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Foundation Problems and Pyrite Oxidation in the Chattanooga Shale, Estill County, Kentucky

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Abstract

Pyrite oxidation in the Chattanooga Shale has caused serious foundation problems in numerous buildings and structures in Estill County, Ky. Pyrite oxidizes and various secondary sulfates form when excavated shale or shale fill are used in foundations. These secondary sulfates are water- and humidity-sensitive and can form when only minor amounts of water are present in foundation materials. These sulfates form by crystal growth and expand by volume change, which causes subsequent soil expansion and heaving of any foundation materials when the materials are confined. Several structures have undergone expensive remediation to repair damaged sidewalks, floors, walls, and foundations. Zones of high concentrations of pyrite occur in the Chattanooga Shale across the state, and these mineral zones may be responsible for the high pyrite content in Estill County.

Introduction

Significant foundation and structural problems have developed in several large buildings constructed in an area of North Irvine, in Estill County, Ky. (Figs. 1–2). The Estill County Middle School, Carhartt factory, and Marcum and Wallace Hospital auxiliary building (Fig. 1) have all had foundation problems such as cracked and heaving floors and cracked walls, ceilings, and sidewalks. Ky. 499 (the Irvine Bypass) has had pavement and heaving problems in segments of the roadway near the schools.

The middle school (Figs. 3–4) was built in 1996 and has had extensive foundation problems and numerous stages of remediation to correct the problems. The Carhartt factory was built in 1994 and has had severe foundation problems since it was constructed; remediation possibilities are currently being evaluated. The hospital was built in 1959, and although the entire history of previous repairs is not known, it is known to have had minor repairs to correct foundation-related problems at the time this report was completed. Ky. 499 was constructed in 2000 and has had swelling problems since the initial construction. Extensive milling and repair work were required. All of these problems appear to be related to their foundations being developed in the Devonian Chattanooga Shale, with the exception of Ky. 499, whose foundation is in the Crab Orchard Formation, a unit that underlies the Chattanooga Shale.

The Chattanooga Shale is black and organic, and is exposed on the surface over a wide area in east-central Kentucky. Generally, the unit is called the Ohio Shale in the northeastern part of Kentucky, the Chattanooga in the southeastern part of Kentucky, and the New Albany in western Kentucky, as discussed in Hamilton-Smith (1993). It contains various clay and iron-sulfide minerals (primarily pyrite) that can react with water to form sulfates and a mild sulfuric acid. This formation of sulfates and sulfuric acid causes the shale to weather very rapidly and degrade into unstable clay and sulfate minerals.

The Chattanooga Shale extends over a large section of the central United States, and Bryant and others (2003) documented 20 additional states that have had expansive or heaving problems in it. Some of these problems were related to pyrite oxidation and sulfate formation, and some were related to expanding clays in the shale.

Geology and Hydrology

Estill County is located along the eastern flank of the Cincinnati Arch and in the west-central part of the Rome Trough in eastern Kentucky. The county seat, Irvine (Fig. 1), is located along the Irvine–Paint Creek Fault System, a northeast-trending basement system. An unnamed northwest-trending fault occurs along the main Irvine–Paint Creek Fault System and lies about 1,000 ft north of the middle school. There were several northwest- and northeast-trending cleats in the outcrop behind the school and in the subcrop beneath the school.

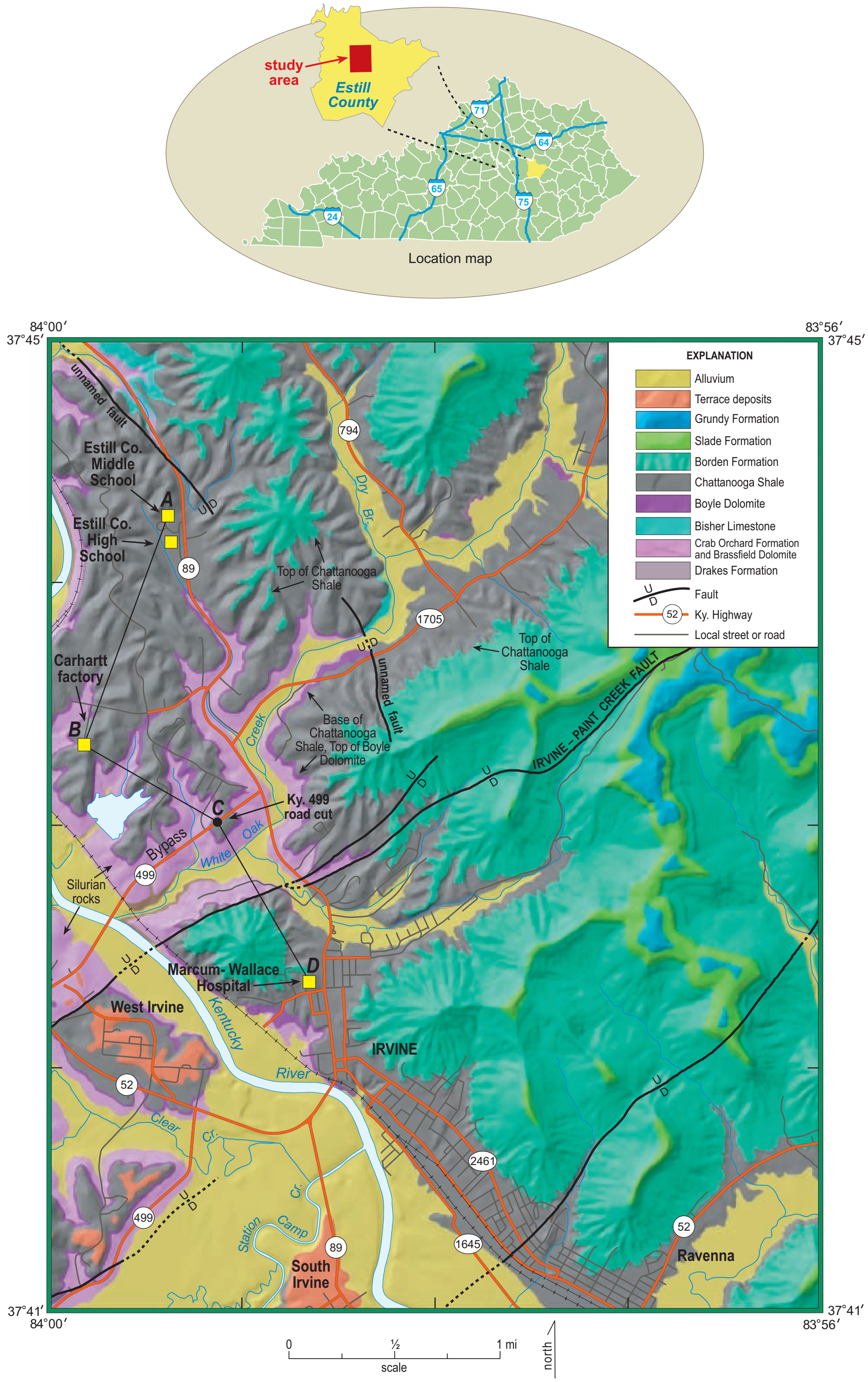

Figure 1. Geology of the North Irvine area, Estill County, Ky. Locations of buildings with foundations in the lower part of the Chattanooga Shale, which have had significant foundation structural problems, are shown. Compiled from Morris and Curl (2000).

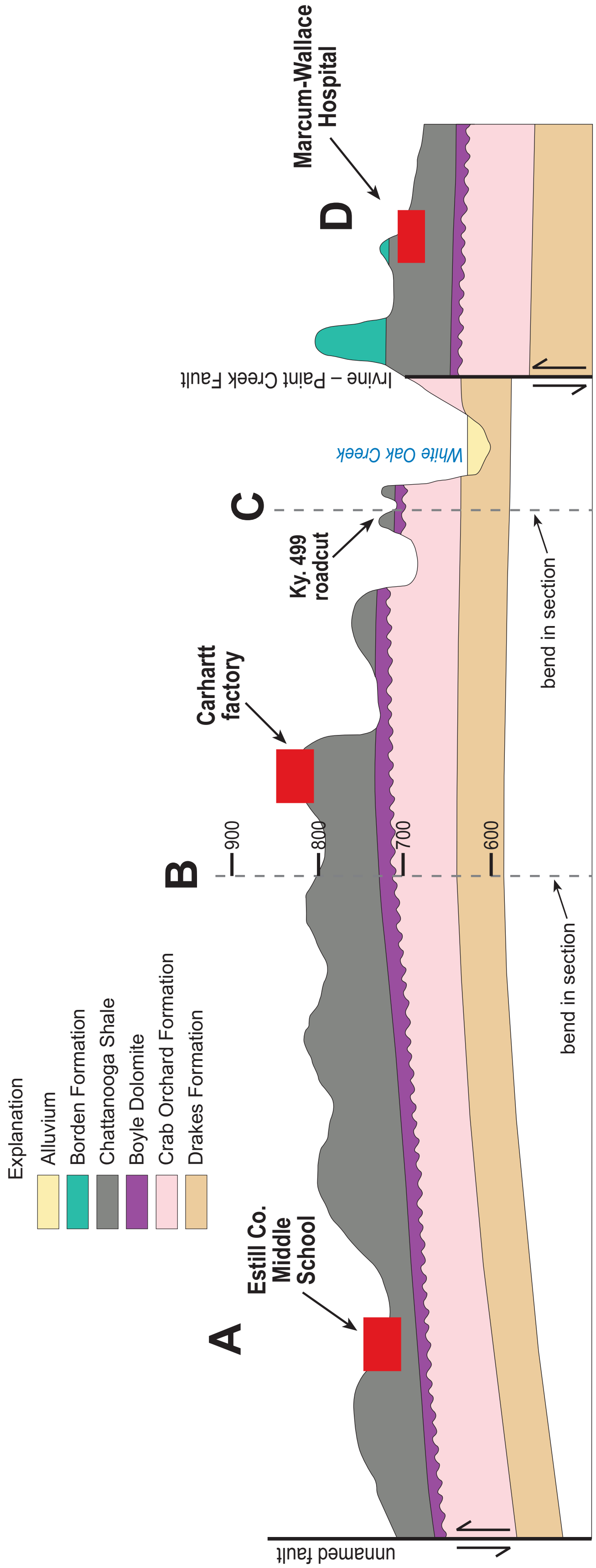

Figure 2. Cross section showing locations of buildings and roadways and position of pyrite zones in the Chattanooga Shale.

Hoge and others (1976) showed that the Chattanooga Shale has been eroded and is flat-lying over a wide area in North Irvine (Fig. 1), and since flat land is desirable for urban development, it would appear to be a good place for building. The shale is not exposed on the surface in other places around Irvine, or occurs on steep slopes and is not appropriate for construction.

The Chattanooga Shale contains abundant pyrite nodules and quartz silt in this area, and it produces water near White Oak Creek (Hoge and others, 1976). Pyrite lenses and nodular zones are common in the outcrops behind the middle school (Figs. 5–8). No obvious fractures or faults were observed in the outcrop at the rear of the middle school, but numerous cleats (Figs. 9–10) appear to be parallel to the northwest-trending fault, and a northeast cleat direction was also noted. These cleats may facilitate the flow of groundwater toward the school, and remediation contractors working at the school noted moisture in some of the subcrop cleats during repair work. No springs were observed on the surface outcrop or subcrop, but Masters Creek, a tributary of White Oak Creek, lies west of the middle school, and the school is at the base of several sloping hills (Figs. 1–2, 5–6), which would channel any surface runoff toward the northwest side of the school. This runoff would accelerate weathering and dissolution in the zone of pyrite nodules, react with the pyrite, and create a mild sulfuric acid in the creek.

Several current and abandoned landfills and an abandoned coal processing plant are in the area, but landfill effluent and surface runoff from these sites does not affect the study area. Several oil and gas fields have been discovered within a few miles of the study area.

Stratigraphy and Mineralogy

The Chattanooga Shale in the study area is between 100 and 160 ft thick (Fig. 11) and is composed of fissile, silty, brownish-black shale with abundant carbonaceous material, limonite, and pyrite nodules. Limestone beds in the shale exhibit cone-in-cone structures.

The mineralogy of the shale consists of 65 to 70 percent clay, 25 to 30 percent quartz silt, 10 percent chlorite, 5 percent pyrite, and some calcite, limestone, and dolomite (Hosterman and Whitlow, 1983). Pyrite occurs as lenses, nodules, and microscopic framboidal or granular particles. Although only mapped as a single unit by Hoge and others (1976) on the geologic map of the Irvine quadrangle, the shale was divided into the upper-

Figure 3. Estill County Middle School (looking northwest).

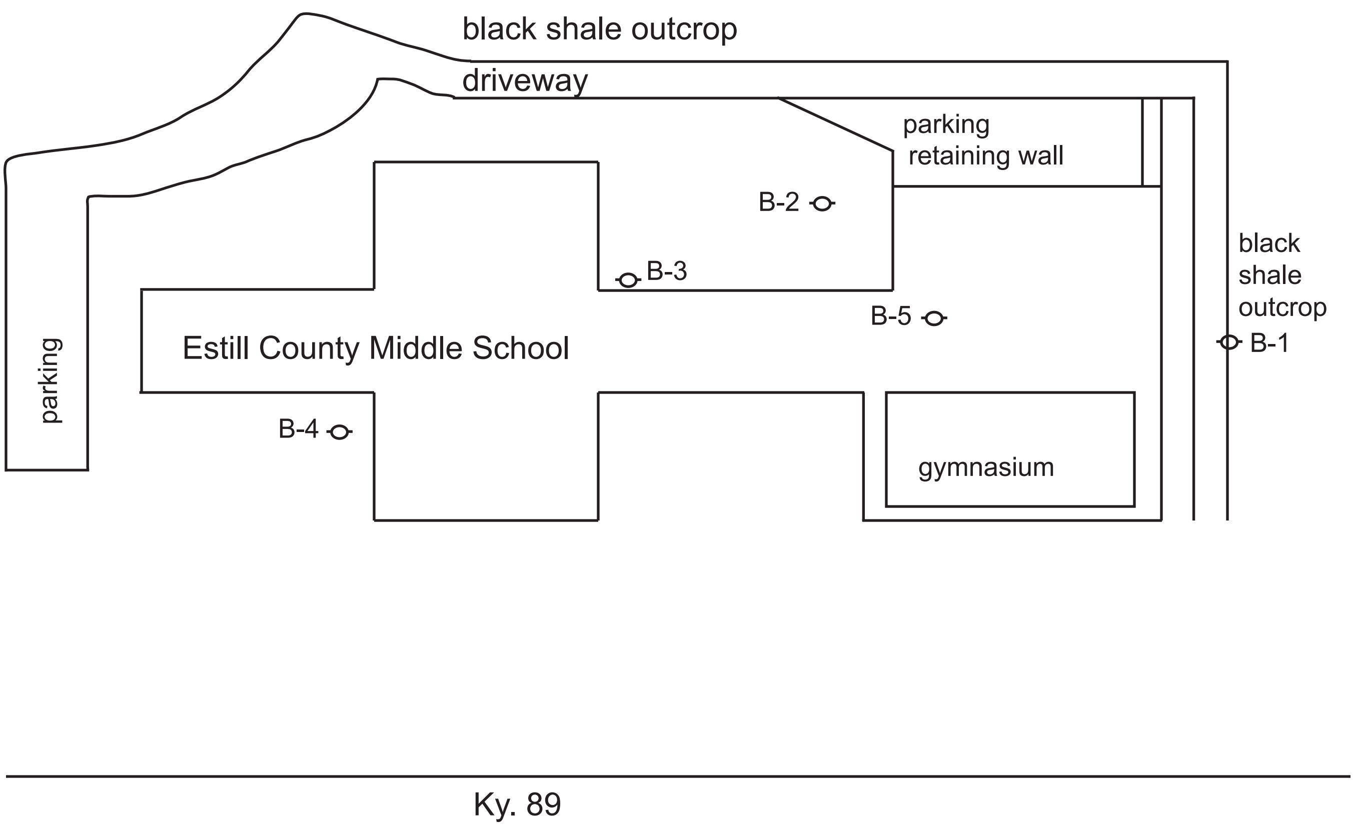

Figure 4. Schematic diagram of Estill County Middle School showing locations of coreholes, outcrops, and the retaining wall.

most Cleveland Member, Three Lick Bed, and Huron Member in this part of Kentucky by Pryor and others (1981). The shale was slowly deposited in an oxygen- and sediment-deprived basin about 400 million years ago. It transgressed over an underlying carbonate sequence, so the lower part of the shale is frequently interbedded with gray and green carbonaceous shales. The coloration of the carbon-rich shale reflects organic content and depositional oxygen saturation. The black shales are more organic and less oxygenated than the green shales. Slow deposition, the abundance of organic material, and the lack of oxygen during diagenesis of the shale allowed sulfide minerals, primarily pyrite, to precipitate between organic matter and along bedding planes. The Huron Member may have been more susceptible to low-oxygen conditions, contributing to increasing framboidal pyrite size (Rimmer and others, 2001; Hawkins and Rimmer, 2002). The organic matter was derived from terrestrial material (Rimmer and Hawkins, 2006). The shale contains minor amounts of iron, uranium, phosphate, vanadium, chromium, and nickel, and is also radioactive, as shown in Figure 11 and as discussed by Tuttle and others (2003).

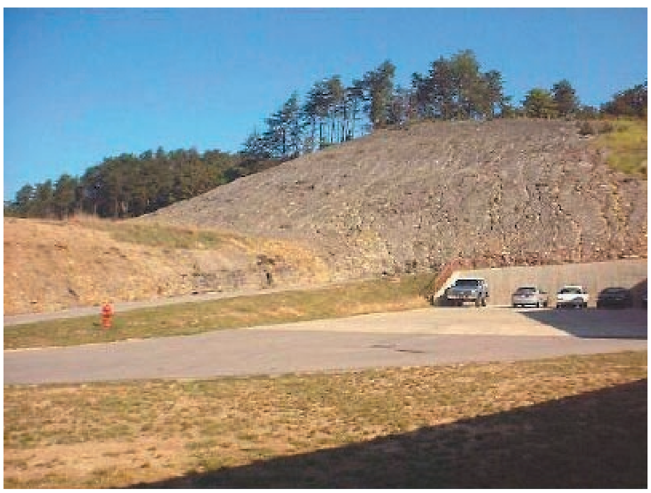

Figure 5. Chattanooga Shale outcrop behind the middle school (toward the north). Note retaining wall.

Figure 6. Outcrop and road behind Estill County Middle School.

Figure 7. Pyrite oxidation, iron oxide, and sulfate staining and precipitate in the Chattanooga Shale at the middle school.

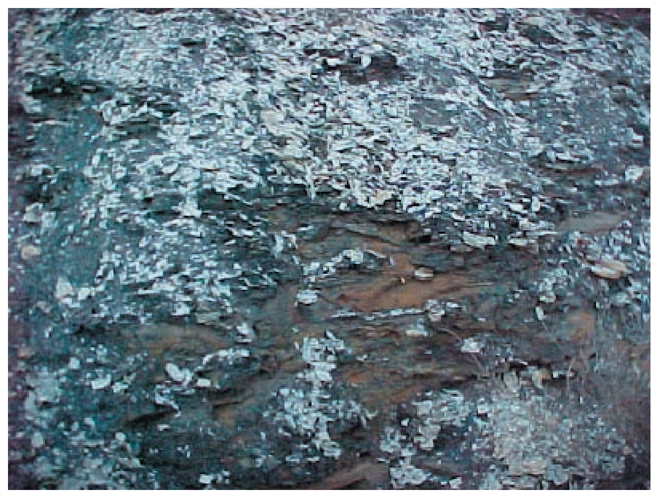

Figure 8. Secondary sulfate coating on Chattanooga Shale outcrop at the middle school.

The clay mineralogy of the Cleveland Member consists of illite (60 percent), illite/smectite (30 percent), chlorite (10 percent), and a trace of kaolinite. The Huron Member primarily contains an illitic clay (60 percent), mixed-layer clay of illite/smectite (20 percent), and chlorite (10 percent) (Hosterman and Whitlow, 1983), and the remainder is kaolinite. The mixed illite/smectite layer could contain some expanding clays. Examples of

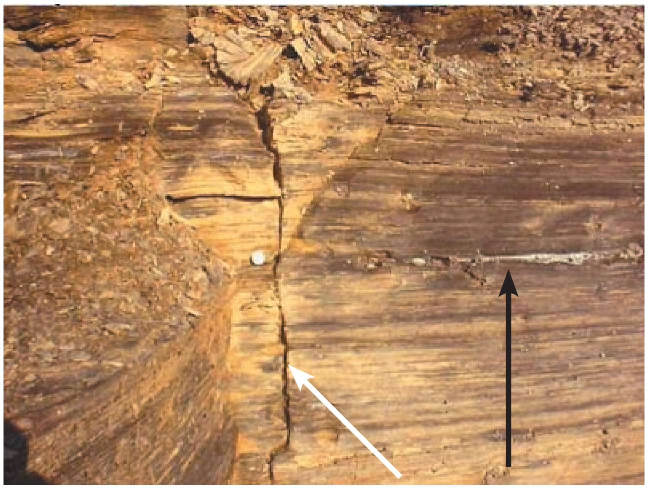

Figure 9. Cleat fractures (white arrow) and pyrite nodule zone (black arrow) in Chattanooga Shale at the middle school.

Figure 10. Intersection of pyrite zone with cleat zone in Chattanooga Shale at the middle school. Note extreme weathering of the shale.

this weathered shale lie in the outcrop drainage behind the middle school (Fig. 10), where it is evident that it has a semiplastic property with little or no shear strength.

The Chattanooga Shale in this area has a high pyrite content, which oxidizes into various efflorescent (powder-like) sulfate minerals. What is commonly called pyrite swelling is actually a chemical oxidation reaction between groundwater and pyrite. Many sulfates form from this chemical reaction, but two of the most common are jarosite and copiapite. Jarosite, an iron sulfate, is a mineral salt and copiapite is a calcium-iron sulfate with a distinctive yellow color.

Underlying the Chattanooga Shale is the Devonian Boyle Dolomite and the Silurian Bisher Limestone and Crab Orchard Formation. The Boyle Dolomite is very thin (less than 20 ft thick). An erosional unconformity at the top of the Silurian may truncate the Bisher Limestone so that the overlying Devonian Boyle Dolomite may reside on top of the Crab Orchard Formation. The Crab Orchard Formation is primarily shale that also contains expandable clays and pyrite (McDowell, 1983).

Geochemical trend maps of Pike, Floyd, Martin, Johnson, and Knott Counties in eastern Kentucky by Negus-de Wys (1981) suggest that pyrite in the Chattanooga Shale may concentrate or occur in specific trends related to original deposition, structure, or stratigraphy. The pyrite concentration can be as high as 8 percent in eastern Kentucky. Although the maps by Negus-de Wys showing high-pyrite trends are of areas outside the current study area, concentration of minerals and metals would be expected in many areas where the shale occurs, particularly in eastern Kentucky. One of these areas of concentration could be in Estill County and account for the high pyrite content.

Stratigraphic Context of the Building Sites

Estill County Middle School was founded near pyrite zones in the lower Huron Member of the Devonian Chattanooga Shale (Fig. 1) (Hoge and others, 1976) and on construction fill derived from the shale. The nearby high school is also founded in the lower shale nearer the contact with the underlying Devonian Boyle Dolomite, but was not founded on fill material (R. Christopher, Estill County Board of Education, personal communication, 2005) and apparently not on a pyrite zone.

The Carhartt factory is located at a higher stratigraphic position than the middle school, in the upper Chattanooga Shale, either the Cleveland or upper Huron Member. Parts of the factory were built on fill, but the parking lot was not. The parking lot does not appear to have any heaving problems.

The Marcum and Wallace Hospital auxiliary office building is situated in the Cleveland Member of the Chattanooga Shale, slightly above the stratigraphic position of the Carhartt factory.

The construction of Ky. 499 occurred south of the middle school, and segments of the road appear to be located in the lower Huron Member of the Chattanooga Shale. Highway construction excavated parts of the Chattanooga Shale, but borehole corings indicate that the base of the road is actually in the Crab Orchard Formation (T. Hopkins, Kentucky Transportation Center, personal communication, 2006). Other segments of the roadway occur in parts of the underlying Crab Orchard Formation, which also contains expanding clays and pyrite. The Crab Orchard also heaves because of expanding

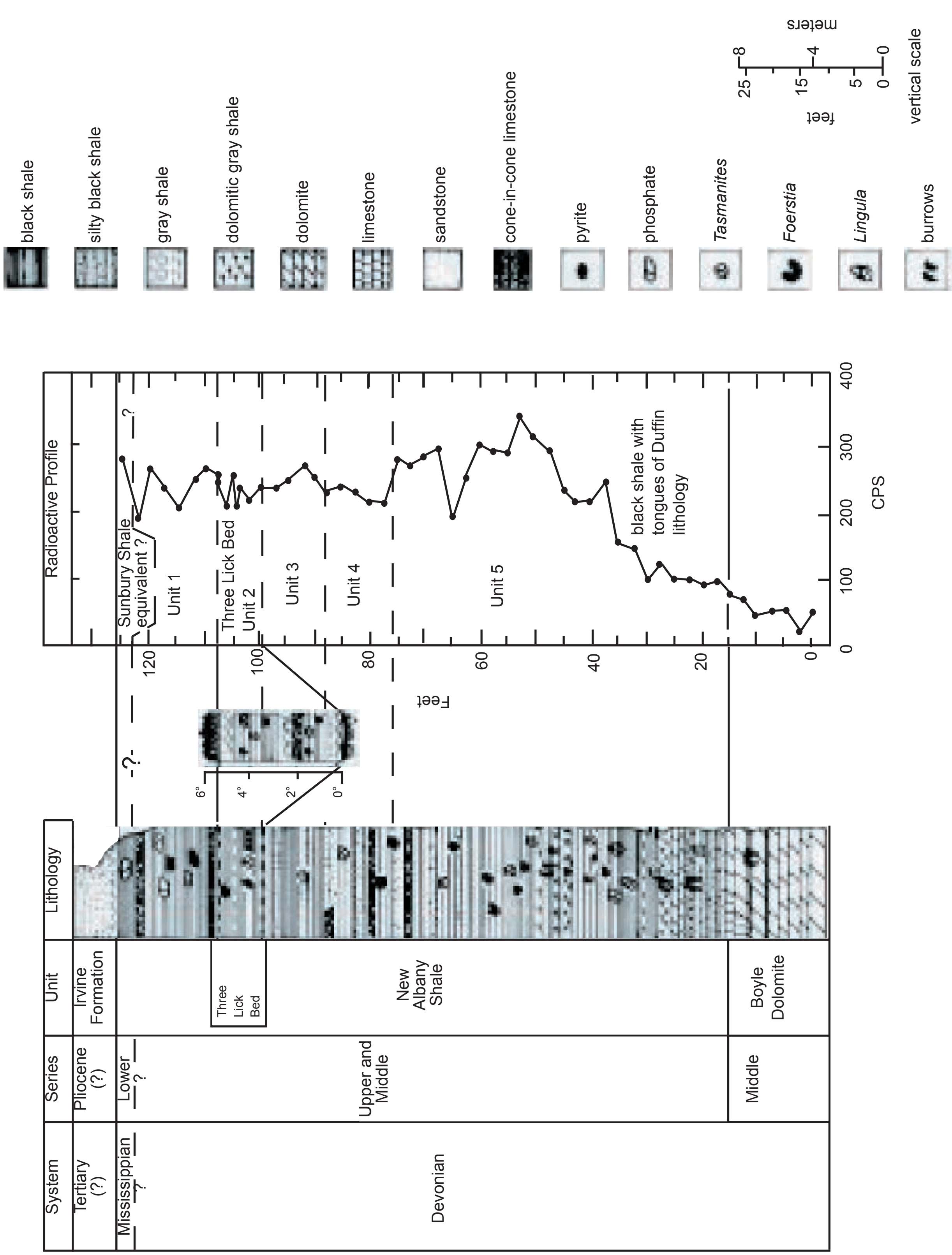

Figure 11. Stratigraphy of the Devonian Chattanooga black shale in Estill County. High radioactivity signatures correspond to the phosphatic zones of the black shale. Modified from Pryor and others (1981).

shale, but pyrite oxidation and sulfate formation in the Crab Orchard were not investigated in this study.

The middle school, factory, and Ky. 499 are located on the north side of the Irvine–Paint Creek Fault System, where the shale is between 120 and 160 ft thick. The hospital lies south of the northernmost fault of the Irvine–Paint Creek system, where the shale is 100 ft thick, which is thinner than at the school. The factory and hospital are located in the upper parts of the shale, whereas the middle school is located in the middle to lower section of the shale. The thickness variability of the shale is related to original deposition and to the Devonian unconformity.

The pyrite zones (Figs. 7–10) within the Cleveland or Huron Member of the Chattanooga Shale appear to be a common factor in the foundation problems in Estill County. Additional pyrite zones in the Chattanooga Shale could cause similar problems. The stratigraphic location of each building and roadway in this study founded on the Chattanooga Shale is shown in Figure 12. Pyrite zones in other shale units such as the Crab Orchard Formation may also cause foundation problems, but were not examined in this study.

Methods

This study inspected the middle school, Carhartt factory, and hospital and their foundations, along with Ky. 499, and examined the Chattanooga Shale in cores and outcrops. The chemistry and mineralogy were analyzed to determine the source of the foundation problems associated with the shale.

Site Inspections

Beginning in 2000, the middle school and factory were both examined for foundation-related failures in interior floors, walls, and ceilings and exterior sidewalks, roadways, parking lots, and retaining walls. In 2006, the hospital and Ky. 499 were also examined. The geology of each site foundation was examined in core and outcrop samples to determine lithologic and mineralogic characteristics of the shale bedrock supporting the foundation and any important associated hydrologic characteristics. Ky. 499, which is located close to the other structures, was examined because swelling pavement and road heaving were reported by Beckham and Hopkins (2005).

Estill County Middle School. As early as the opening of the middle school, problems were noted with the floors, walls, and doors. Several cosmetic repairs have been made to masonry cracks in the walls, concrete floors, and along door frames, including cracks around the frame of the only elevator in the building. Many sections of exterior concrete walkways have been replaced because of the severity of cracking. The middle school has had gaps in the tile floors, cracks in the ceramic floor, and 1-in. offsets in brick and concrete-block walls (Fig. 13). The gymnasium floor has also heaved considerably, and the raised relief of the gym floor was impeding the opening and closing of the bleacher seats in 2000 (Fig. 13). The gym floor (Fig. 14) was excavated in 2005; all flooring and foundation material was removed, and the subcrop bedrock foundation was sealed with an asphaltic fiber resin to prevent further oxidation and heaving. Subsequent remediation in 2006 in other parts of the school (Figs. 15–18) removed additional concrete floors and utility lines and replaced them with concrete columns, steel beams, and joists to create a subfloor above the shale. The damage apparently has not penetrated to the second floor; only minor damage was noted there.

A 10-in. poured-concrete retaining wall in the parking lot shows signs of bulging, confirmed by tension fractures along its face (Fig. 19). Mineral precipitates in the tension cracks and drainholes along the wall (Fig. 20) confirm the presence of sulfate minerals.

An outcrop behind the school exhibits sulfates, pyrite nodules, and pyrite lenses (Figs. 5–10). The sulfate formation is visible in the core, as described in Table 1 (samples 1 to 4), in the subcrop foundation of the school (Figs. 15–17), and in the outcrop behind the school (Figs. 7–8). Massive pyrite oxidation occurring in the shale leaches minerals, including sulfates, sulfur, and iron, into Masters Creek, resulting in low pH, high sulfate, and significant iron-staining in the creek. The outcrop behind the school is red-stained with iron oxide precipitates.

The southeastern corner of the school near the location of core B-4 has some exterior masonry cracks on the brick veneer, and there is a report of a drawer in a teacher's desk that will not remain closed, but slides open by gravitational forces, implying subsidence on the southeastern corner of the school. Shale fill was used in this part of the school.

Estill County High School. The Estill County High School is located several hundred feet south of the middle school and is approximately 30 to 40 ft lower in elevation. The high school has had no apparent foundation problems. The Masters Creek tributary behind the high school drains the landscape of both schools and is a "red" creek, implying that it is iron-rich and sulfurous, containing acidic water.

Carhartt Factory. The Carhartt factory, located in an industrial park about 1 mi southwest of the middle school and north of Ky. 499 (Fig. 1), had similar foundation problems as the middle school. The factory is sited higher in the stratigraphic column, in the Cleveland

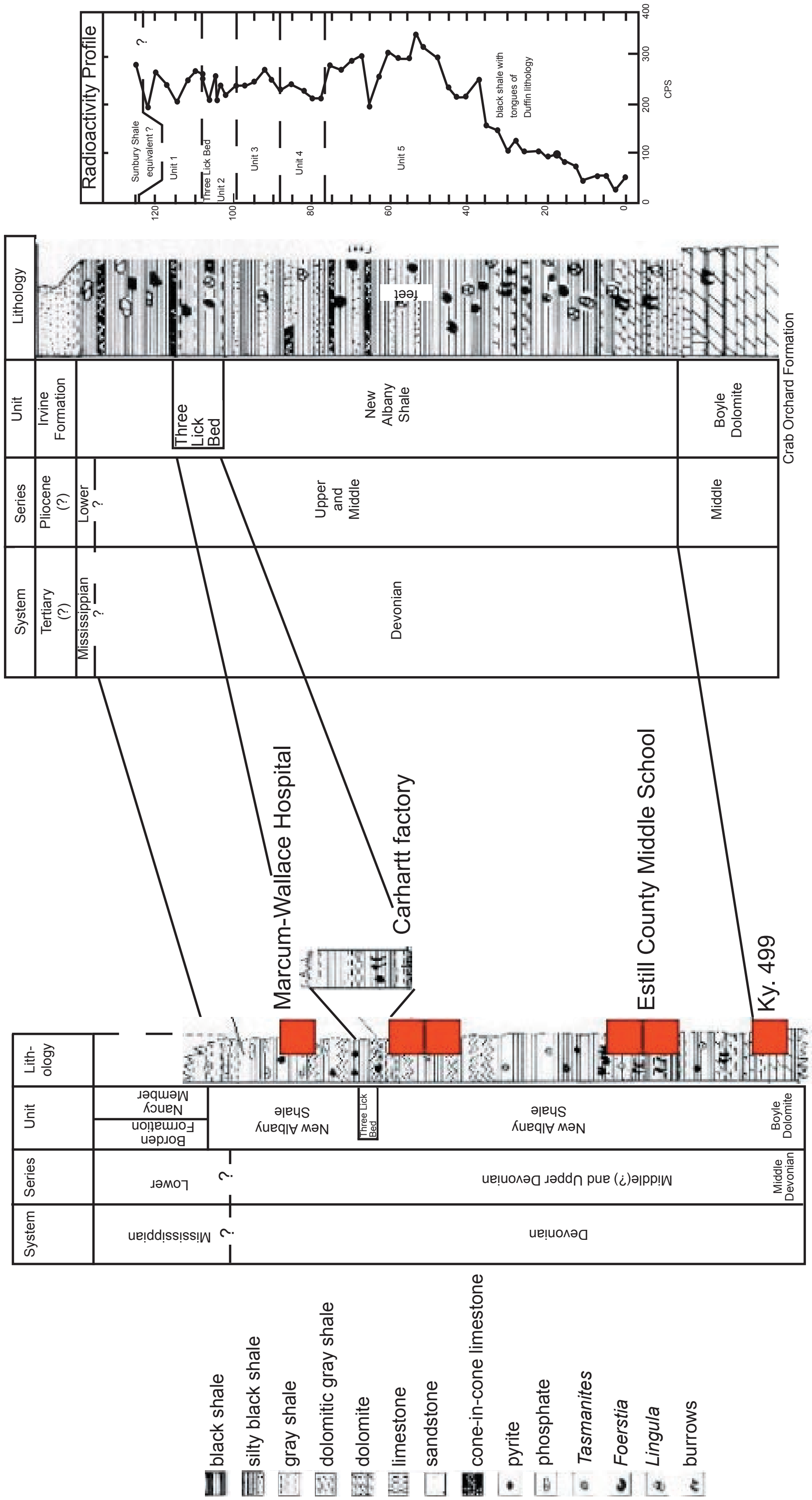

Figure 12. Stratigraphic column showing location of buildings examined in this study. Stratigraphic columns modified from Swager (1978).

Figure 13. Repaired masonry block cracks.

Figure 15. New trench constructed in shale subcrop beneath the middle school. The sulfate mineral copiapite has formed in cleats. Note that load-bearing walls on the right side of the photograph and in the background do not show any signs of failure.

Member of the Chattanooga Shale. Floor heaving was considerable: 4 in. adjacent to the load-bearing walls. There were also cracks near doorways, ceilings, and in floors (Figs. 21–22). Doorways have been cut to allow functionality (Fig. 23). In the truck-loading area, steel inclines had to be installed so that forklifts could be driven over heaved flooring (Fig. 24). Although no major remediation was conducted in 2006, options for repair are being evaluated.

Marcum and Wallace Hospital. The hospital's location in the upper Chattanooga Shale contributed to some of its foundation problems. Interior floors and nonload-bearing concrete-block walls have cracked and heaved considerably, bending and breaking copper water lines and radiators and breaking ceiling plaster. Exterior load-bearing walls did not have any major cracks or fractures in exterior brickwork. Water runoff from the shale outcrop at the rear of the hospital and a roof drainage system that channels runoff into an area within 15 ft of the foundation could be the reason many of the floors were heaving. Cleat directions, iron stains, and water marks indicate that sulfate-rich waters are seeping into the hospital foundation bedrock from these drains and

Figure 14. Repair of heaving floors in middle school gymnasium. The original foundation and fill had to be removed and sealed with a resin to prevent further oxidation and heaving of the shale. Photograph by John F. Stickney, Kentucky Rural Water Association.

Figure 16. Multidirectional cleat fractures coated with secondary sulfate precipitates such as jarosite, copiapite, and melanterite in the Chattanooga Shale beneath flooring at the middle school. The sewer drain tile was broken by heaving floor slabs, and subsequently was removed. Rebar is being inserted into reinforced concrete columns.

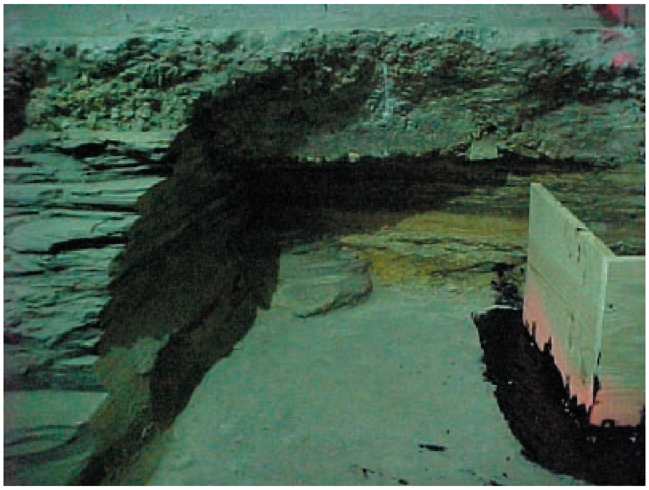

Figure 17. Cleats with copiapite in shale subcrop beneath the middle school, along with newly constructed concrete column forms.

facilitating the chemical reaction of pyrite, water, and shale. These precipitates leave iron stains and other mineral residues such as sulfates in the basement flooring and are evidence that sulfates could be the cause of floor heaving and foundation problems.

The primary foundation problems were repaired by reinstalling water lines and radiators, replacing drywall and ceiling tile, and patching cracked concrete-block walls. But unless the drainage system is modified, heaving problems in floor slabs could continue. Damage appears to be restricted to nonload-bearing walls, since damage to exterior load-bearing walls was not observed (Figs. 25–28).

Figure 18. Cleats with sulfate precipitation in shale subcrop beneath the middle school, along with forms for construction of new concrete columns.

Figure 19. Tension fractures (arrows) along exterior retaining wall and iron-stained drainholes.

Ky. 499. The eastern segment of Ky. 499, located south of the middle school near North Irvine, is situated in the upper Crab Orchard Formation (Beckham and Hopkins, 2005). Field investigation and discussions with Tommy Hopkins (Kentucky Transportation Center, personal communication, 2006) indicated that heaving in this segment is caused by expanding clays in the Crab Orchard and that pyrite oxidation from the Chattanooga Shale has only minor impact on the road base. Although the actual road base is in the Crab Orchard, the cut banks adjacent to the highway are lower Chattanooga Shale. This means that water from the Chattanooga Shale could have low pH and that any pyrite in the outcrop could oxidize and contribute to the swelling problems. Kentucky Transportation Center engineers used a hydrated lime to stabilize the subgrade, which may hinder any pyrite oxidation. The lime raises the pH of the water and restricts the iron and sulfur oxidation. If the Chattanooga Shale contributed to the swelling problem, the lime and high pH essentially halted the reaction, so that the sulfate formation was reduced. Bryant and others (2003), however, cautioned against using hydrated lime in a sub-base in unstable soils with montmorillonite, because the combined chemical reaction can produce many other expansive sulfates such as ettringite. No samples were analyzed from the Ky. 499 location to determine the presence of ettringite. Because Ky. 499 transects the Crab Orchard Formation, swelling is the result of expanding clays such as montmorillonite. Detailed geotechnical investigation of the problems with Ky. 499 is in Beckham and Hopkins (2005).

Other roads in the area that have a foundation in the Chattanooga Shale could exhibit severe foundation problems such as swelling and heaving caused by pyrite oxidation.

Figure 20. Drain-pipe precipitates (sulfates).

Figure 21. Substantial floor cracks in Carhartt break room.

Table 1. Core and outcrop descriptions and analysis for the study area.

Sample No.	*Core*	*Footage*	*Description*
		Cores near the exterior foundation of the middle school (Fig. 3)	
1	B-1	1 ft, 9 in.–14 ft, 10 in.	Shale, black, fissile, fresh, with ¼-in. pyrite nodule; 1/16-in. pyritic lens at 7 ft, 6 in. Pyrite lens at 12 ft, 6 in. and 14 ft, 7 in.; slightly phosphatic.
2	B-2	2 ft, 5 in.–3 ft, 8 in.	Shale, black, fissile, fresh, with traces of pyrite.
3	B-3	2 ft, 0 in.–3 ft, 9 in.	Shale, black, fissile, weathered, with visible amounts of copiapite, gypsum, and melanterite, and scattered pyrite and phosphate grains.
4	B-4	1 ft, 9 in.–3 ft, 4 in.	Shale, black, fissile, wet(?), weathered, with visible copiapite and a zone of pyrite nodules.
		Core from inside the middle school	
5	B-5	1 ft, 0 in.–2 ft, 5 in.	Shale, black, weathered, some visible sulfate, in part unweathered.
		Samples from behind the middle school	
6			Shale, black, weathered, with blooms of melanterite and copiapite; high sulfate content.
7			Pyrite nodules, secondary sulfates visible, melanterite, copiapite. From outcrop.
8			Sulfate precipitates from drain tile in retaining wall—11300. 200 ppm SO_4, 200 ppm Ca, 200 ppm Fe, 200 ppm Mg.
9			Calcareous nodule zone in outcrop; calcium carbonate.

Figure 22. Large cracks (1 in.) in concrete block adjacent to doorway at Carhartt factory.

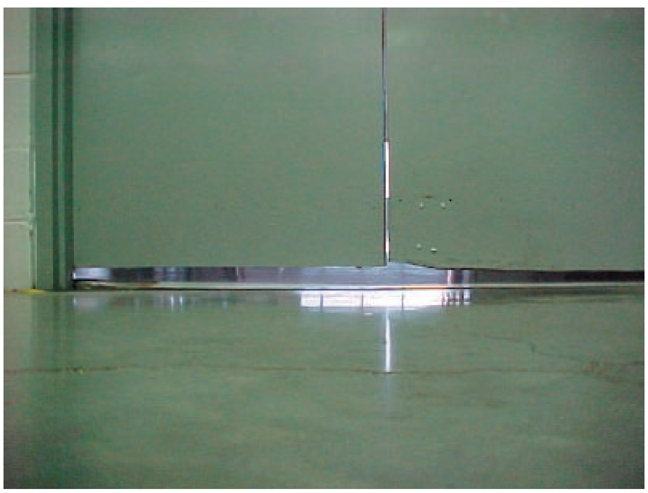

Figure 23. Doors in the Carhartt factory were cut so they could open and close.

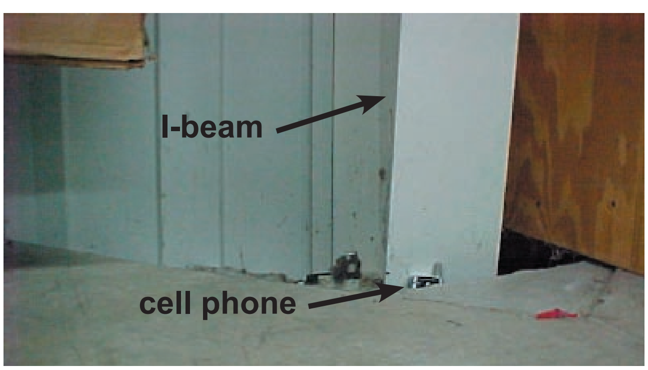

Figure 24. Heaved floor adjacent to load-bearing wall on main floor of the Carhartt factory. Note the top of a cell phone near the I-beam, which shows that the main floor was heaved upward about 4 in.

Excavations of the black shale in the vicinity of the schools are numerous; ball fields and practice fields are located west of the schools, and South East Coal Co. processing plants and a landfill are located about 1 mi southwest; another landfill is located to the east. The surface drainage of these excavations and landfill effluent is generally away from the schools and factory, and does not appear to influence the foundation problems.

Analytical Methods

Five cores were collected at the middle school; one was from an interior hallway and the others were from the exterior perimeter of the school foundation. Detailed core descriptions were compiled to identify lithologic and mineralogic characteristics of the shale. Additional outcrops along the western side of the school were examined and described, as well as outcrops near the factory, hospital, and Ky. 499.

Preliminary visual mineral identification was conducted on sample sets from core and outcrop, and confirmed by X-ray diffraction and fluorescence. Shale was analyzed by X-ray fluorescence to determine whole-rock chemistry, and clay-mineral analysis was determined by X-ray diffraction. These analyses determined the percentage of calcium, iron, silicon, aluminum, potassium, magnesium, sodium, and sulfur: the principal elements in sulfate minerals. Sulfate analysis was conducted by X-ray diffraction to determine mineralogical composition. Mössbauer spectroscopy was conducted on pyrite samples to determine the variations in iron and sulfur composition. Induced coupled plasma spectroscopy on

Figure 25. Exterior of the Marcum and Wallace Hospital office wing and outcrop of the Cleveland Member of the Chattanooga Shale. Note the absence of cracks or offsets in exterior brickwork near windows, even though behind these windows, interior floor heaving was extensive.

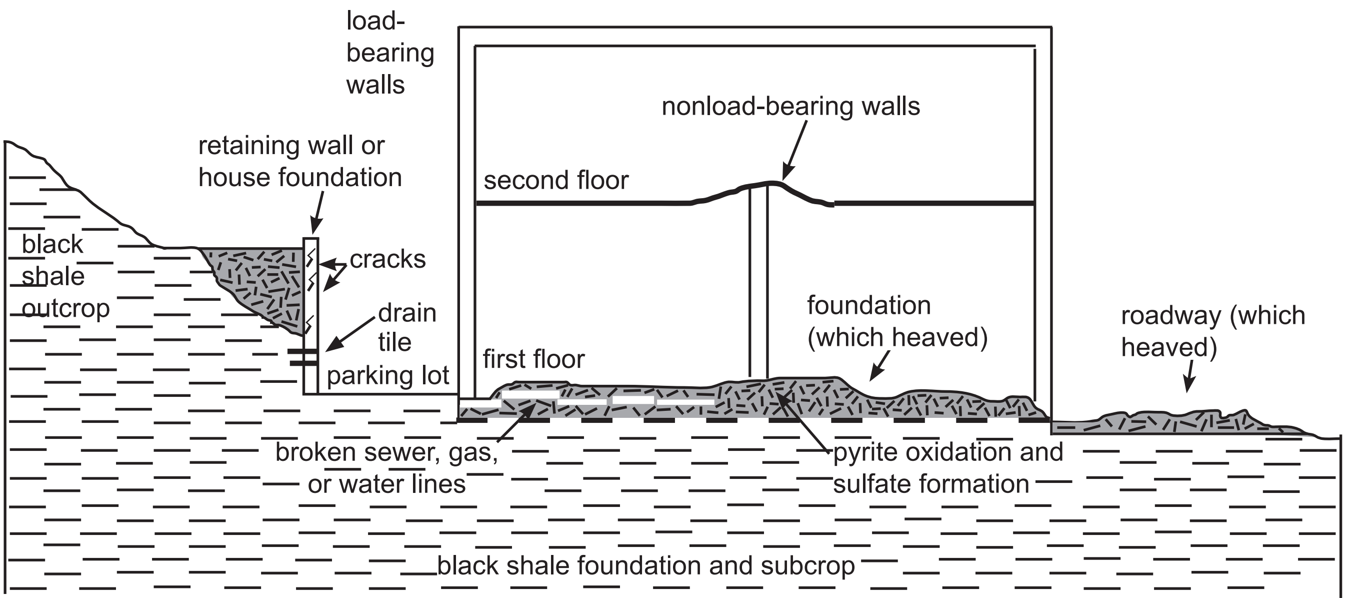

Figure 26. Schematic diagram of Chattanooga Shale outcrop, demonstrating pyrite oxidation and sulfate formation. Floors heave because sulfate forms and puts pressure on load-bearing walls. Roads, nonload-bearing walls, and retaining walls could be affected by continued pyrite oxidation and sulfate formation.

Figure 27. Displacement of ceiling wallboard at hospital along nonload-bearing walls caused by floor heaving.

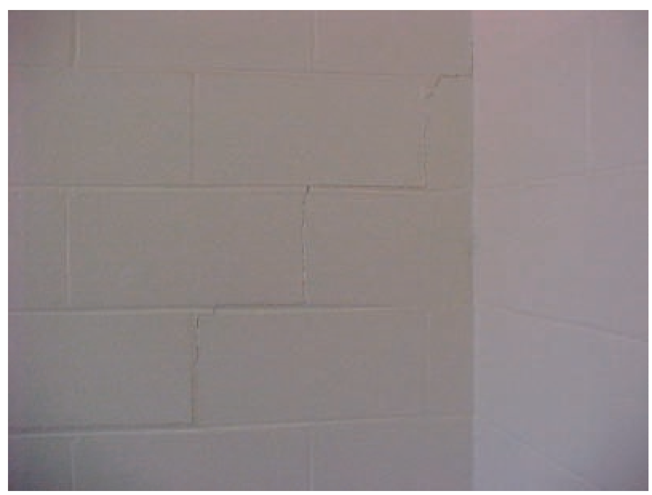

Figure 28. Cracks in concrete blocks at hospital.

major elements in the core and water samples determined overall major- and minor-element composition. Variance in each component mineral is important to determine areas of chemical reactions involving shale, pyrite, and sulfates.

Results

Core and Sample Descriptions

The cores used for analysis at Estill County Middle School were fresh rock samples, cored on August 30, 2000, by Marshall Miller and Associates. Upon examination, most samples appeared fresh, although some weathering was noted in physical description of three cores (B-2, B-3, and B-4) (Table 1).

Analytical Results

Shale Analysis. The mineral composition of the shale foundation material at the middle school was analyzed by X-ray diffraction and fluorescence. The shale is composed of clay (60 percent), quartz silt (30 percent), pyrite nodules (5 percent), and some calcite (less than 5 percent). The most important thing revealed by the analysis is that the shale is composed of 60 percent clay minerals and 5 percent pyrite. Raw sulfur values in the shale ranged from 2.95 to 5.47 weight-percent (Table 2), but sulfur can be bound as either a sulfate or sulfide. The high pyrite and sulfur content contribute to the formation of sulfates such as jarosite and copiapite. Numerous secondary sulfates and a minor amount of phosphate were also noted in the core descriptions and analysis.

Chemical analyses for major oxides in the shale were determined by X-ray fluorescence. Elemental concentrations are shown in Tables 2 and 3, which indicate that cores B-1 and B-2 had variable levels of calcium and iron. This implies that major oxidation has started at these locations. Chemical and mineralogical analyses of core B-3 indicate lower values of calcium in the shale there, suggesting that the chemical and mineralogical transition to sulfates has begun. Iron values were constant in core B-3 (Table 3). Chemical and mineralogical analysis of core B-4, located in the southeastern part of the site, indicates low values of calcium and iron in the shale there. This core is high in iron and sulfur, in the form of sulfate minerals (jarosite and copiapite), however, which suggests accelerated weathering and decomposition of the shale, oxidation of pyrite, and formation of sulfate. Jarosite and other sulfates are forming at the expense of pyrite. All of the bedding planes in this core had visible oxidizing, demonstrated by the presence of efflorescent sulfate minerals. All of the bedding planes and cleats in the subcrop of the school also contained efflorescent sulfate minerals (Figs. 15–17). Analysis of core B-5 showed that the uppermost section of the core contained extremely high values of calcium, which suggests the formation of calcium sulfate minerals such as jarosite or copiapite.

Clay Mineralogy. The clay mineralogy of the Huron Member of the Chattanooga Shale is primarily illitic clay (65 percent) and a mixed-layer clay of illite/montmorillonite/muscovite (20 percent), with minor chlorite and kaolinite (less than 10 percent) and undetermined components (5 percent). Illite is a nonexpanding clay mineral, but it does weather rapidly into soft, pliable clay. The mixed-layer clay contains approximately 20 percent expanding clays, based on X-ray diffraction and fluorescence, which swell when in contact with water. All five cores analyzed had a similar clay-mineral composition at the time of analysis (September 7, 2000, and July 6, 2006). Samples were stored in a controlled, standard-humidity environment at room temperature.

X-ray diffractograms (Fig. 29) for each of the five core samples look similar, showing the zones of both illite and smectite clays. Cores B-1, B-3, and B-4 also showed evidence of illite, chlorite, kaolinite, montmorillonite, and smectite.

Pyrite Analysis. Mössbauer spectroscopy indicates all pyrite in core samples had similar chemistry. Pyrite was more than 85 percent iron, except as noted. Other iron sulfides such as marcasite or pyrrhotite were not detected in large quantities (Table 4).

The weight-percent of pyritic sulfur in pyrite was also analyzed for several core samples and results suggest that pyritic sulfur content fluctuated in the cores. Most pyritic sulfur averaged about 5.26 weight-percent. Pyritic sulfur for core B-4 was 3.69 percent, which is low compared to the other samples. Percentage of iron in the mineral jarosite in core B-4 was about 5.5 percent, which was high compared to the other samples (about 2 percent). This suggests that pyrite was oxidizing more rapidly in core B-4, which is confirmed in the diffractogram (Fig. 29); jarosite is forming at the expense of pyrite in this core. This process is a critical chemical reaction; the oxidation of pyrite and subsequent growth of secondary sulfates in the shale causes crystal growth and resultant volume change (heaving/expansion) in foundation bedrocks.

Additional information on pyrite and trace elements in pyrite in east-central Kentucky is in Tuttle and others (2003). They discussed availability and mobility of many trace elements in addition to iron, calcium, and sulfur.

Sulfate Analysis. The sulfate minerals jarosite, melanterite, copiapite, gypsum, alunite, kalinite, pickeringite, and epsonite—oxidation products of pyrite—were detected visually and by X-ray diffraction (Figs. 30–31). Other minerals may also occur. Tuttle and others (2003) determined that melanterite, haliotrichite, and szomolnokite occurred in the Middle Huron at a sample site 7 mi north and east near Clay City in Powell County. The abundance of trace elements and pyrite in the shale produces many elements for the formation of various secondary sulfates. These sulfates are humidity- or water-sensitive and can change chemistry hourly. Each rainfall will remove or alter existing sulfates, promoting new crystal growth.

Cores B-1, B-3, and B-4 showed a marked difference in the sulfate content at the 15 degrees, 2-theta, zone of sulfate when identified by X-ray diffraction. The comparative diffractograms (Fig. 29) of intervals in cores B-1, B-2, B-3, and B-4 show variable activity in the sulfate region of each core, implying sulfate formation in the various sampled intervals.

Induced coupled plasma spectroscopy of the sulfate precipitate sample indicated 200 ppm each of iron, magnesium, calcium, and sulfate, all common ele-

Table 2. Major- and minor-element analysis of shale samples using X-ray diffraction. Sulfur analysis was conducted separately and represents raw sulfur in shale. SO_3 values are from ash residue.

Sample	*SiO_2 (%)*	*Al_2O_3 (%)*	*Fe_2O_3 (%)*	*Na_2O (%)*	*MgO (%)*	*P_2O_5 (%)*	*K_2O (%)*	*CaO (%)*	*TiO_2 (%)*	*MnO (%)*	*SO_3 (%)*	*LOI (%)*	*S (Wt %)*
B1 126	52.25	15.31	6.89	0.29	1.38	0.07	4.13	0.71	0.72	0.02	0.47	16.88	5.01
B1 147	52.22	14.00	8.18	0.31	1.31	0.08	3.69	1.17	0.71	0.02	0.46	17.58	3.78
B1 59	53.46	13.75	7.17	0.31	1.30	0.09	3.79	0.84	0.70	0.02	1.19	17.19	3.90
B1 76	56.96	14.07	6.70	0.32	1.30	0.08	3.89	0.50	0.71	0.02	0.83	14.59	5.47
B2 25	57.83	16.29	7.78	0.34	1.56	0.09	4.39	1.24	0.81	0.02	1.23	8.39	4.05
B2 36	53.63	15.67	7.76	0.31	1.47	0.07	4.16	0.88	0.73	0.02	0.76	14.29	4.60
B3 20	55.36	17.22	6.44	0.30	1.36	0.07	4.37	0.16	0.74	0.02	0.20	13.64	3.45
B3 36	55.31	16.49	6.59	0.31	1.49	0.07	4.51	0.63	0.76	0.02	0.68	12.95	3.65
B4 19	58.01	15.10	5.49	0.30	1.12	0.07	4.02	0.11	0.77	0.01	0.05	14.73	3.58
B4 30	56.50	15.27	5.65	0.31	1.16	0.06	4.04	0.11	0.77	0.01	0.32	15.62	3.29
B5 10	52.13	13.97	6.00	0.31	1.45	0.07	3.82	3.55	0.74	0.03	2.76	15.04	3.57
B5 17	57.16	16.87	5.80	0.32	1.55	0.07	4.65	0.79	0.76	0.02	0.82	10.93	2.95
B5 21	52.38	14.52	7.53	0.32	1.38	0.09	3.88	0.85	0.74	0.02	0.80	17.37	4.85

Sample	*Ba (ppm)*	*Co (ppm)*	*Cr (ppm)*	*Cu (ppm)*	*La (ppm)*	*Mo (ppm)*	*Nb (ppm)*	*Ni (ppm)*	*Pb (ppm)*	*Rb (ppm)*	*Sr (ppm)*	*Th (ppm)*	*U (ppm)*	*V (ppm)*	*Y (ppm)*	*Zn (ppm)*	*Zr (ppm)*
B1 126	440	25	71	39	38	77	14	74	22	151	98	11	22	123	29	50	159
B1 147	413	28	81	44	36	84	13	72	22	119	77	10	24	100	28	41	145
B1 59	443	27	73	45	35	112	13	111	19	131	84	11	37	121	29	83	150
B1 76	474	25	71	47	36	101	14	100	18	142	82	11	35	130	29	37	156
B2 25	430	25	70	43	37	89	14	69	20	142	97	11	25	119	29	75	169
B2 36	414	27	68	32	32	61	15	40	19	134	72	11	17	105	28	49	153
B3 20	468	23	71	34	37	60	15	86	20	164	105	12	22	124	31	56	160
B3 36	454	22	71	40	36	66	14	49	22	166	98	12	20	124	29	49	155
B4 19	405	23	72	44	28	65	17	63	20	157	62	12	35	126	29	252	183
B4 30	406	22	70	44	32	71	16	64	20	161	74	12	27	110	29	294	194
B5 10	393	20	68	42	35	63	15	51	18	138	98	11	20	112	29	76	179
B5 17	480	19	71	36	35	56	14	52	21	177	112	12	19	116	29	50	154
B5 21	418	27	67	44	34	86	14	75	23	132	91	11	23	109	29	46	152

Table 3. Calculated elemental analysis determined from major oxides in shale samples from Estill County Middle School. Range of Ca and Fe analysis for cores B-1 through B-4 is from two X-ray fluorescence analyses in 2000 and 2006, and shows variability as sulfates form.

Sample (Footage)	*Al*	*Si*	*K*	*Ca*	*Fe*
SDO 1 (standard)	7.4	21.1	2.8	0.74	5.5
B-1 (5 ft, 9 in.–6 ft, 0 in.)	8.4	25.2	3.2	0.52–0.51	4.0–4.9
B-1 (7 ft, 6 in.–6 ft, 0 in.)	8.2	25.2	3.1	0.99–0.84	4.0–5.8
B-1 (12 ft, 6 in.–12 ft, 9 in.)	8.8	24.4	3.2	0.65–0.60	4.2–5.1
B-1 (14 ft, 7 in.–14 ft, 10 in.)	8.8	23.9	3.2	0.59–0.35	4.1–4.7
B-2 (2 ft, 5 in.–2 ft, 11 in.)	8.9	24.5	3.4	0.72–0.89	4.1–5.5
B-2 (3 ft, 6 in.–3 ft, 8 in.)	8.6	22.4	3.2	0.61–0.63	5.3–5.5
B-3 (2 ft, 0 in.–2 ft, 6 in.)	9.1	23.8	3.3	0.29–0.11	4.0–4.6
B-3 (3 ft, 6 in.–3 ft, 9 in.)	9.2	23.6	3.2	0.16–0.45	4.1–4.7
B-4 (1 ft, 9 in.–2 ft, 1 in.)	8.8	25.7	3.1	0.04–0.08	3.1–4.0
B-4 (3 ft, 0 in.–3 ft, 4 in.)	9.1	25.4	3.3	0.04–0.08	3.2–4.1
B-5 (1 ft, 0 in.)	7.3	24.4	3.2	2.5	4.2
B-5 (1 ft, 7 in.)	8.9	26.7	3.9	0.56	4.1
B-5 (2 ft, 1 in.)	7.7	24.5	3.2	0.61	5.3

ments in secondary sulfates. Cleat joints in the outcrop, subcrop, and bedding planes in the core samples also provide visual evidence of rapid oxidation to sulfates, suggesting that pyrite occurs along these surfaces and is easily weathered. Oxidation of pyrite is a chemical reaction that results in crystal growth of various sulfates, expansion and volume change at or near the site of the pyrite, and release of mild sulfuric acid and iron. The reaction is:

$$\underset{\text{Pyrite}}{2FeS_2} + \underset{\text{Water}}{3H_2O} + \underset{\text{Lime}}{CaCO_3} + 6O_2 \rightarrow \underset{\text{Sulfate}}{FeCa(SO_4)} + \underset{\text{Sulfuric Acid}}{3H_2SO_4} + CO_2 + \underset{\text{Iron}}{Fe}.$$

The crystal structure of sulfates is larger than that of pyrite, and this increase in volume can be substantial, resulting in heaving and other movement of structures. The volume change from pyrite to sulfate can be on the order of 10 to 100 times, depending on the amount of sulfate that is forming. The expansion can, and does, exert pressure from crystal growth, and is the major cause of floor heaving and expansion in all structures described in this report. These sulfates grow where the shale and pyrite have been exposed to weathering and water. The drain tile in the retaining wall of the middle school has sulfate mineral precipitates (Figs. 30–31). Other foundation drain tiles that are buried around the school are likely filled with these minerals, and are therefore not functioning as designed. Excavated shale was apparently used in the southeastern part of the building as foundation fill. Excavated shale weathers extremely rapidly and could lead to significant subsidence.

Hydrogeochemistry

Sulfides are easily oxidized when exposed to the atmosphere or water, as occurs in the study area. High sulfate values and low pH in White Oak Creek (Table 5) suggest a vibrant chemical reaction with the pyrite (Table 4). As the surface water reacts with the exposed pyrite, the pH of the surface water decreases and further reacts with pyrite, causing the pyrite to oxidize rapidly. The pH of the water in the tributary of White Oak Creek (Masters Creek) was approximately 1.5. This is very low, indicative of the amount of chemical reaction occurring between the pyrite, shale, and groundwater. Lower pH can increase the speed of oxidation. Analysis of a water sample from the creek behind the high school confirms high levels of sulfate (800 ppm) in the water system. Tuttle and others (2003) described other streams near Clay City as having a pH of 7 to 8, considered a normal pH. The low pH in White Oak Creek is probably the result of extensive excavation at the school for playgrounds and ball fields, which has exposed much pyrite to weathering and oxidation.

Summary

All the structures examined in this investigation that were founded in the pyrite zones of the Chattanooga Shale had extreme foundation problems. The swelling in the pavement of Ky. 449 is related to expanding clays in the Crab Orchard Formation, and any effects from the black shale appear to be minor at this location.

A contributing factor is that many of the structures were built on Chattanooga Shale fill material, which weathers rapidly, and causes the pyrite to oxidize

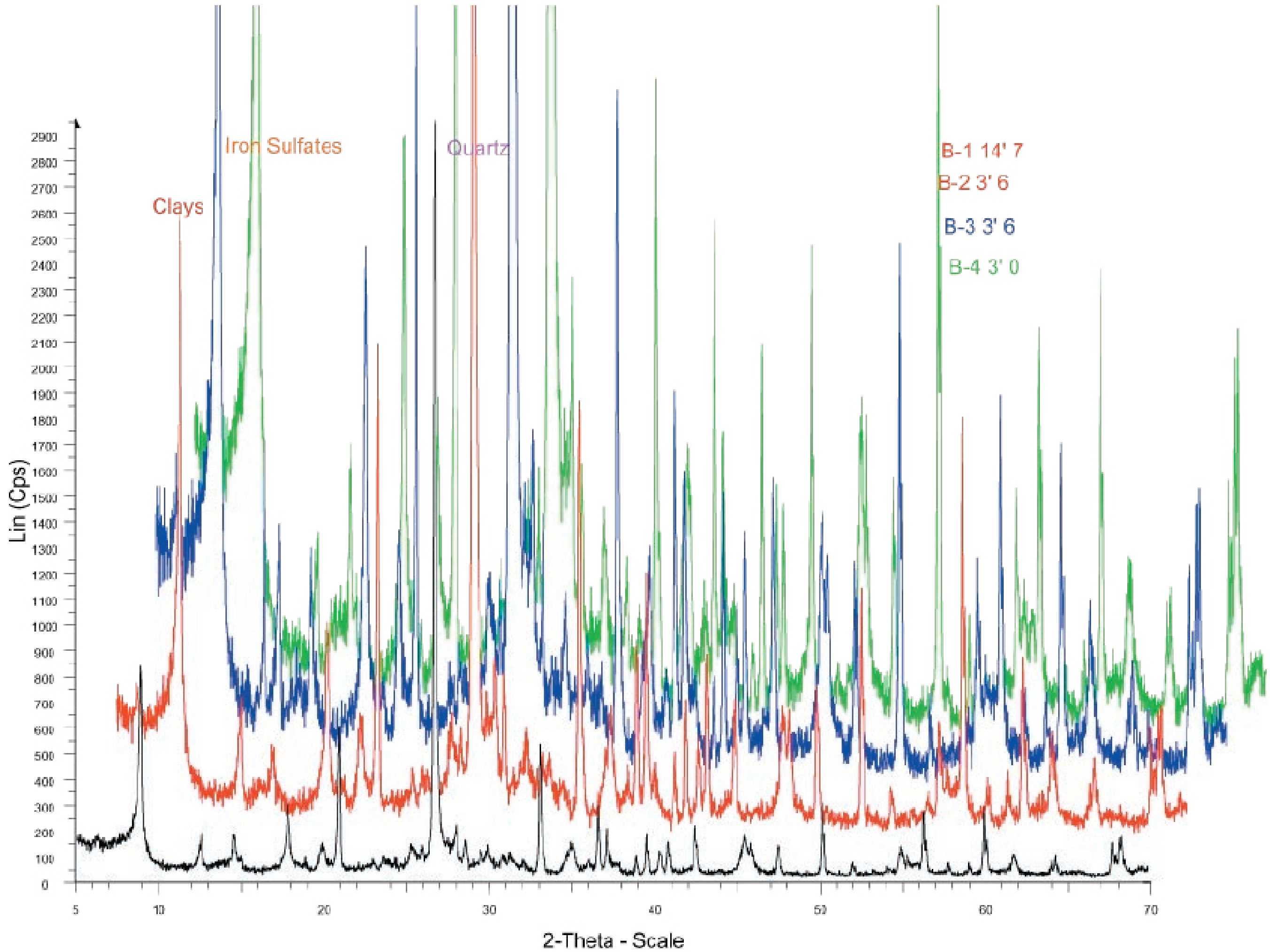

Figure 29. Diffractograms of cores in the study area show regions of clay minerals and sulfate activity between 10-20 2-theta. Data is projected in a three-dimensional view.

to sulfates very rapidly. The primary cause of these structural failures is pyrite oxidation, also called pyrite swelling, which creates secondary sulfate growth beneath the slab foundation, causing floor heaving, wall and flooring cracking, and structural instability. This pyrite oxidation leads to crystal growth that can crack concrete and lift foundations. Normally, the load-bearing walls in these structures exert enough load or pressure on the expanding pyrite to balance the strength of crystal growth within the sulfate in the shale, so that the load-bearing walls do not move, but the adjacent slab flooring does move.

The stratigraphic column in Figure 12 shows the elevation, location, and approximate stratigraphic position of the buildings and roads inspected during this investigation. Figures 1 and 12 show that the entire Chattanooga Shale contains pyrite. Therefore, caution should be used when building in the North Irvine area. Geochemical trend examples (Negus-de Wys, 1981) demonstrate that high pyrite content in the shale can occur in other areas of the state and suggest that some of these anomalous concentrations are occurring in North Irvine.

Excavation and weathering of pyrite-bearing shale make it unstable for fill material or as a foundation for load-bearing structures or highway construction. Water draining toward the construction sites may contribute to pyrite oxidation and formation of mild sulfuric acid.

Sulfates erode rapidly on the outcrop, whereas they are confined beneath the school foundation. Under the confined conditions, oxidation creates large-volume growth of sulfate crystals and subsequent heaving of

Table 4. Mössbauer spectroscopic analysis for iron and weight-percent sulfur in pyrite.

Sample	*Mineral (%)*	*Total Iron (Wt. %)*	*Pyritic Sulfur*
B-11	Pyrite	89	5.11
	Fe^{2+}/clay	11	
B-12	Pyrite	90	5.29
	Fe^{2+}/clay	10	
B-13	Pyrite	87	4.9
	Fe^{2+}/clay	11	
	Jarosite	2	
B-14	Pyrite	86.5	5.74
	Fe^{2+}/clay	11	
	Jarosite	2.5	
B-41	Pyrite	86.5	3.7
	Fe^{2+}/clay	8	
	Jarosite	5.5	
B-42	Pyrite	85.5	3.69
	Fe^{2+}/clay	9	
	Jarosite	5.5	

floors. A minor contributing factor to the structural problems is the presence of expandable clays in both the Cleveland and Huron Members, which could enhance any floor heaving if the clays are exposed to water. Another factor is that mild acid reacts with concrete sidewalks or limestone aggregate fill and accelerates dissolution and weathering, creating large voids in the outcrop and beneath the foundation.

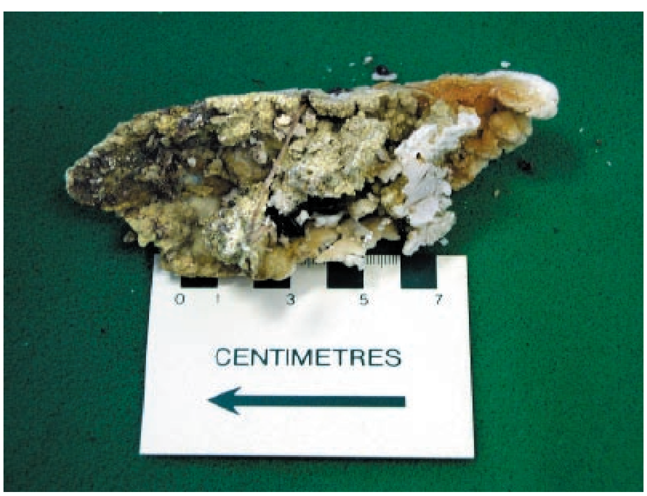

Figure 30. Secondary sulfates copiapite and melanterite derived from retaining-wall drain tiles at rear of middle school.

Causes of Foundation Failure

1. Oxidation of pyrite and growth of secondary sulfates in the shale is the primary cause of foundation problems in this part of Estill County. Pyrite oxidation leads to crystal growth and resultant volume change of crystals, creating heaving/expansion of the concrete-slab foundation and retaining walls. The oxidation of pyrite and formation of sulfates also releases a mild sulfuric acid into the creeks and tributaries. This acidic creek water is a contributing factor to the foundation problems.
2. The shale degrades into various clay and sulfate minerals and has a lack of shear strength when subjected to loads. The behavior of the weathered clay minerals in the shale makes the shale very unstable. The shale moves through compression and expansion, which may be the major problem with structural stability at the school. There may be a lens of smectite or expanding clays in the shale. When this clay comes into contact with water it will also expand and heave the foundation; when the shale dries out, the site will then collapse. This would be a perpetual problem, but based on our analysis of the clay minerals in the shale, the smectite problem is minor compared to the sulfates.
3. Parts of the middle school and factory appear to be constructed on shale fill, which weathers more rapidly than shale bedrock. The floor of the factory and the southeastern corner of the school therefore have a good potential for heaving. The factory and school location and surface grade around the school allow for significant amounts of water to saturate the shale, causing these problems.

Figure 31. Evidence of heaving by growth of secondary sulfate copiapite in the Chattanooga Shale.

Table 5. Analysis by ICAP of water collected from Masters Creek south of the high school next to the running track. Note the low pH and high sulfate, calcium, and sulfur content.

Element	*Cl*	*Mg*	*NO_3*	*K*	*SO_4*	*Si*	*Ca*	*Fe*	*Na*	*S*	*pH*
Result (ppm)	5	35	0.3	11	800	4	220	80	8	240	1.5

Recommendations

Preconstruction Prevention

1. Avoid construction and excavation in the pyrite zone of the Chattanooga Shale. Avoid using Chattanooga Shale aggregate as construction fill. Conduct minimal excavation into the shale to reduce pyrite oxidation.
2. Keep water away from the foundation, preferably through the barrier method. Drainage ditches or drain tile can still accumulate sulfates from weathered shale material and cause heaving. Drainage ditches and tile did not solve the middle school problem.

Remediation Solutions

1. Remove foundation material and fill, and replace them with a barrier impermeable to moisture. Build new subfloor bearing walls or piers, and refill with nonshale aggregate.
2. Add micropilings or specialty grouts to the Boyle Dolomite, which underlies the shale (probably less than 60 ft deep in this area). This might stabilize the foundation by transferring loads to formations with a higher bearing capacity.
3. Another remedy would be treating the foundational materials under distress. A suite of balanced stabilizing grout slurry could be injected to remove sulfates and "tighten" the formation to residual permeability and shear strength values.
4. Applying lime would raise the pH of the surface and near-surface groundwater and would act as an acid-reducing additive, which might slow or prevent additional pyrite oxidation. This would be similar to spreading lime across fields. Bryant and others (2003) cautioned against using any lime or agricultural lime, however, since introducing additional calcium in unstable soils might stimulate other sulfates to form.

A comprehensive geochemical and geotechnical investigation of the shale should be conducted prior to completing any remediation. The same investigations should be completed prior to planning and construction of future projects.

Future Work

Although the foundation problems analyzed were local to Estill County, the Chattanooga Shale crops out over a wide area of eastern and west-central Kentucky. Pyrite zones in the shale could induce foundation failures in other areas as well. Adequate preconstruction geologic investigation and using construction practices that follow the geologic recommendations are essential when foundations are made in the Chattanooga Shale, particularly in pyrite zones. The problems encountered in this study suggest that the extensive excavation of the building foundations or roads near the pyrite zone in the shale predisposed the pyrite to oxidize. Avoiding these zones may aid in foundation stability because remediation techniques are expensive, disruptive, and time-consuming.

Although foundation problems in other areas of the state could occur in the Chattanooga Shale, this report examined only the foundation problems near North Irvine. Similarly, private homes and residences were not examined in this study, but foundation problems would be possible there also.

Additional statewide detailed mineral and lithostratigraphic investigations of the Chattanooga Shale would assist in understanding the larger geographic extent and potential for this type of problem. Determination of pyrite geochemical trends in the outcrop belt would aid in sound engineering and construction practices for future planning and development and reduce the need for costly repairs and maintenance.

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References Cited

Beckham, T.L., and Hopkins, T.C., 2005, Swelling pavements: Ky. 499, Estill County, Kentucky: University of Kentucky, Kentucky Transportation Center, Report KTC-05-01SPR270-03-11, 14 p.

Bryant, L., Mauldon, M., and Mitchell, J., 2003, Geotechnical problems with pyritic rock and soil: Virginia Polytechnic Institute and State University, Center for Geotechnical Practice and Research, Charles E. Via Department of Civil Engineering, 88 p.

Hamilton-Smith, T., 1993, Gas exploration in the Devonian shales of Kentucky: Kentucky Geological Survey, ser. 11, Bulletin 4, 35 p.

Hawkins, S., and Rimmer, S.M., 2002, Pyrite framboid size and size distribution in marine black shales: A case study from the Devonian-Mississippian of central Kentucky [abs.]: Geological Society of America North-Central and Southeastern Section annual meetings, gsa.confex.com/gsa/2002NC/finalprogram/abstract_33902.htm [accessed 5/4/2007].

Hoge, H.P., Wigley, P.B., and Shawe, F.R., 1976, Geologic map of the Irvine quadrangle, Estill County, Kentucky: U.S. Geological Survey Geologic Quadrangle Map GQ-1285, scale 1:24,000.

Hosterman, J.W., and Whitlow, S.I., 1983, Clay mineralogy of Devonian shales in the Appalachian Basin: U.S. Geological Survey Professional Paper 1298, 31 p.

McDowell, R.C., 1983, Stratigraphy of the Silurian outcrop belt on the east side of the Cincinnati Arch in Kentucky with revisions in nomenclature: U.S. Geological Survey Professional Paper 1151-F, 27 p.

Morris, L.G., and Curl, D.C., 2000, Spatial database of the Irvine quadrangle, Estill County, Kentucky: Kentucky Geological Survey, ser. 12, Digitally Vectorized Geologic Quadrangle Data DVGQ-1285. Adapted from Hoge, H.P., Wigley, P.B., and Shawe, F.R., 1976, Geologic map of the Irvine quadrangle, Estill County, Kentucky: U.S. Geological Survey Geologic Quadrangle Map GQ-1285, scale 1:24,000.

Negus-de Wys, J., 1981, Strataspecific geochemical trend maps for eastern Kentucky: U.S. Department of Energy, Morgantown Energy Technology Center, DOE/ET/12138-1374, 169 p.

Pryor, W.A., Maynard, J.B., Potter, P.E., Kepferle, R.C., and Kiefer, J., 1981, Energy resources of the Devonian-Mississippian shales of eastern Kentucky (guidebook and roadlog, annual field conference of the Geological Society of Kentucky): Kentucky Geological Survey, ser. 11, 44 p.

Rimmer, S.M., and Hawkins, S., 2006, Terrestrial organic matter in Devonian marine black shales: Implications for organic carbon accumulation, terrestrial ecosystems, and paleo-atmospheric oxygen levels [abs.]: Geological Society of America North-Central Section annual meeting, gsa.confex.com/gsa/2006NC/final program/abstract_103642.htm [accessed 5/4/2007].

Rimmer, S.M., Thompson, J., Goodnight, S., and Hawkins, S., 2001, Organic matter accumulation in Devonian-Mississippian black shales, east-central Kentucky [abs.]: Geological Society of America annual meeting, gsa/confex.com/gsa/2001AM/finalprogram/abstract_27900.htm [accessed 5/4/2007].

Swager, D.R., 1978, Stratigraphy of the Upper Devonian–Lower Mississippian shale sequence in the eastern Kentucky outcrop belt: Lexington, University of Kentucky, master's thesis, 116 p.

Tuttle, M., Breit, G.N., and Goldhaber, M.B., 2003, Geochemical data from the Chattanooga (Ohio) Shale, Kentucky: A study in metal mobility during weathering of black shales: U.S. Geological Survey Open-File Report 03-207, 57 p.