone Service, Inc.). It seems likely that some of the metal spheres may have become lodged in the irregular stone surface during the finishing of the stone. Once they were exposed to rain, the spheres rusted, leaving a red-brown surficial discoloration that locally disfigures but does not seem to affect the integrity of the stone.

DISCUSSION

In addition to characterizing the alteration crusts at the Cathedral of Learning, this study was undertaken to see whether the characteristics of the crusts might reveal something about the environmental exposure of the building. The characteristics of the gypsum crystals in the black alteration crusts reflect the conditions under which they have grown, and the particles trapped by the gypsum crystals may provide some information about the air-borne pollutants in the local environment. Samples collected from specific locations around the building could also provide some insight into the environmental exposure of the building in its urban setting.

In addition to providing an understanding of the building's exposure history, characterizing the surficial discoloration at a building is a first important step if a cleaning program will be undertaken at the building. Examination of the crusts not only helps to identify the constituents of the alteration crust, it also aids assessments of how tightly the crusts are adhered to the underlying stone. Examination of the crusts may be helpful in assessing their affect on the integrity of the underlying stone.

VARIETY OF GYPSUM CRYSTALS

The gypsum particles that comprise the black surficial crusts present a variety of forms, ranging from blocky to long and thin, that reflect the conditions under which the crusts developed (McGee, 1992). The gypsum crystals in these samples are generally blocky and elongate with rounded edges and corners. The crystals range in size from small fairly crisp-edged grains 5 microns long to more massive grains, up to 50 microns, that appear to be several crystals that have grown together (Fig. 3). The rounded edges and blocky shape of the gypsum crystals suggests that they grew slowly, and probably remained moist for extended periods. A moist or damp environment would encourage slow growth of gypsum crystals; the resultant crystals are likely to be wide and have rounded edges. In contrast, gypsum that has grown where evaporation is relatively rapid, tends to form thin, needle-like crystals (McGee, 1992). The overall appearance of the gypsum crystals at the Cathedral of Learning differs from that of the gypsum crystals that grew on fresh limestone samples in exposure site studies conducted by the National Acid Precipitation Assessment Program (NAPAP). In the NAPAP experiment gypsum crystals that grew on fresh limestone samples were generally thinner and more elongate than those that grew on marble under identical exposure conditions (McGee, 1996). The shapes and especially the rounded edges of the gypsum crystals at the Cathedral of Learning resemble those slowly grown in a moist environment on the fresh marble samples from the NAPAP study.

Many of the gypsum crystals in the Cathedral of Learning samples are intergrown at random angles. This pattern suggests that there is a progressive growth from isolated individual grains to a mass that eventually covers an entire area (Fig. 7). Another typical occurrence for the gypsum crystals is as a mass that has grown outward (or up) from the surface of the stone to form a small protrusion (Fig. 3). At the Cathedral of Learning some protrusions are large enough to be seen by eye when examined closely. They can also be felt as small bumps when the blackened surface is touched. The details of the gypsum crystals in the protrusions reveal a coalescing growth pattern (Fig. 7B) and they seem to form a typical occurrence of gypsum in these samples. These growth patterns also suggest long, slow periods of crystal growth that have not been interrupted by dissolution or by long dry periods.

PARTICLES AND POLLUTANTS

Since gypsum is a white mineral, the particles that become trapped in the network of gypsum crystals are significant because they contribute to the color of the alteration crust which may disfigure the building. The types and features of the particulates trapped in the alteration crust also provide information about the pollutant history of the building because they are a record of some of the pollutants to which the building has been exposed. Another reason the nature of the particles is of interest is that some types of particles may contribute to the development of gypsum alteration crusts by catalyzing gypsum crystal growth (del Monte and Vittori, 1985; Camuffo, 1986).

Many of the samples collected from the Cathedral of Learning have small angular grains that resemble fragments of minerals scattered on the surface of the larger grains in the sample. Because of their small size, these particles are difficult to analyze reliably. However some of the particles contain silica and (or) aluminum which suggests that they may be clay or soil fragments. Many particles also contain calcium and sulfur. These may be fragments of the gypsum and calcite in the samples that broke up when the sample was collected. Because most of the small angular grains appear to be mineral fragments, they indicate that the air may have been dusty, but they do not provide much information about pollutant particles.

Spherical particulates are a striking component in the samples that does appear to come from urban air pollution. These spheres occur in large numbers, nestled among and on the gypsum crystals (Fig. 2, 8). The spheres range in size from 1 to nearly 15 microns in diameter. Some spheres have a smooth, glassy surface, while others have a rough irregular surface that looks as though it was covered by small crystals. Some spheres appear to be hollow (Fig. 9). Based on their chemical composition, the spheres form two groups: those that are Fe-rich, and those that are Si- and Al-rich. The particle composition of both groups is variable; in addition to Si, Al, and Fe they may contain S, K, Mg, and Ti (Fig. 10). The smooth glassy spheres are more likely to be the Si- Al- rich type and the irregular surfaced spheres are more likely to be Fe-rich; but neither the size of the particles nor their surface features consistently correlate with the composition of the spheres. Some spheres even seem to be transitional between the groups because they contain varied proportions of Si, Al, and Fe. Both the composition and the appearance of the spheres suggest that they are fly ash particles. Given the industrial history of Pittsburgh, it is not surprising to find this type of particle on the building surfaces.

Fly ash particle spheres are the only significant pollutant component in the Cathedral of Learning samples. However, there seems to be only one factor that correlates with the presence of the fly ash spheres: the fly ash particles are most abundant on the black alteration crust samples. The spheres are present but less common on the red-brown samples and a few of the spheres are even present on some of the light samples. This suggests that at some point the fly ash particles were probably an abundant and widespread component of the local air pollution. The spheres are randomly distributed on the samples. Some occur in small clusters, others are isolated, and they are commonly nestled between the gypsum crystals. Because of the way the spheres occur on the samples, it is not possible to accurately assess relative abundance of the types of spheres on the various samples. There appears to be no striking difference in the abundance of spheres when samples are compared from various positions around the building. The Fe-rich and Si- Al-rich spheres occur together in all the samples where fly ash spheres are present. Thus, there does not appear to be a relation between the type of sample (black, red-brown, or light) and the types of fly ash spheres that are found on the sample.

The relationship of the particles to the gypsum crystals may indicate whether the particles have a role in the gypsum growth on the building surfaces. It has been suggested (del Monte and Vittori, 1985; Camuffo, 1986) that pollutant particles serve as catalysts for gypsum growth on carbonate stone. However, it seems unlikely that these pollutants acted as catalysts for gypsum growth. The particles most visible in these samples do not seem to be an integral part of the gypsum crystals. The particles are located in small indentations and are trapped between some of the gypsum crystal. Many of the fly ash spheres only loosely adhere to the sample surface; during examination in the SEM some of the spheres move out of the field of view when the electron beam is placed on them. In many places there are spherical hollows in the gypsum crystals where fly ash spheres formerly sat (Fig. 11). Although the hollows suggest that the gypsum crystals grew around the spheres, the gypsum crystals appear unaffected by the presence of the spheres.

Position Around the Building

Samples were collected for this study at locations around the building to obtain as complete a picture as possible of any characteristics that might vary with the position of the alteration crusts around the building (McGee, 1995). The most complete set of positions was obtained on the fifth floor level because black alteration crusts are widespread at this level and several areas were readily accessible for sampling. Black crusts are less prevalent at higher levels on the building and there are no black crusts on the roof level. Although black crusts are common on the ground level and the crusts are readily accessible, there is a high probability these crusts have been affected by factors other than the pollution environment. For example, the ground level walls are readily accessible to defacement or damage from people, and several entrances were being cleaned when the sample set was collected. Since the fifth floor patio area is one of the main locations for the deposition and environmental monitoring studies conducted by Davidson and his students, the samples for this study were concentrated on the fifth floor level to facilitate comparisons with those studies.

The fifth floor level samples were collected from five orientations: three facing streets (Forbes, Bellefield, and Fifth) and two facing corners (Bigelow and Fifth; Bigelow and Forbes) (Fig.12). Samples were collected from only one location on the 16th floor level, but the orientation of the four samples from this level corresponds with the orientation of one set of samples from the 5th floor level, thus enabling a comparison between heights on the building. Although five samples were collected from the 40th floor level, there are no black crusts at that level. However, the red-brown and light samples collected from the 40th floor level are similar to those respective types of samples from other levels.

All of the black crust samples examined from various locations on the fifth floor level contain gypsum with abundant fly ash spheres. The 16th floor black samples also contain gypsum and fly ash spheres. However, although the morphology of the gypsum crystals in the samples is varied, the shapes and habits of the gypsum crystals are not distinctive from one side or location on the building compared with another. In many cases the morphology and characteristics of the gypsum crystals vary as much within one sample as they do between samples. Similarly, the presence and types of pollutant particle spheres also do not correlate with the side of the building from which the sample was taken.

Position Pairs

The Cathedral of Learning has a very irregular shape (Fig. 12), so the exposure geometry of any particular location may be very complex. In order to compare exposures that are identical except for the side of the building, samples were collected from several specific locations. For example, on the 5th floor level a wall protruding at a 45° angle presents an identifiable location for some of the samples (CL801-11 & 17, CL801-18, 10, & 2; Fig. 12). Another set of samples was collected from a specific area around a window that was similarly located on two sides of the building (CL801-23 & 14; Fig. 12). Pairs of samples from identical locations were examined both optically and with the scanning electron microscope to compare their characteristics. No significant features were found in these samples that distinguished one from the other. Also, no features were found that could be used to specifically identify the sample's location on the building. There appears to be as much variation in gypsum crystal habit within one sample as there is among the various samples. Even comparisons of the samples collected by scraping the stone with those collected by prying off a small piece shows that the gypsum crystal habits appear the same regardless of the sampling method used.

Stone Integrity

Marble with thick black alteration crusts is commonly severely disaggregated under the crusts, so the removal of the crusts endangers the integrity of the encrusted feature (Amoroso and Fassina, 1983). Since the black alteration crusts on limestone buildings are similar to the crusts on marble, it is of interest to determine whether the stone under the crusts on limestone buildings is similarly disaggregated. Most of the black alteration crusts sampled at the Cathedral of Learning adhere tightly to the limestone surface. Even when the stone was scraped with a knife, a residue of surficial crust typically remained on the stone. Where the crust could be pried off in small flakes, the stone underneath also seemed to be intact. From these observations it appears that limestone integrity is not affected by the accumulation of surficial alteration crusts.

One explanation for the apparent integrity of the limestone under the black crusts is that the surficial crusts are not yet thick enough to cause the stone to disaggregate. However, thickness of the alteration crust on carbonate stone does not necessarily correlate with friability of the stone underneath. Both marble and limestone briquettes at NAPAP stone exposure sites developed gypsum alteration crusts under identical exposure conditions; but even though the limestone developed thicker crusts than the marble (McGee, 1996), the marble is more friable than the limestone. It seems more likely that the limestone has remained intact because moisture is not likely to be trapped in the pore spaces of the limestone. In general, marble has a lower porosity and is much less permeable than limestone. At the Merchant's Exchange in Philadelphia, two marbles with differing permeability have surficial blackened alteration crusts. While the less permeable marble has disaggregated beneath the alteration crusts, the more permeable marble appears to be intact (McGee, 1992). Since permeability influences the movement of water in stone, water is less likely to be trapped in stone with higher permeability. Therefore, the cumulative effects of temperature cycles on moisture trapped in intergranular spaces are not likely to disaggregate stone with a high permeability, such as limestone.

CONCLUSIONS

This study had four main goals: to characterize the alteration crusts, to identify pollutant particles in the crusts, to determine if the crusts differed depending on their position around the building, and to determine whether the crusts seemed to have a deleterious effect on the building. The Cathedral of Learning has three types of surfaces: light, black, or red-brown. The light areas are typical of limestone that is regularly washed. The red-brown areas appear to be areas of local discoloration from metal spheres lodged in the irregular surface of the stone. The black crusts at the Cathedral of Learning are typical of most black crusts on limestone or marble buildings. In addition to the gypsum that forms the alteration crusts, fly ash sphere particles that are either Si-Al- rich or are Fe-rich are the main pollutant component of the crusts. Although the gypsum characteristics and fly ash particle populations both vary, the characteristics of the alteration crusts do not seem to vary with their position on the building and they are not correlated with exposure in a particular direction or location. It does not appear that the crusts are hurting the integrity of the limestone, but because the black crusts are very tightly adhered to the stone attempts to remove the crust might injure or severely affect the outermost surface of the stone.

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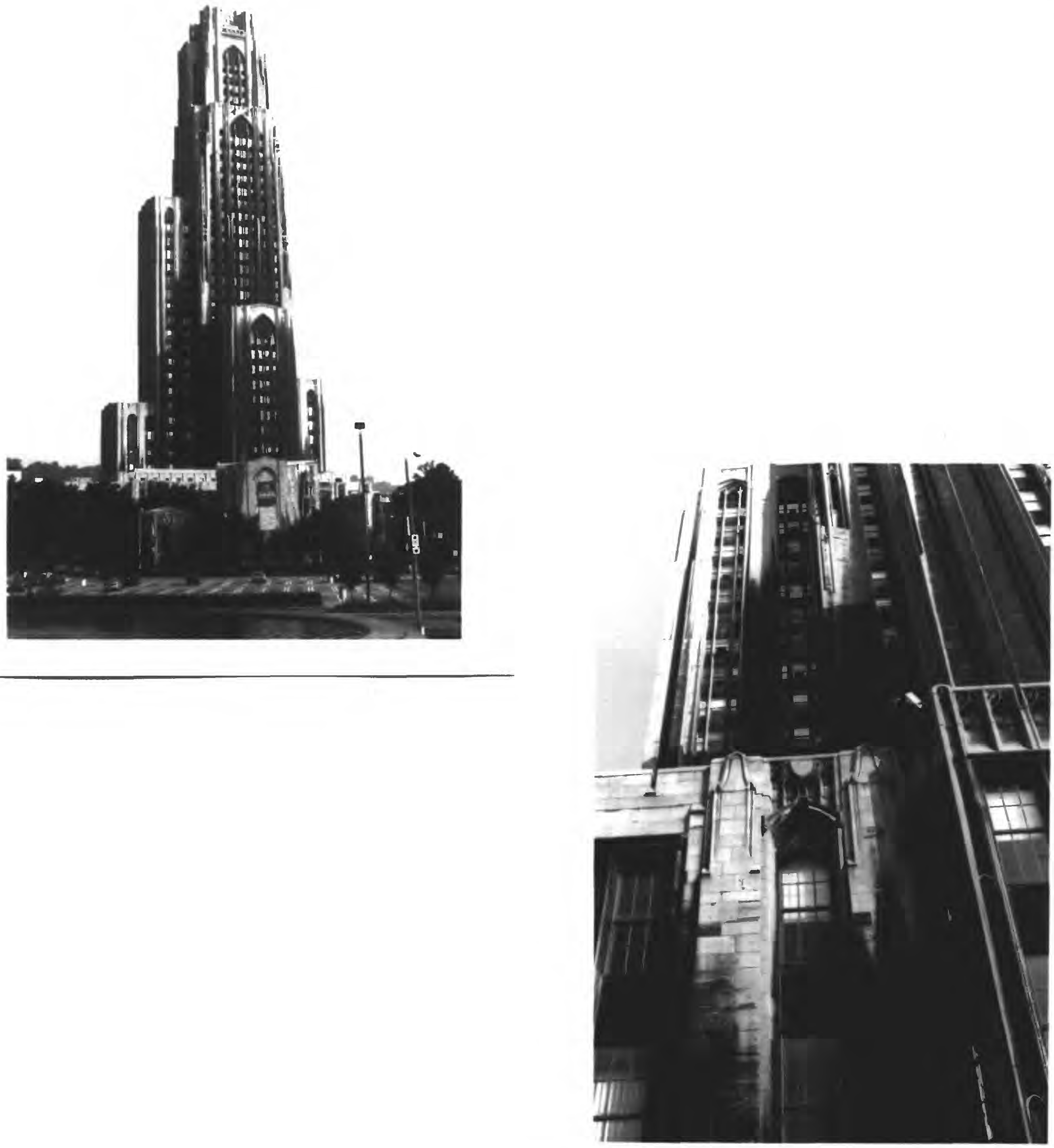


Figure 1. The Cathedral of Learning in Pittsburgh, Pennsylvania has distinctive patterns of dark and light areas that are readily visible even from a distance. **A.** The building as seen from Forbes Avenue. **B.** Detail of "V" drip pattern, on the Forbes Avenue side of the building.

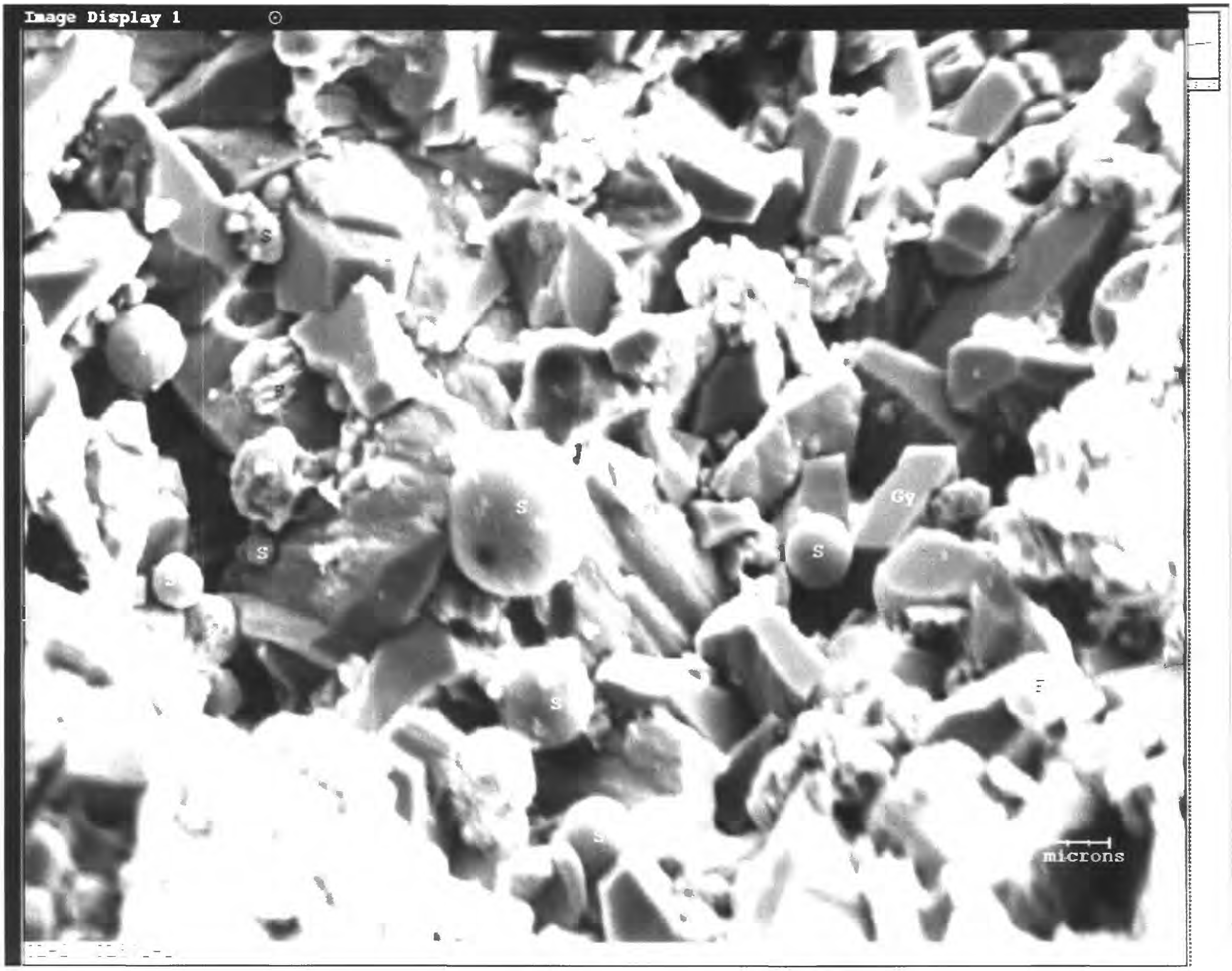


Figure 2. Scanning electron micrograph of gypsum crystals in a black alteration crust. Fly ash particle spheres sit on and between the gypsum crystals. Gy = gypsum, S = Si- Al-rich particle, F = Fe-rich particle.

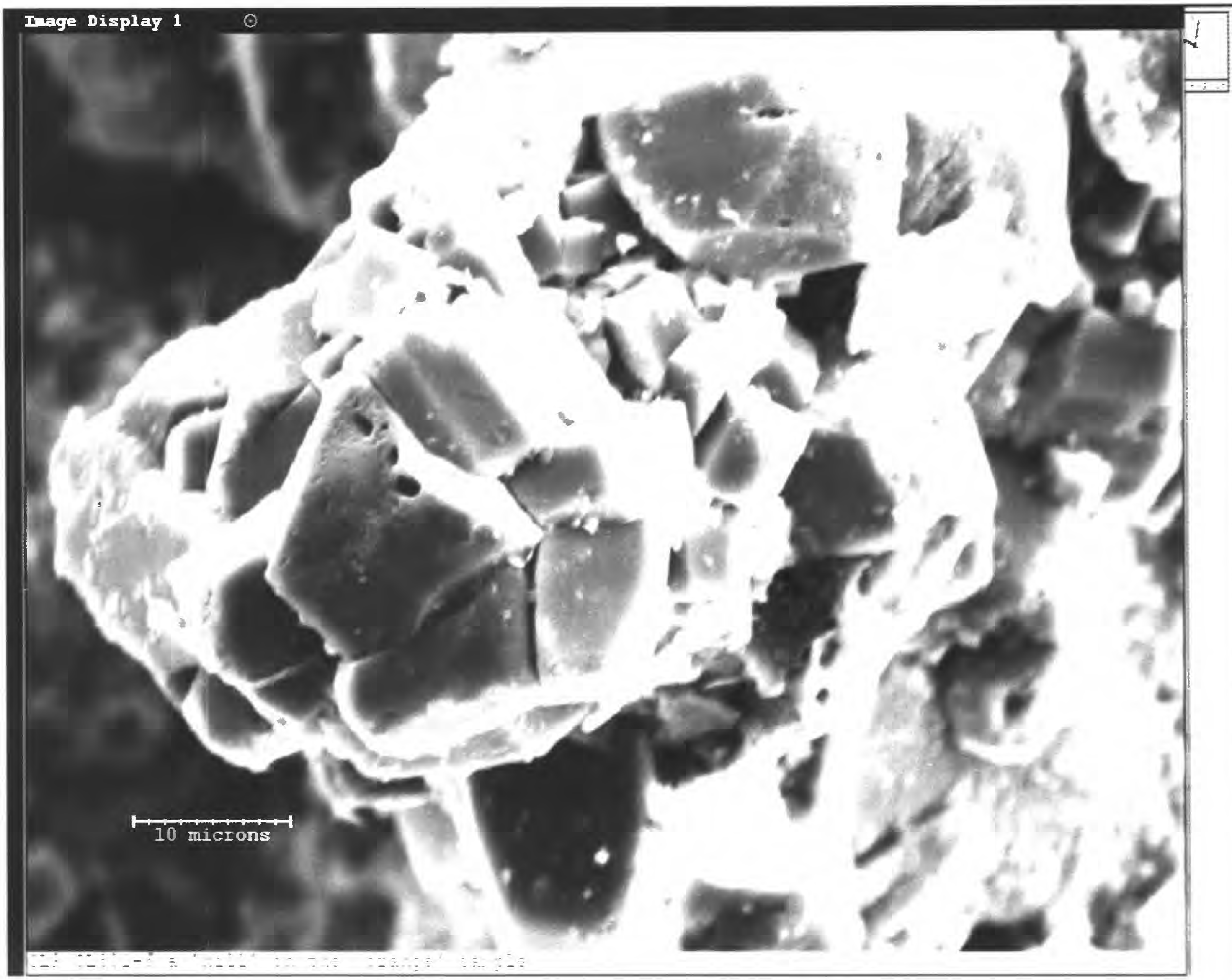


Figure 3. A large cluster of gypsum crystals that have grown together protrudes above the stone surface.

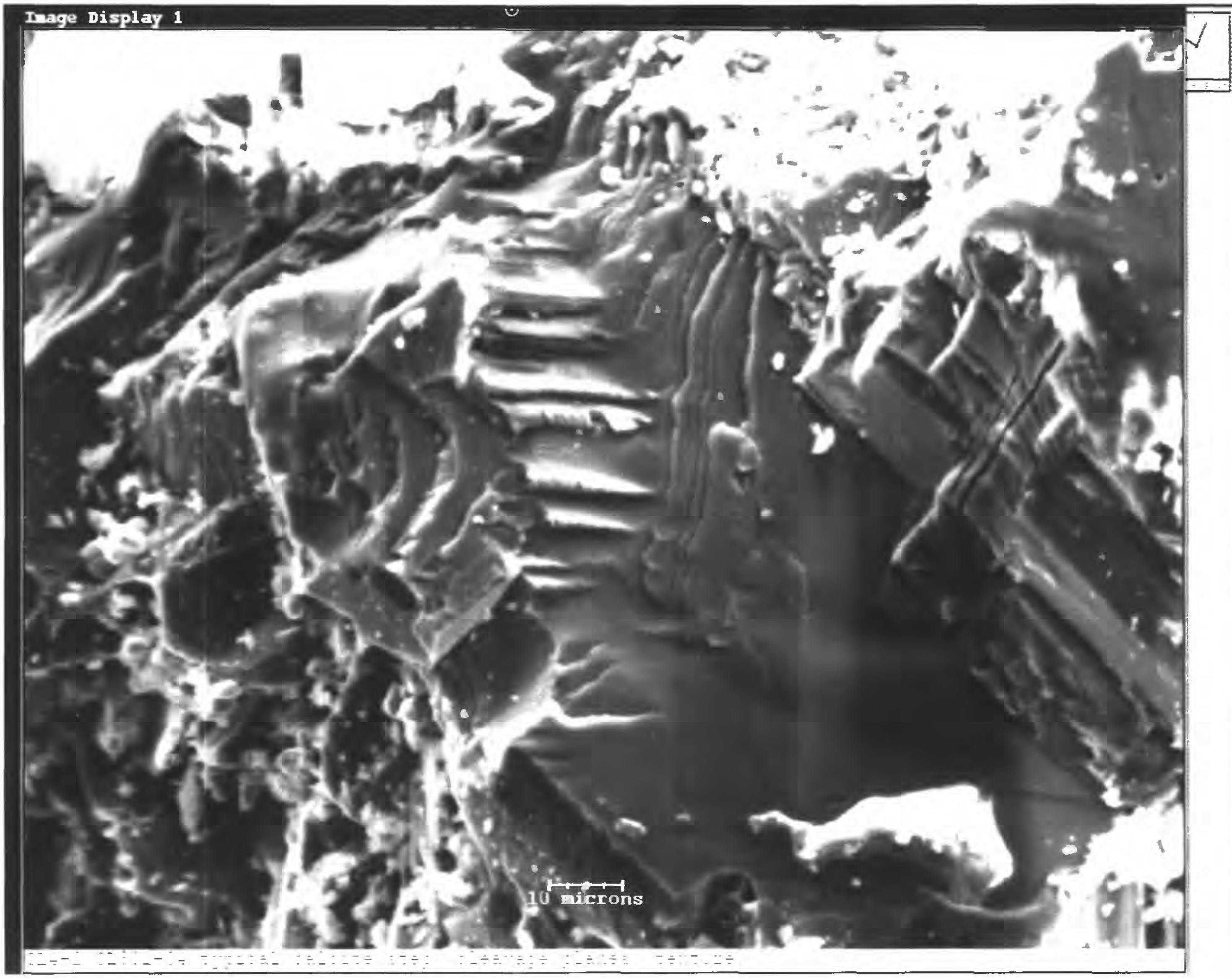


Figure 4. Stepped edges that result from calcite cleavage surfaces are typical on light samples.

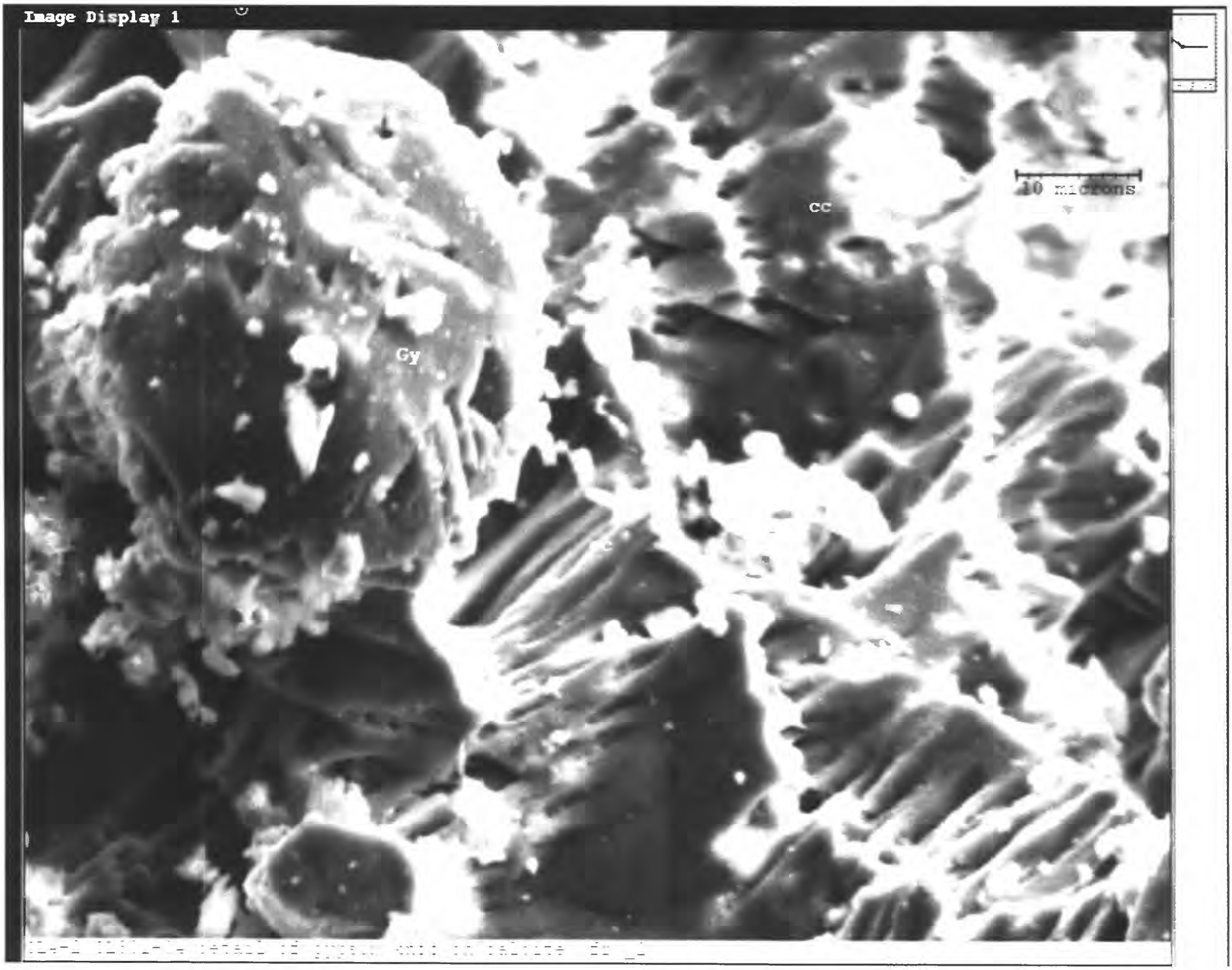


Figure 5. Small clusters of gypsum form bumps on the calcite in light sample CL801-4.

Figure 6. Red brown discolorations stand out on many of the light blocks of limestone. They may occur as small isolated spots, or may cover large areas of a single block of stone. The black area at the left edge of the photo is an area of black surficial crusts.

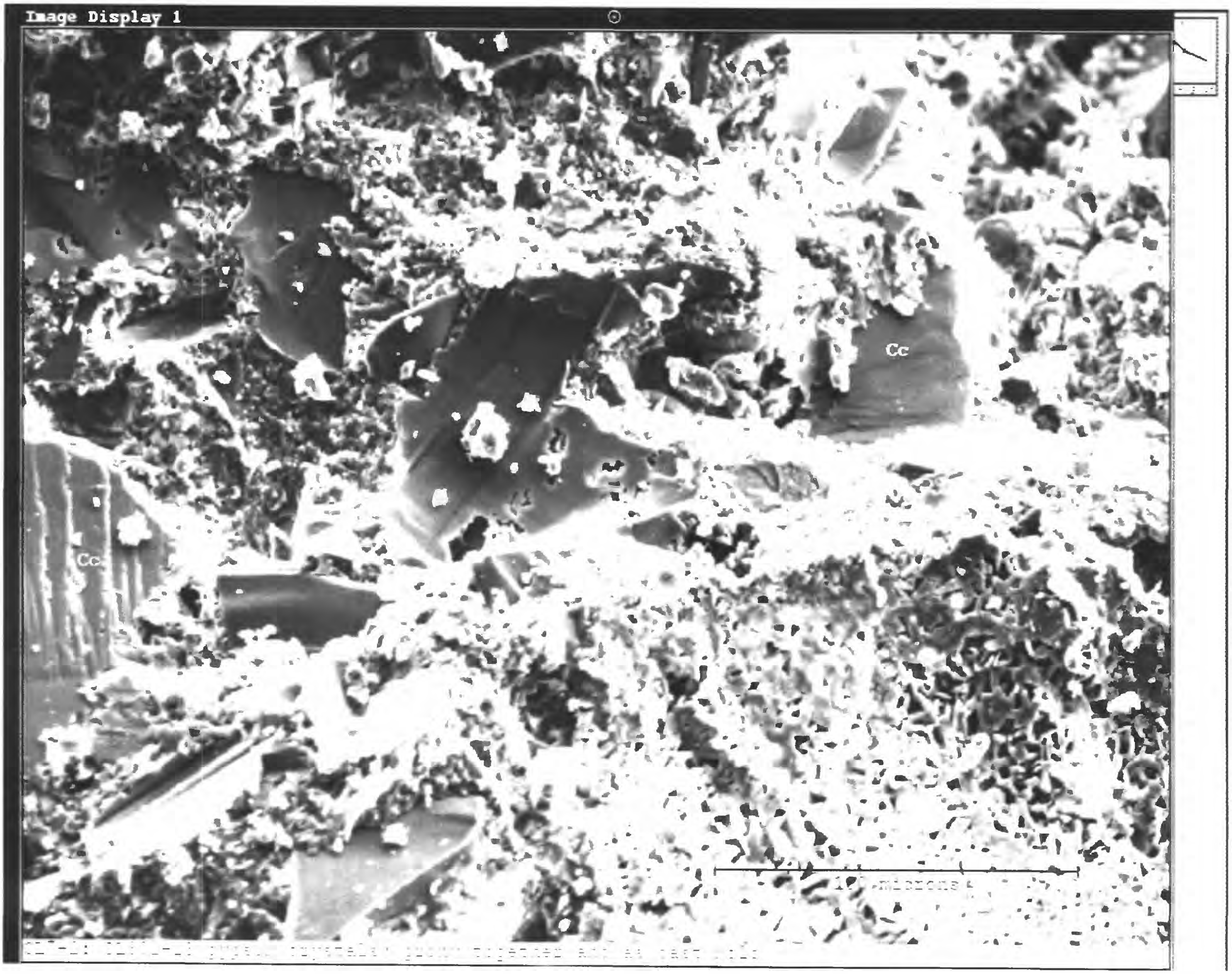


Figure 7. A sample pried from the wall shows how gypsum crystals cover the stone surface. In several areas the gypsum crystals are coalescing and growing together so individual grains become indistinct. **A.** Large area of the sample CL801-13; cc = calcite, the rest of the grains are gypsum.

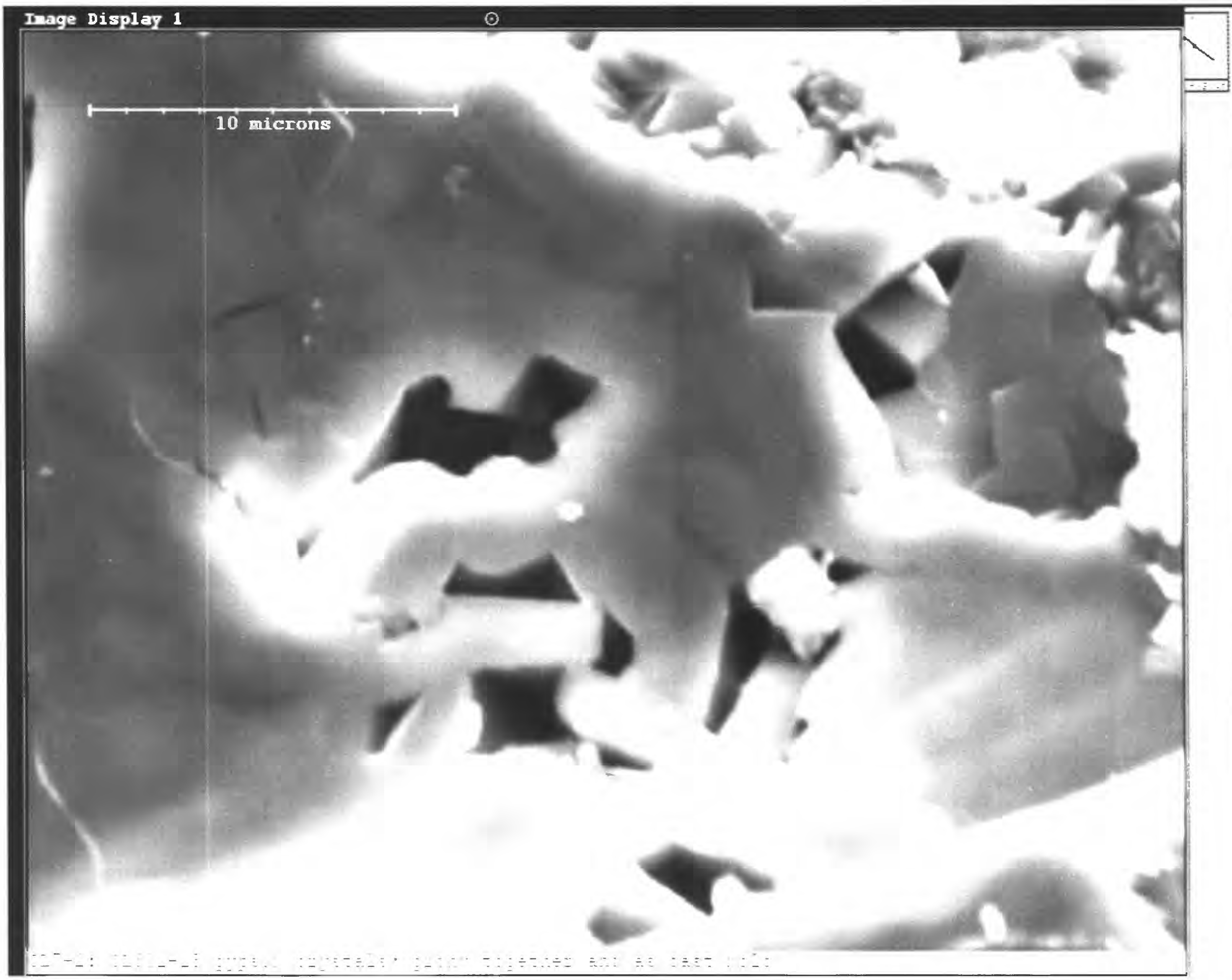


Figure 7. B. A detail of the area at the center of A, shows how gypsum crystals become indistinct as they grow together.

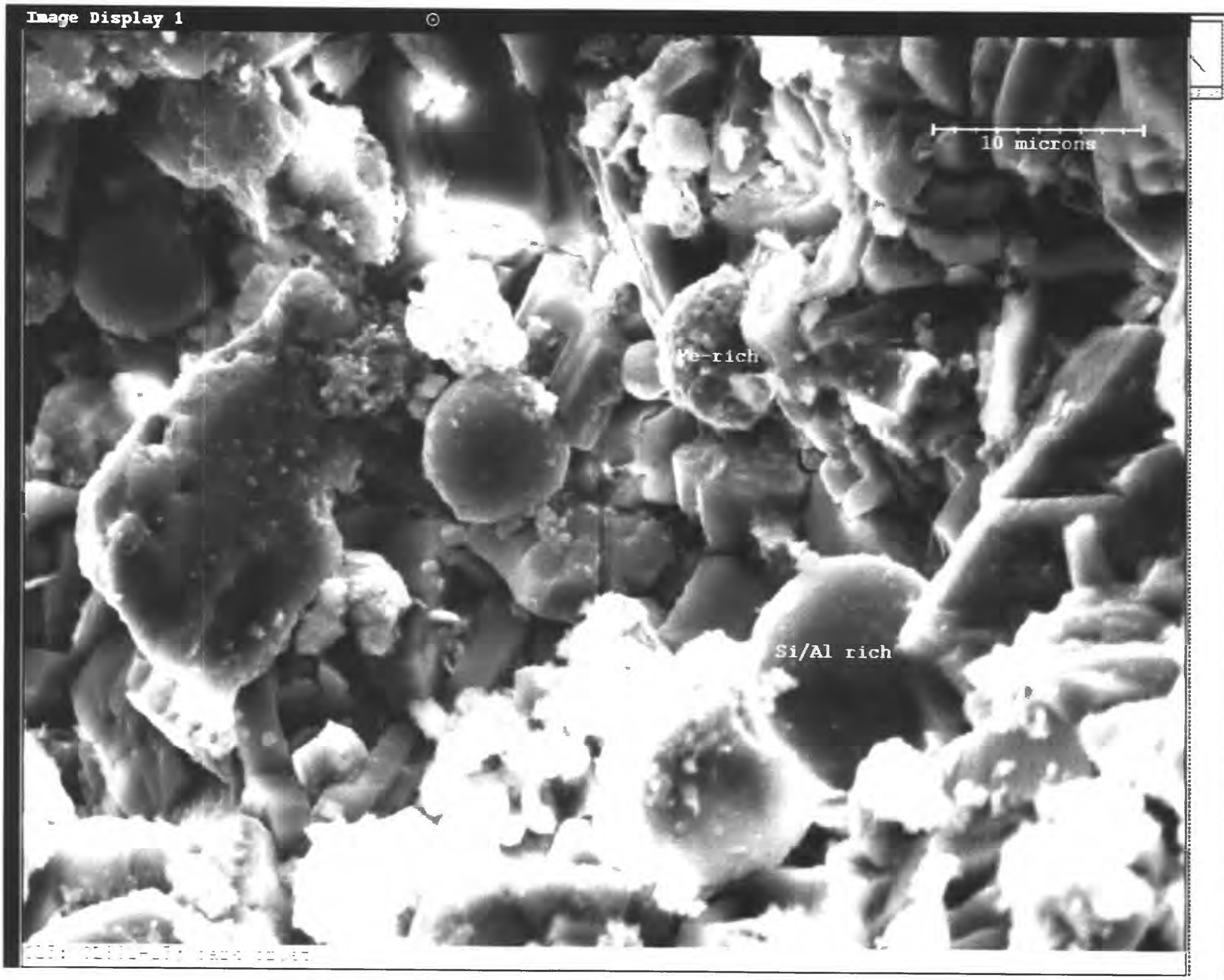


Figure 8. Spheres with a range of surface textures are the most common pollutant particle trapped among the gypsum crystals. The Si- Al-rich spheres are commonly smooth and glassy and the Fe-rich spheres are commonly rough; but surface textures do not always correlate with sphere composition.

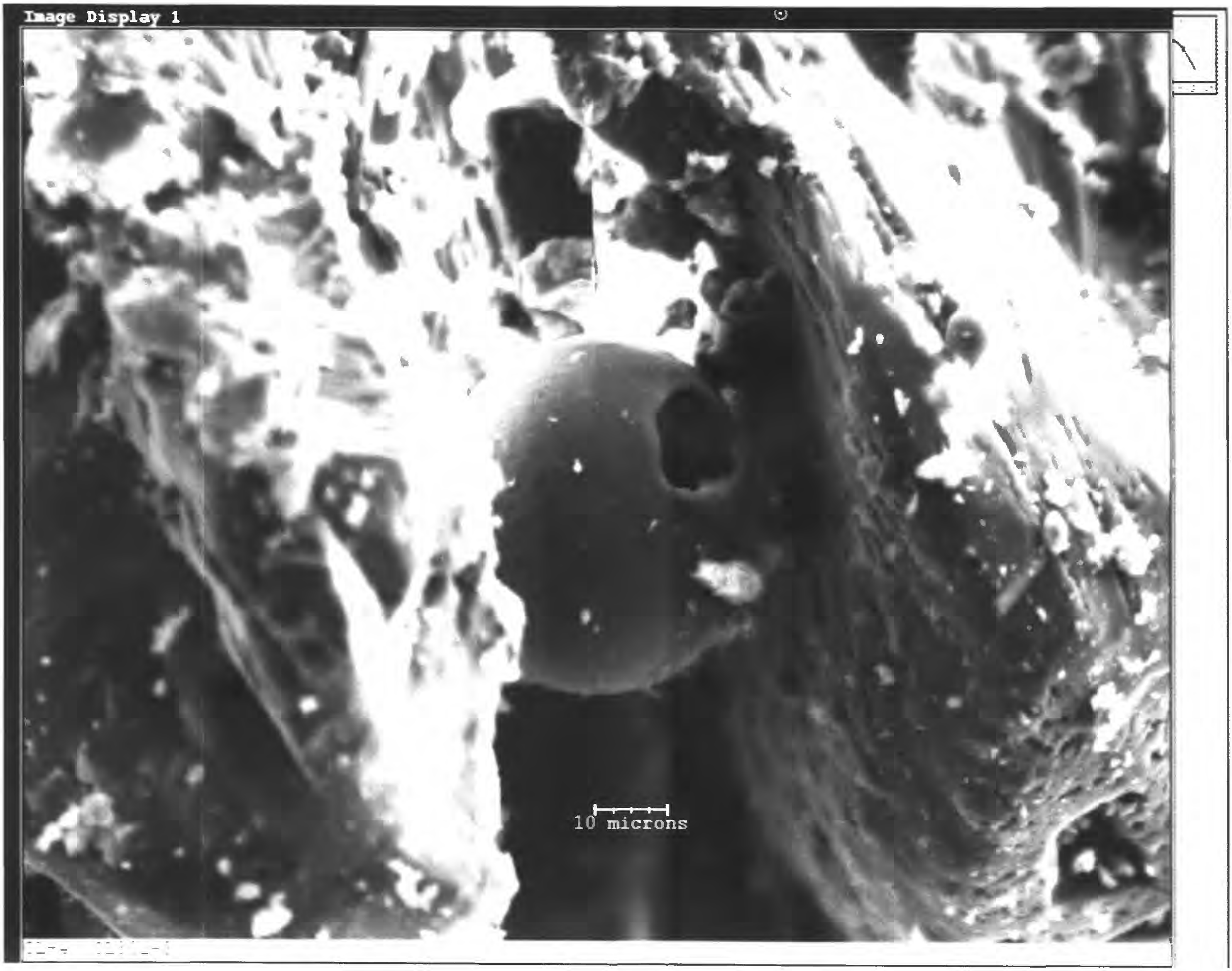
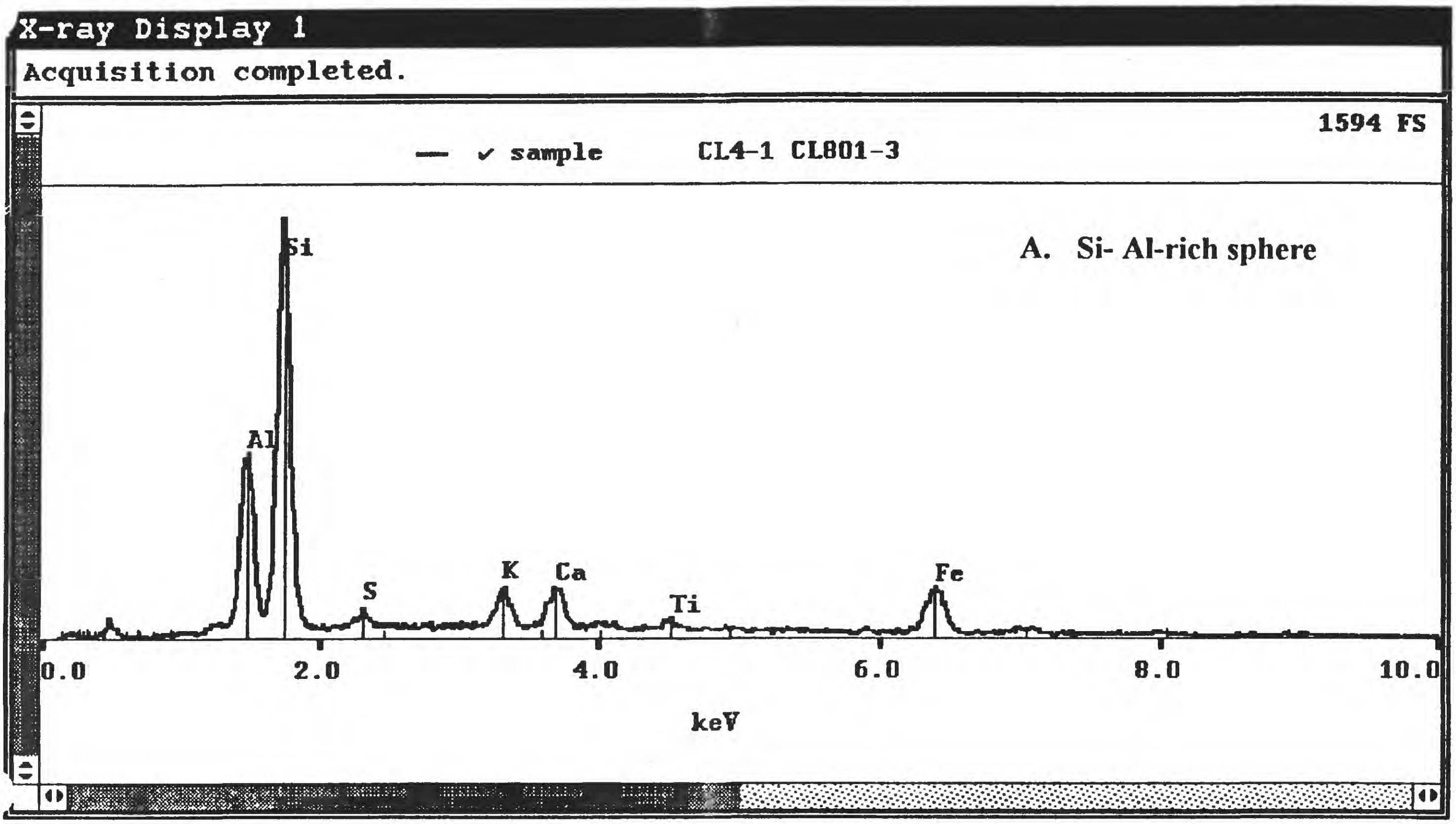


Figure 9. A hollow fly ash sphere with a smooth glassy surface is also Si- Al-rich.



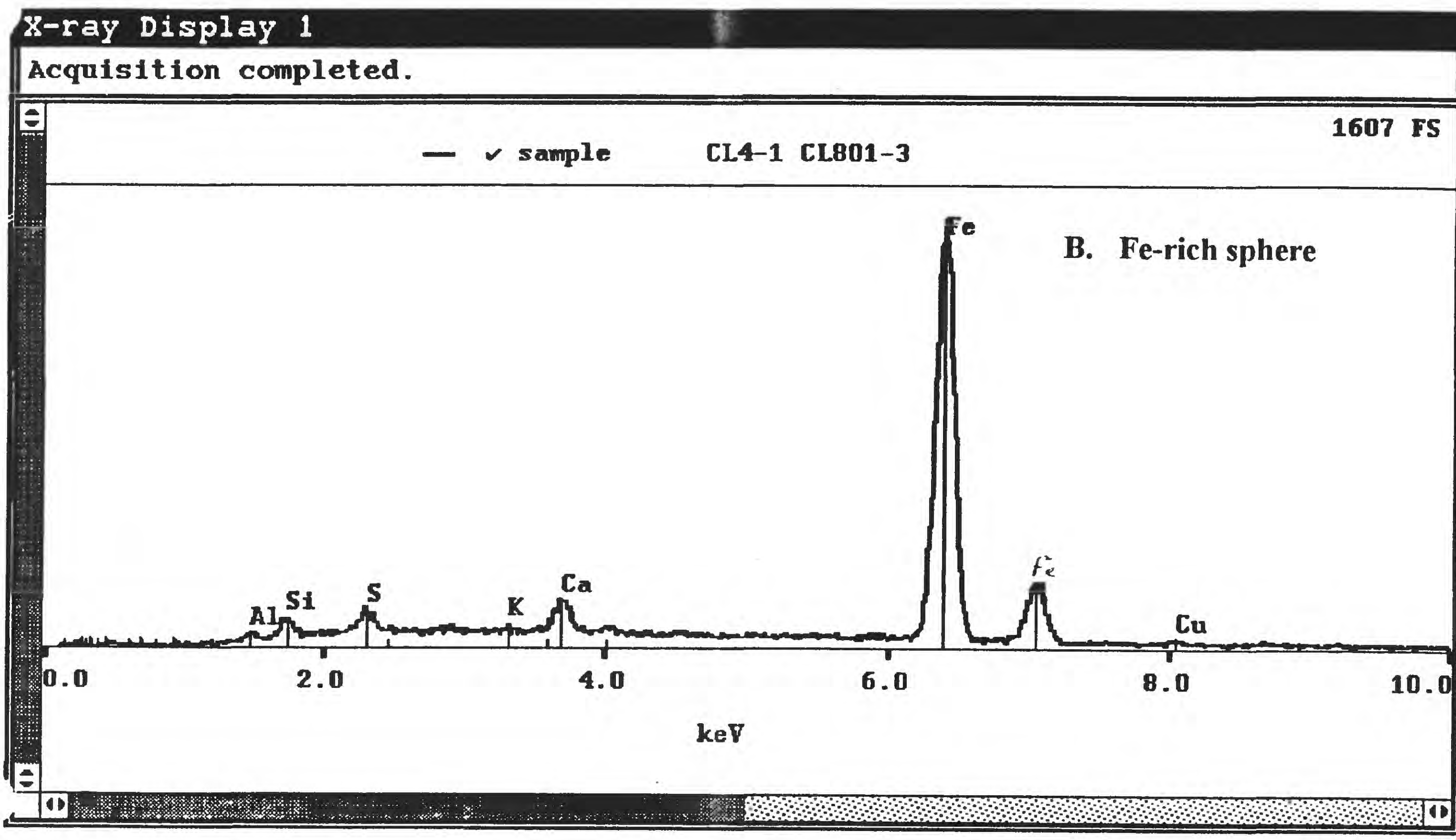


Figure 10. Energy dispersive X-ray (EDAX) spectra for two typical fly ash particles. **A**. Si-Al-rich sphere. **B**. Fe-rich sphere.

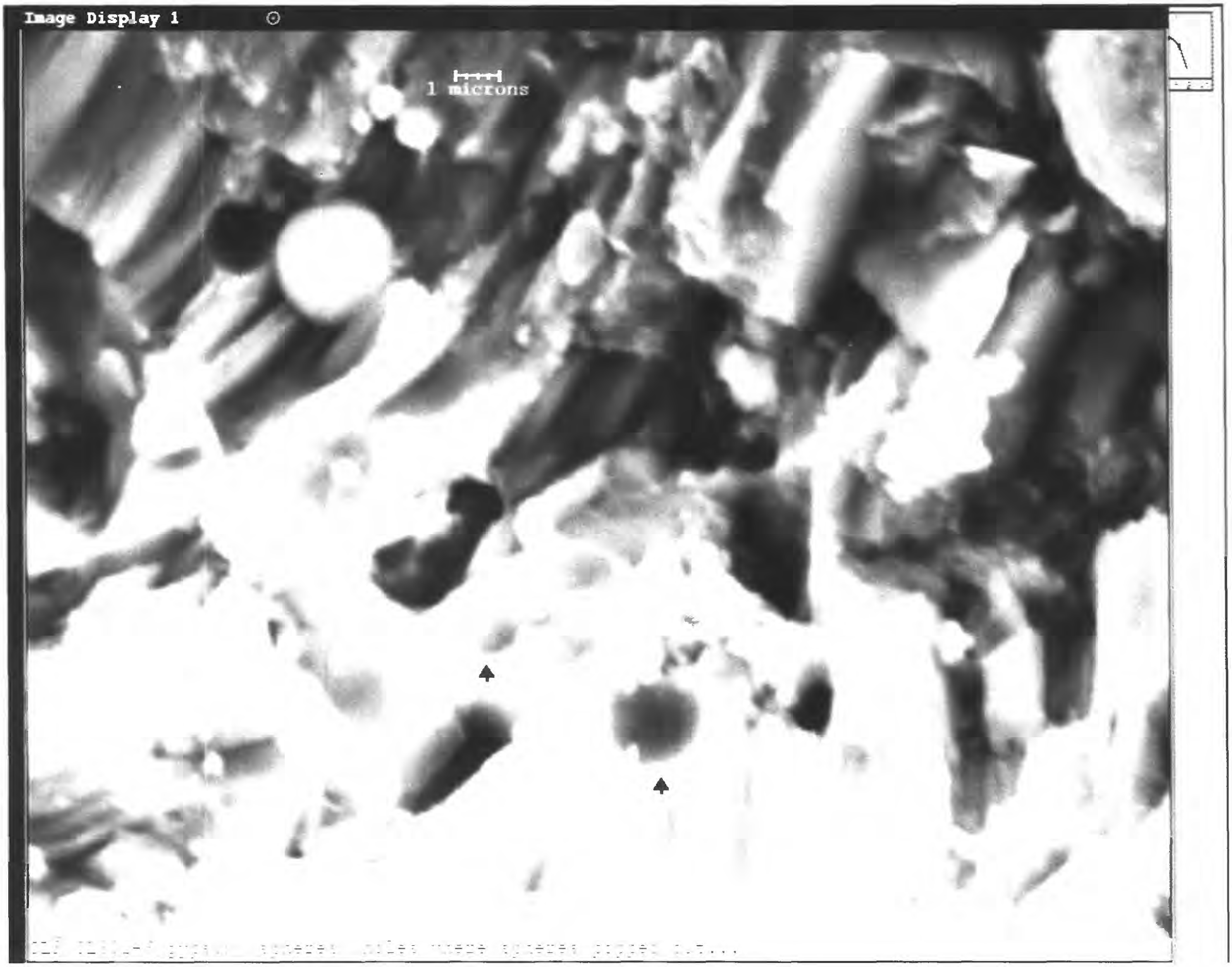


Figure 11. Spherical hollows (shown with arrows) in the gypsum crystals suggest that the gypsum grew around fly ash particles with little or no interaction between the gypsum and the pollutant particles. One fly ash sphere is still present in the upper left of the photo.

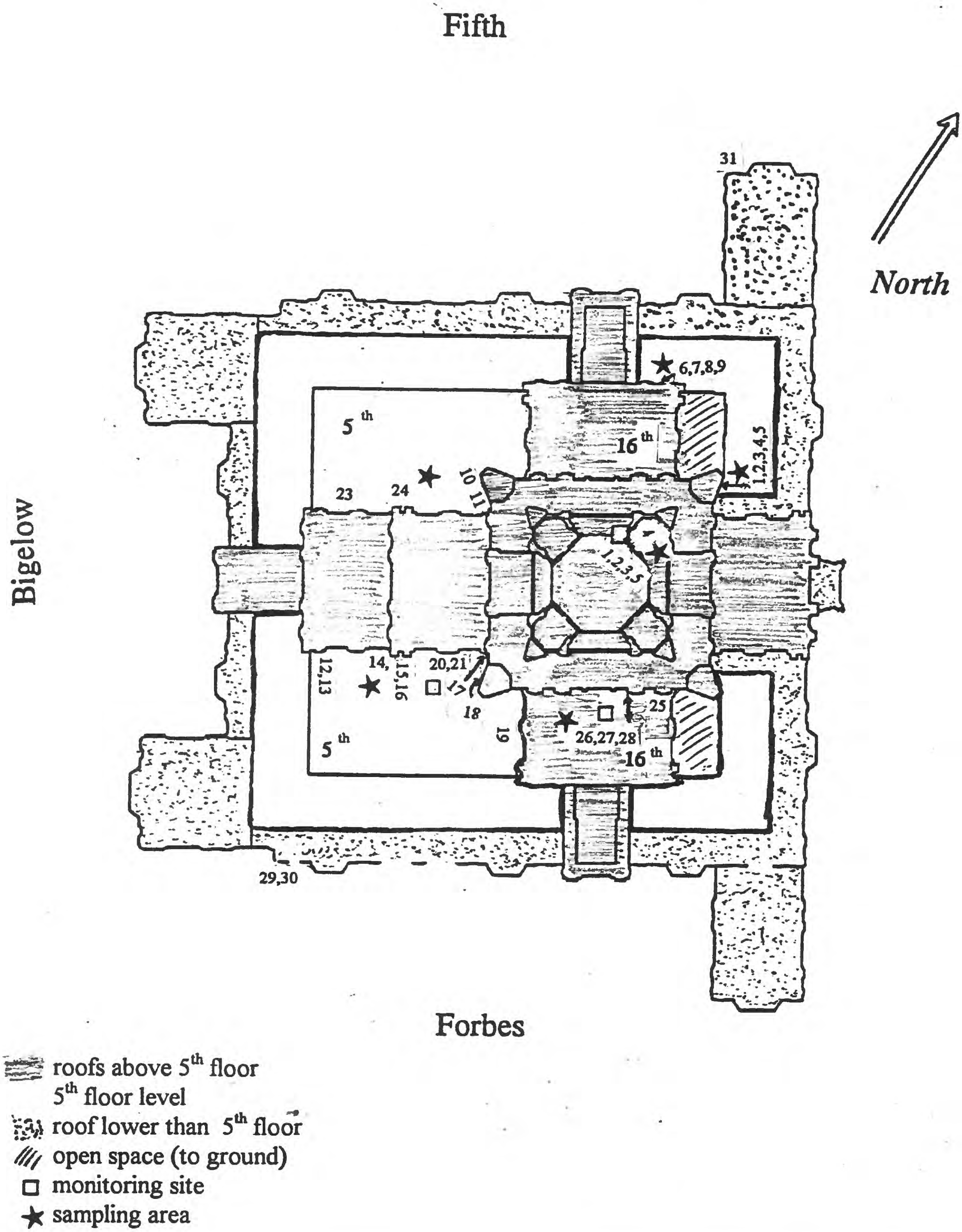


Figure 12. Plan view of the Cathedral of Learning shows the irregular shape of the building and the distribution of sampling sites around the building.