ON THE ORIGIN AND SIGNIFICANCE OF PYRITE SPHERES IN DEVONIAN BLACK SHALES OF NORTH AMERICA

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ABSTRACT: **Devonian black shales deposited on the North American craton contain abundant *Tasmanites* cysts that are typically preserved as flattened circular discs on bedding planes. Work by the present authors shows that cysts can be preserved as pyrite-infill casts that are expressed as sand-size whole and geopetal half-spheres of pyrite. At the bases of thin black shale layers these occur *in situ* at many stratigraphic levels in the distal prodelta facies of the Catskill Delta complex of New York, as well as in laterally equivalent black shales in Tennessee and Kentucky. Reworked pyrite casts, usually dominated by whole spheres, form lenticular lag accumulations and hydraulic placers, together with plant debris and phosphatic particles (bone debris, conodonts).**

An earlier model for the formation of pyrite spheres in gas bubbles is rejected in favor of formation within uncompressed *Tasmanites* cysts. Direct observation of cyst cuticle in association with pyrite spheres suggests that localized bacterial sulfate reduction in *Tasmanites* interior voids led to formation of localized pyrite deposition, in a manner similar to that described from certain ammonoid chamber settings. Cyst fill commenced with formation of framboidal pyrite, followed by later diagenetic pyrite cementation between framboids. These fills show geopetal features and appear to have formed within the redox zone below the sediment–water interface.

Although described here from the Upper Devonian, comparable pyrite textures are also known from Proterozoic, Cambrian, Ordovician, and Silurian sediments. They probably occur throughout the sedimentary record, and in mudstone successions they may prove to be an important source of sand-size grains in areas far removed from the basin margins. As such they may be important for detection of erosive events and strong bottom currents, and provide valuable information about the depositional history of mudstone successions.

INTRODUCTION

Devonian black shales contain a wide variety of diagenetic pyrite morphologies, including disseminated fine crystalline pyrite, framboids, concretions, and sand-size pyritic spheres. The latter, unusual because of their spherical shape and large size, were first described by Baird and Lash (1990) and Baird and Brett (1991) from Devonian black shales of the northeastern U.S. Baird and Brett (1991) suggested two possible diagenetic modes of formation for pyrite spheres: infill of gas bubbles within the sediment, and infill of *Tasmanites* cysts. The question of the origin of pyrite spheres was not resolved.

We present here conclusive evidence that these pyrite spheres formed within *Tasmanites* cysts during early diagenesis, and in addition explore the shape spectrum of pyrite-filled cysts. Pyritized burrow tubes, pyritized fecal pellets, small reworked pyrite nodules, and pyrite ooids are also present in lag deposits (Schieber 1998), but are not discussed in this contribution.

The significance of these pyrite spheres lies in the fact that they constitute a sand-size population of sedimentary particles that forms far offshore in shale successions, and that they have implications regarding hydrodynamics, energy conditions, and oxygenation of the water column. For example, the fact that iron was able to migrate through the sediment to accumulate within cysts implies, somewhat paradoxically, that the overlying water column must have been oxygenated (Brett and Allison 1998). The concentration of these grains into lag deposits of several centimeters thickness implies reworking and winnowing of a considerable thickness of previously deposited carbonaceous muds and substantial current velocities to accomplish their erosion (Schieber 1998). Cross-bedding within these lags further attests to strong bottom currents and may provide paleocurrent information. In absence of these *in situ* grains, the conditions implied above would most likely be missed, especially in offshore muds where the grain sizes to form readily interpretable bedforms are typically lacking. Thus, in mudstone successions, pyrite spheres and pyrite sphere lags can provide a wealth of information about depositional conditions.

A related question is whether these Devonian pyrite spheres represent an isolated occurrence or whether the conditions of their formation extend through the sedimentary record to the present. Reasons to believe that the latter is the case are (1) the fact that *Tasmanites* ranges in age from the Precambrian to the Holocene (Tappan 1980), and (2) the observation that texturally comparable pyrite spheres occur in sediments of various ages. Also, candidates for modern analogs have been described from recent sediments (Bertolin et al. 1995; Bailey and Blackson 1984; Bailey, personal communication 1998). We believe therefore that the described process of pyrite sphere formation is uniformitarian, and will eventually be identified in modern basins.

GEOLOGIC SETTING

This study is based on petrographic examination of black shale samples from the Upper Devonian Chattanooga Shale (central Tennessee and southern Kentucky), and from various Givetian through Fammenian localities in New York (Fig. 1). These shales were deposited in the Appalachian and Illinois basins, and their exposed thickness varies from less than 10 m in central Tennessee to hundreds of meters of aggregate thickness in New York (Rickard 1981). Although these shales commonly are interpreted as having accumulated in stagnant and comparatively deep water (e.g., Potter et al. 1982), recognition of submarine erosion surfaces, hummocky cross-stratified (HCS) silt and sand beds, mud tempestites, and widespread bone beds (Conkin and Conkin 1980) suggests that at least intermittently the water was comparatively shallow (Schieber 1994, 1998).

The black shales in question are the distal facies of a westward-thinning clastic wedge. In its thinnest and most distal part, in central Tennessee and south-central Kentucky, the average accumulation rate of these shales was on the order of 10^{-3} mm/yr. This figure is based on thickness of stratigraphic sections, conodont data (Ettensohn et al. 1989), and age calibrations of Devonian conodont zones (Harland et al. 1990; Fordham 1992).

Throughout, these black shales contain sporelike microfossils that commonly are referred to as *Tasmanites* (e.g., Winslow 1962). *Tasmanites* probably represents the cyst stage (phycoma) of fossil algae with affinities to the modern planktonic green alga phylum Prasinophyta (Tappan 1980). Prasinophytes can take on two distinct appearances during their life cycle, changing from motile quadriflagellate cells to cysts in which new motile cells develop (Tappan 1980). Whereas the motile cell has no skeletal mineralized structures and so has little chance to become fossilized, the cyst walls consist of a complex ''lipoid'' substance that resists chemical breakdown (Tappan 1980). What is found in the geologic record are probably cysts that settled to the bottom after their contained motile cells were released (Tappan 1980).

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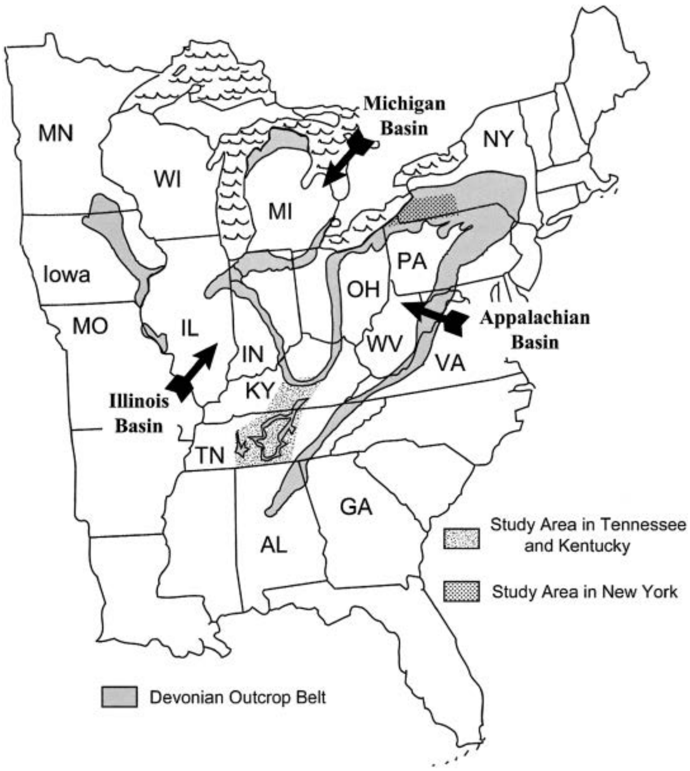

FIG. 1.—Location map that shows extent of the outcrop area of Devonian black shales (gray shading) in the eastern U.S. Study areas in New York and Tennessee/Kentucky are marked with stipple pattern and mezzotint pattern, respectively.

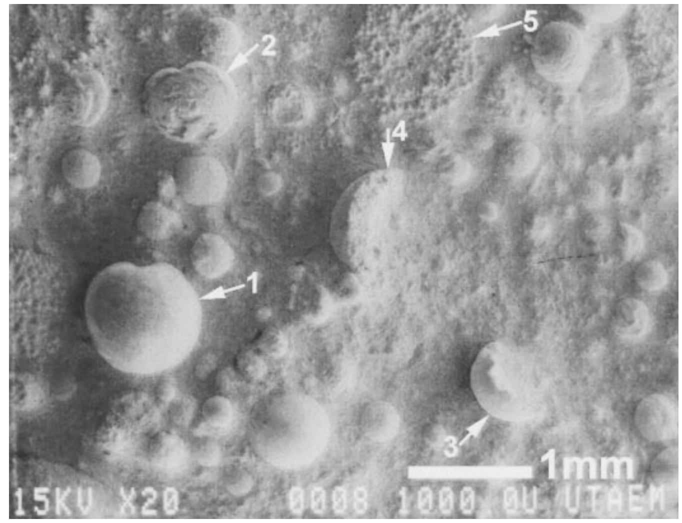

FIG. 2.—SEM photo of pyrite spheres and related grains on bedding plane (lag deposit). Note that pyrite grains range in size from almost 1 mm to approximately 0.1 mm. Not all grains are perfectly spherical (arrows 1 and 2), and a number of grains are actually half-spheres (arrows 3, 4, 5). Arrow 5 points to a half-sphere whose flat side is oriented towards the viewer (note bumpy surface). Note that half-spheres are randomly oriented.

Tasmanites and similar forms (Family Tasmanitaceae) are found in deposits from the Precambrian to the Holocene (Tappan 1980) and are spherical prior to compaction. Winslow (1962) recognized several genera and a number of different species of *Tasmanites* in Upper Devonian rocks of eastern North America, ranging from 0.05 to 0.81 mm in diameter.

Stratigraphic Distribution of Pyrite Spheres

Materials examined from Tennessee (Fig. 1) were found on various erosion surfaces in the Dowelltown and Gassaway members of the Chattanooga Shale (Schieber 1998). Pyrite spheres from Kentucky (Fig. 1) were recovered from lag deposits at the base of the Camp Run and Clegg Creek members of the New Albany Shale (Ettensohn et al. 1989). Samples from New York (Fig. 1) come mostly from the Upper Devonian (Fammenian) Gowanda Shale Member of the Canadaway Formation. Additional New York material was obtained from strata comprising the uppermost part of the Hanover Shale Member of the Java Formation and superjacent beds comprising the base of the Dunkirk Shale Member of the Canadaway Formation (Baird and Brett 1991). One example of hydraulically concentrated pyrite spheres occurs in uppermost Givetian deposits at the base of a siltstone bed near the base of the Sherburne Member of the Genesee Formation at Tinkers Falls Ravine near Tully, Onondaga County, New York.

In the southeastern U.S. pyrite spheres are typically found on erosion surfaces within black shales (Schieber 1998). In the northeastern U.S., however, they typically occur in thinly interlayered black shale and gray-green mudstone layers (''zebra facies'') that constitute the distal prodelta facies of the Catskill Delta Complex (Baird and Brett 1991). Although they occur throughout Upper Devonian strata of the eastern U.S., they appear to be most common in carbonaceous mudstones of Fammenian age.

METHODS

Textural features of pyrite spheres and lag deposits were examined by binocular and petrographic microscope (transmitted and reflected light) in a collection of hand specimens and polished thin sections. A high-resolution digital camera was used to produce the images used in this study. In order to enhance pyrite textures in thin sections, some sections were etched with concentrated HNO_3 for about 30 seconds. Polished as well as broken portions of thin section blocks were also examined by scanning electron microscope (secondary electron images). Where needed, an attached energy dispersive X-ray analyzer was used to verify presence of other minerals. Several of these samples were etched with HNO_3 for variable lengths of time (30 seconds to 2 minutes), in order to study textures that emerged with increasing depth of etching. After etching, samples were gently rinsed with distilled water to remove residue and surface coatings prior to observation. Because the observed pyrite textures (framboids, blocky cement) are well documented in the literature (O'Brien and Slatt 1990), and because the etching enhances only textures that are already present in the unetched sections, we are confident that none of the described features are etching artifacts.

OBSERVATIONS

Spherical pyrite grains in the Chattanooga and New Albany Shale occur in two principal modes: (1) within a black shale matrix, and (2) within lag deposits above erosion surfaces (Schieber 1998). In both cases pyrite grains generally range in size from 0.1 to 0.9 mm in diameter. Shale-enclosed spheres, however, have organic ''skins'' that are of amber color in thin section (Schieber 1996) and behave isotropically under crossed polarizers, whereas pyrite grains in lags generally lack this organic ''skin''. When present, these ''skins'' are barely recognizable in reflected light because they do not provide much contrast, but they are readily visible in transmitted light, where they stand out because of their amber-brown color.

In New York, pyrite spheres occur at numerous levels within a distinctive thinly interlayered succession of alternating green-gray and black shale beds that is also characterized by occasional thin siltstone and fine sandstone layers. This facies is characteristic of the uppermost Hanover Member to basal Dunkirk Member interval, as well as of the upper part of the

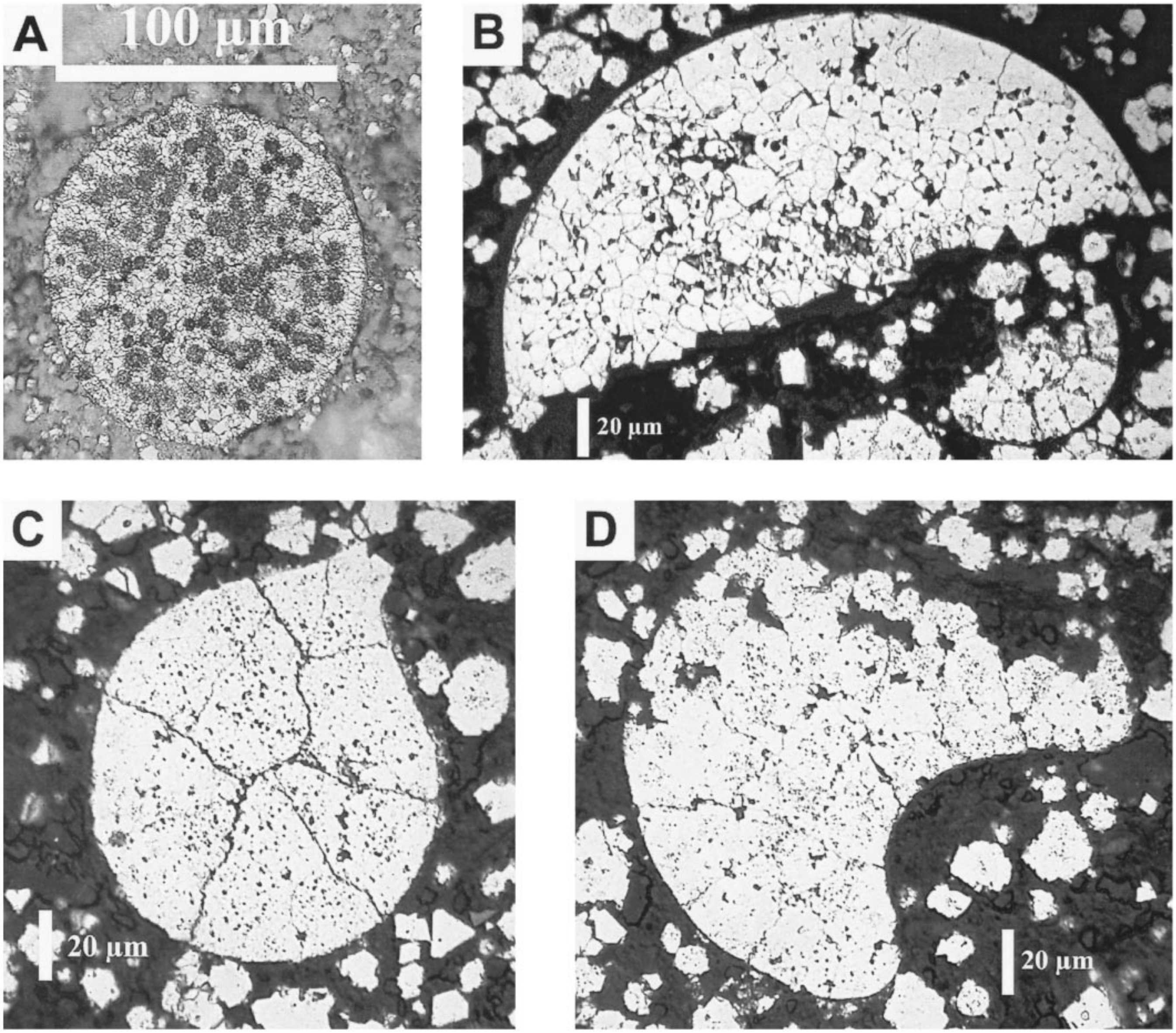

FIG. 3.—**A)** Photomicrograph (reflected light) of polished thin-section view of perfectly spherical pyrite sphere. Smaller, round spots within sphere are framboids that have been revealed by etching with HNO_3. The cement between framboids is coarser crystalline and more resistant to etching. The framboids are mostly of the same size throughout, but sectioning exposes variable portions of framboids and produces an apparent larger range of framboid sizes. Photo is from a lag deposit. **B)** Photomicrograph (reflected light) of polished thin-section view of pyrite half-spheres in a lag deposit. Note variable orientation and size of half-spheres. Sample has not been etched. The small pits between pyrite crystals were plucked out during polishing. **C)** Photomicrograph (reflected light) of polished thin-section view of irregular but still rounded pyrite grain in a lag deposit. This grain was not etched, and thus framboids are not visible. **D)** Photomicrograph (reflected light) of polished thin-section view of irregular pyrite grain. Upper part of grain has irregular outline, probably because cementation did not go to completion, and cyst wall collapsed during compaction.

Gowanda Member. Black–gray–green shale couplets repeat at intervals of a few centimeters to decimeters, imparting a striking banded appearance on fresh surfaces. Contacts between light and dark layers are often sharp, although the upper contacts of the black layers are sometimes diffuse and irregular owing to bioturbation. Baird and Lash (1990) and Baird and Brett (1991) coined the term ''zebra facies'' to denote this distinctly banded type of deposit that characterizes many intervals within the dysoxic to anoxic, slope to basin facies transition within the Upper Devonian succession.

Because they approximate perfect spheres, spherical pyrite grains are very conspicuous when seen on bedding planes (Fig. 2) or in thin sections (Fig. 3A). Nonetheless, when examined in detail, many samples show a large proportion of grains that are not perfectly spherical (Fig. 3B, C, D). Many of these are half-spheres (Fig. 3B), and are found both in shale matrix and in lag deposits. In addition, it is also possible to observe hollow spheres (Fig. 4A) and apparent hollow spheres that have collapsed (Fig. 4B).

In the Chattanooga and New Albany Shale, pyritic half-spheres in shale matrix are typically oriented with the convex hemisphere oriented downward and the flat face upward. In lag deposits, however, half-spheres are oriented randomly. Similarly, in the ''zebra facies'' of New York, *in situ* half spheres are consistently oriented convex down when found within a gray shale matrix. These half spheres typically occur in the uppermost 0.5 to 2.0 mm of gray shale layers below the sharp lower contacts of black shale layers (Fig. 5A). The underlying intervals within the gray shale layers usually do not contain spheres and half-spheres. As such, when a black

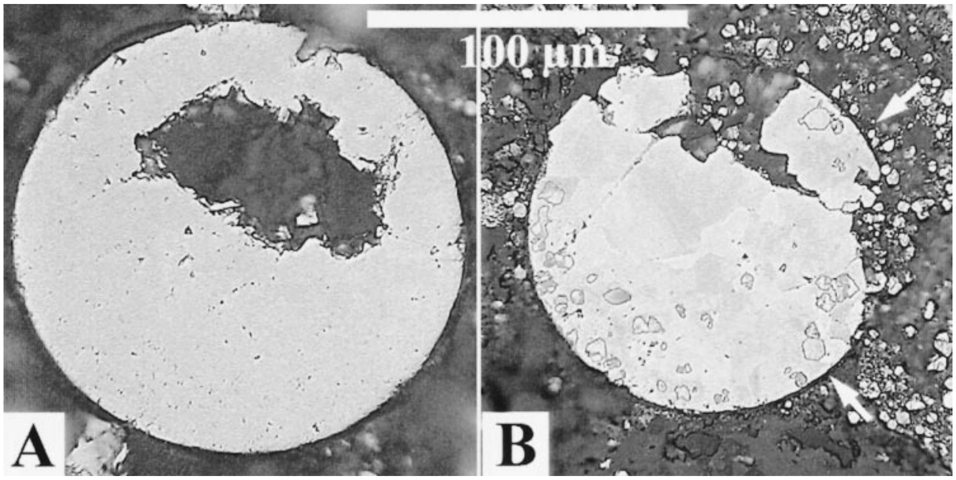

FIG. 4.—**A)** Photomicrograph (reflected light) of hollow pyrite sphere in lag deposit. The ''hollow'' can be filled with dolomite or quartz, or it may remain empty. In the latter case it may be crushed during compaction and lead to a ''collapsed'' hollow sphere. This is shown in **(B),** where the walls of the ''hollow'' (white arrows) have been broken and rotated on top of the main pyrite body. In case of a sphere with a large void, this may produce the appearance of a half-sphere.

shale layer is peeled up from the underlying gray shale layer, the parting often develops along the top of the horizon of half spheres, revealing a pavement of flattened spheres when seen from above (Fig. 5B). Alternatively, the parting may develop along the lower boundary of the half-sphere horizon, revealing a pavement of shiny ''bubbles'' when seen from below (Fig. 5C). When half spheres are observed within the basal part of overlying black shale layers, they are often randomly oriented (Fig. 2). In places, small *Planolites* traces may be found in the basal parts of these black shale layers.

Internally, pyrite spheres and related grains consist of clusters of fine-crystalline framboidal pyrite that have been cemented by a later, coarser crystalline form of pyrite (Figs. 3A, 6). Because of this cementation, framboidal pyrite is usually not observed in freshly polished sections of pyrite spheres. When thin sections are etched with HNO_3, however, they invariably reveal framboidal aggregates. The interiors of some pyrite spheres show an uneven distribution of framboids vs. pyrite cement, where framboids are concentrated in one side of a sphere, and coarser cement in the opposite side (Fig. 7A). If this occurs in shale-enclosed spheres, framboid

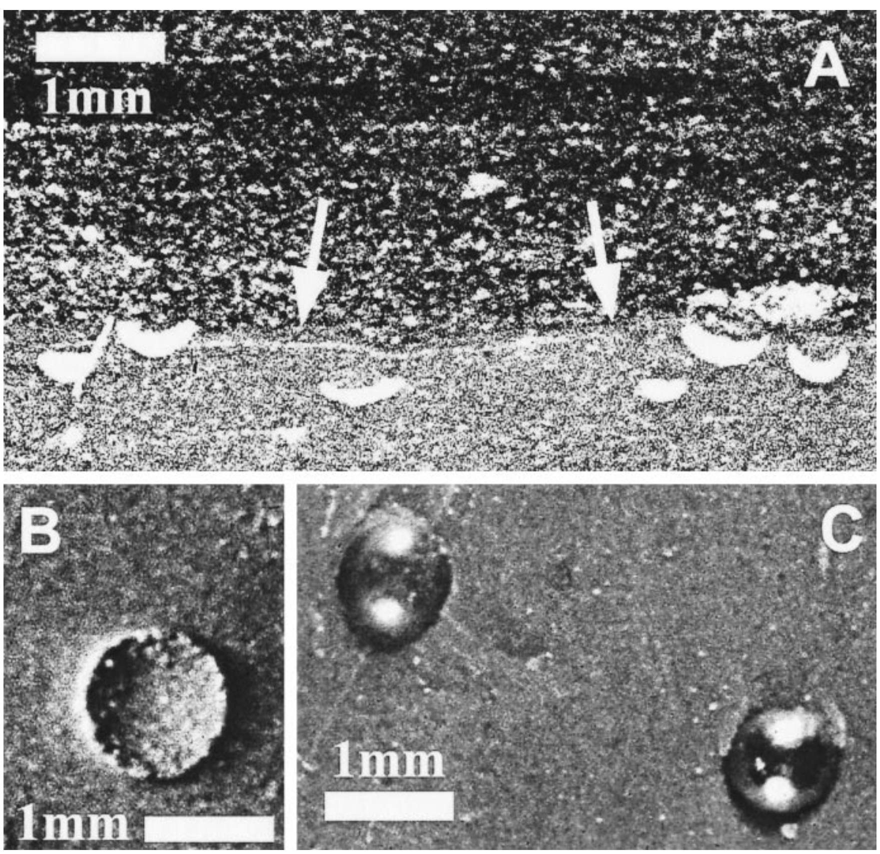

FIG. 5.—**A)** Pyrite half spheres from ''zebra'' shale facies. The contact between gray shale (bottom) and black shale (middle and upper part) is marked with arrows. The half spheres are all oriented concave down and occur close to the contact. **B)** View of a bedding plane split from above, showing flat upper surface of half sphere. **C)** view of a bedding plane split from below, showing the lower halves of shiny half spheres.

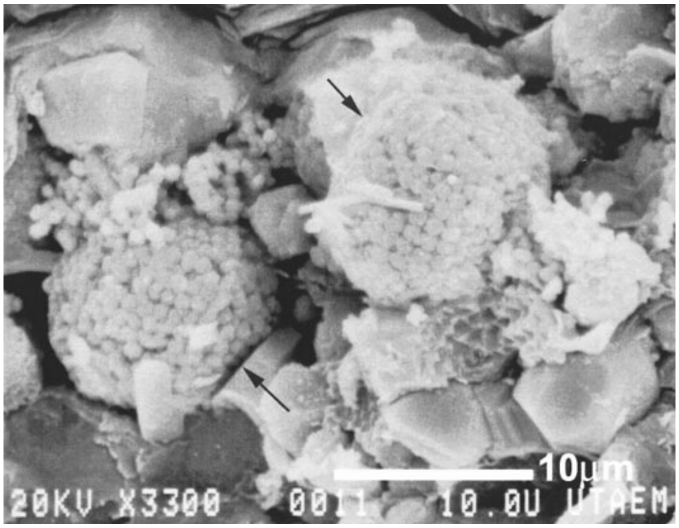

FIG. 6.—SEM photo of pyrite sphere interior, showing finely crystalline spherical framboids (arrows) that are surrounded and held together by much more coarsely crystalline pyrite cement.

enrichment is found in sphere bottoms, whereas in lag deposits the framboid-enriched portions are randomly oriented.

Although pyrite spheres in most cases have a smooth surface (Fig. 7B), they may also show surface wrinkles of the type illustrated in Fig. 7C. These wrinkles form a concentric pattern (Fig. 7C), much like parallels of latitude on a globe. In addition, this type of sphere is oblate in shape (Fig. 7D). When wrinkles are observed on shale-enclosed spheres, the plane of the wrinkles is usually parallel to bedding. In contrast, when wrinkled spheres occur in lags, the planes of wrinkling are randomly oriented (Fig. 7D). Pyrite spheres may also show a ''bumpy'' surface morphology produced by closely packed framboids (Fig. 8A). In most instances, ''bumpy'' surfaces are seen only over parts of the sphere surface (Fig. 7D).

When spheres and half-spheres in shale matrix are examined carefully, it is usually possible to detect thin organic membranes that enclose the pyrite (Fig. 8B). These membranes have previously been identified as the walls of *Tasmanites* cysts (Schieber 1996), an identification based on published descriptions of *Tasmanites* in Devonian strata by Winslow (1962) and Tappan (1980). Although in cross section the cyst walls are simply a thin cover that separates the pyrite from the surrounding sediment (Fig. 8B), and might also be interpreted as a diagenetic cover, in transmitted light they have the same color and optical properties that have been described from *Tasmanites* in other studies (e.g., Conant and Swanson 1961; Winslow 1962; Tappan 1980; O'Brien and Slatt 1990). Furthermore, when these shales are disaggregated for conodont separation, the surfaces of the organic covers of pyrite spheres can be examined microscopically, and reveal the same punctate surface textures (see Fig. 8C) as shown in illustrations of *Tasmanites* by Winslow (1962) and Tappan (1980). The great majority of spheres and half-spheres in lag deposits do not show such an organic membrane. Careful search, however, revealed that lag deposits with pyrite spheres always contain a small proportion of spheres and half-spheres that are in fact encased in an organic membrane attributable to *Tasmanites* (Fig. 8C, D). Also, in some thin sections of lag deposits deformed fragments of *Tasmanites* cysts were observed, probably the remains of cyst walls that were removed from pyrite spheres during reworking.

In the Chattanooga and New Albany shales, enrichments of pyrite spheres and half-spheres are typically found in lag deposits (Schieber 1998), where they are mixed to various proportions with quartz grains, fish bone fragments, conodonts, glauconite grains, and carbonized wood debris. Within thicker lag deposits, pyrite spheres are not randomly distributed, but instead are concentrated in discrete laminae.

In New York, thinner concentrations of pyrite spheres occur as localized patchy lags along the bases of silt- and sand-rich black shale beds. These black shale beds may grade laterally into thick siltstone–sandstone beds with sharp erosional bases. Concentrations of pyrite spheres also occur at the bases of fine sandstone beds that occur sporadically within ''zebra facies'' intervals. Typically they form density-segregated concentrations in groove and flute casts (Fig. 9) or in larger scour channel fillings where lenticular pyrite sphere concentrations (0.5 to 6.0 centimeters thick) occur in association with carbonized wood debris and cross-laminated sand (Fig. 10). In the Givetian occurrence mentioned above, complex cross-lamination is well developed within a lenticular concentration of pyrite spheres (Fig. 11). This detrital pyrite lentil, occurring at the base of a fine sandstone bed (8 to 10 cm thick), also contains carbonized wood, conodonts, and bone debris.

Although pyrite overgrowth is the predominant cement that forms between and within pyrite framboids (Figs. 3, 6, 8C, 8D), such spaces may also be filled with quartz. Although it is typically a minor constituent, in places quartz can actually form a matrix that surrounds pyrite crystals and holds them in place (Fig. 12).

Origin of Pyrite Spheres

That pyrite spheres found in shale matrix originated through pyrite precipitation in *Tasmanites* cysts is indicated by the observation that the organic, amber-colored membranes that surround these pyrite spheres have the same optical and textural properties as *Tasmanites* cysts elsewhere in these mudstones (Schieber 1996, 1998, 1999). Pyrite spheres on bedding planes and in lag deposits also show the same kind of organic membrane (Fig. 8B, C) and probably formed in the same way. Several other observations also suggest that pyrite spheres in lag deposits are of this origin.

Pyrite spheres in shale matrix and in lag concentrates, for example, are both composed of pyrite framboids that are held together by variable amounts of coarser-grained pyrite (Fig. 6, 7A, 8A, 8C, 8D). Pyrite spheres with uneven distribution of cement and framboids (Fig. 7A; ''filled'' half-spheres of Fig. 13), and pyrite half-spheres (Figs. 3B, 13) are probably of related origin. The fact that in shale matrix, pyrite spheres always show framboid enrichment at the bottom (Fig. 7A), and half-spheres are always oriented convex down (Baird and Brett 1991), is indicative of geopetal processes. Early-formed framboids settled in the bottom of the cyst cavity, and somewhat later coarser crystalline pyrite filled the rest of the void. If compression occurred before the remainder of the cyst was filled with pyrite cement, half spheres resulted (Figs. 3B, 13). The random orientation in lag deposits of half-spheres and of framboid enrichment in pyrite spheres is consistent with reworking of these grains from underlying shales.

The surface wrinkles that are observed on some spheres (Fig. 7C) from lag deposits are also suggestive of a cyst origin. A plausible explanation for these wrinkles is that they formed when an originally spherical cyst that was loosely filled with pyrite framboids underwent minor compaction (Fig. 13). Subsequent fill of the rest of the (now wrinkled) cyst with pyrite cement (Fig. 6) led to preservation of the wrinkled surface, even after the cyst wall had been removed during reworking. This model implies that these wrinkles on *in situ* spheres are a geopetal, bed-parallel, feature. Random orientation of wrinkles in lag deposits (Fig. 7D) indicates that the wrinkles formed prior to exhumation. Formation of wrinkles by compactional compression of cysts also implies that the cysts show shortening (flattening) perpendicular to the ''wrinkle parallels'', that the largest degree of wrinkling occurs on vertically oriented parts of *in situ* cysts (the ''equatorial belt''), and that the largest pressures between cyst fill and cyst wall occur in the ''polar'' regions. That this is indeed the case is illustrated in Fig. 7D. The cysts are flattened perpendicular to the ''wrinkle parallels'', the wrinkles are best developed in the ''equatorial belt'', and in the ''po-

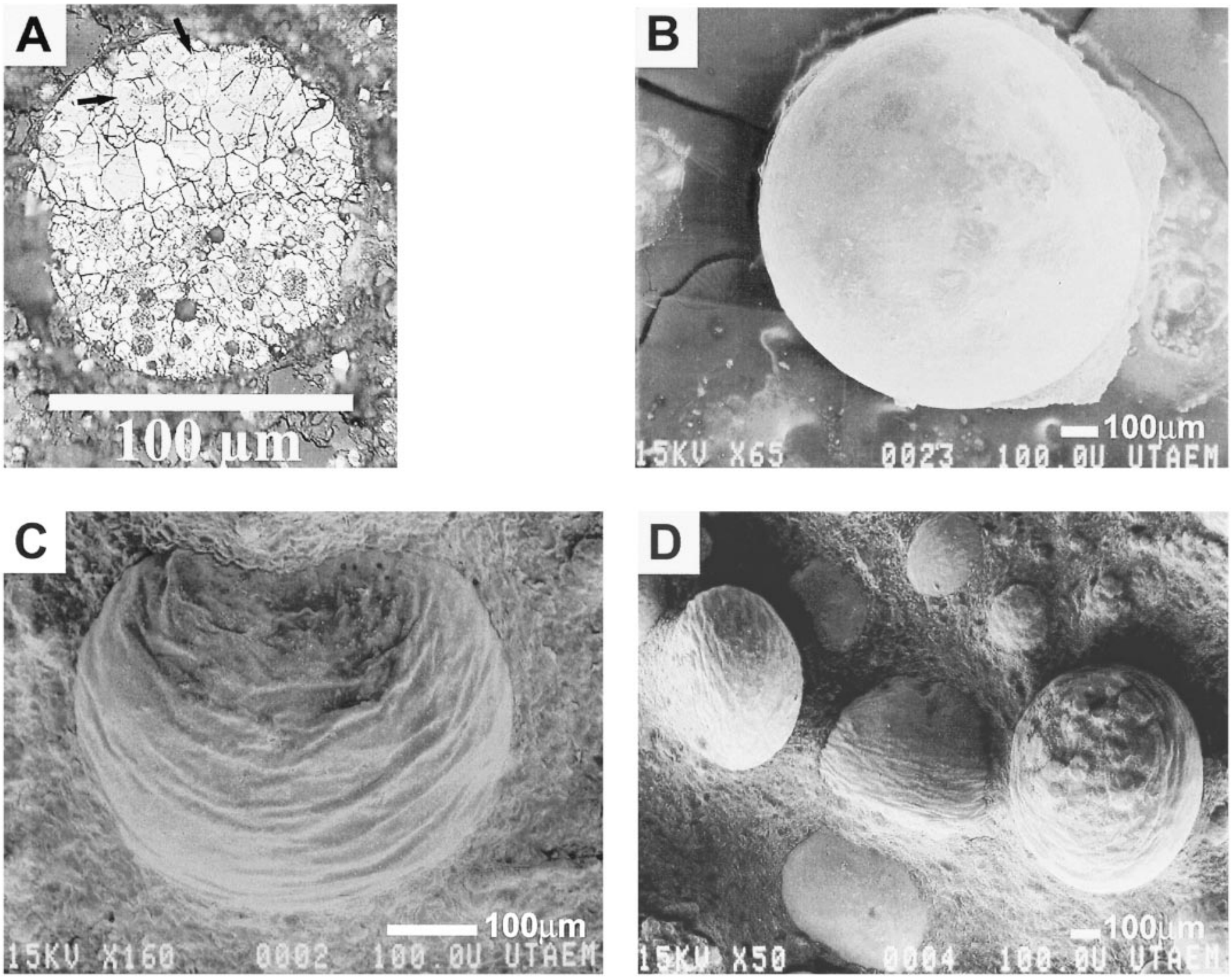

FIG. 7.—**A)** Photomicrograph (reflected light) of polished thin-section view of pyrite sphere in shale matrix. Note that framboids (smaller, round spots, revealed by HNO_3 etching) are concentrated in the lower half of the sphere, and that cement in upper half is more coarsely crystalline in upper half of sphere. Black arrows point to growth-related zonation in the void-filling, coarser, pyrite cement. The accumulation of framboids in the bottom suggests that framboids formed first and settled in the bottom of the sphere, thus representing a geopetal feature. The framboids are mostly of the same size throughout, but sectioning exposes variable portions of framboids and produces an apparent larger range of framboid sizes. **B)** SEM photo of pyrite sphere with characteristically smooth surface. **C)** SEM photo of pyrite sphere with surface wrinkles. These wrinkles are arranged like parallels of latitude on a globe, and suggest shortening of the sphere along the ''polar'' axis. The polar region has a more bumpy appearance, probably because there compressive pressures were largest and pushed cyst walls and framboidal fill together. **D)** SEM photo of lag-deposit bedding plane with several wrinkled pyrite spheres. Note the variable orientation of the planes defined by the ''wrinkle parallels'', a result of reworking and reorienting of these grains. Note also the bumpy surfaces in the ''polar'' regions of these grains.

lar'' region we see a bumpy surface texture. The bumpy surface indicates that this was the region of highest pressure where the initial framboidal fills and the cyst walls were pressed into each other prior to pyrite cementation.

Irregular pyrite grains with smooth rounded outlines exist both in shale matrix and as particles in lag concentrates (Fig. 3C, D). Because these grains are enclosed in *Tasmanites* cysts when found in shale matrix, and generally lack this organic ''skin'' when found in lag deposits, it is likely that these organic membranes were removed by abrasion and flaking off during reworking, analogous to our reasoning for the pyrite spheres. In summary, the textural observations all point to the conclusion that pyrite spheres and related grains found in lag deposits of Upper Devonian black shales are the diagenetic infills of uncollapsed or partially collapsed *Tasmanites* cysts.

Depth and Timing of Pyrite Deposition

Framboidal pyrite as found in the interiors of *Tasmanites* cysts and pyrite spheres (Figs. 3A, 6, 8A, 8D) is considered an indicator of early diagenetic pyrite formation at shallow burial depth (Berner 1969; Love 1967; Rickard 1970). Observations by various researchers suggest that framboid formation definitely occurs within the uppermost few meters of the sediment column (Berner 1969; Love 1967; Suits and Wilkin 1998).

Textural observations of the clay matrix surrounding pyrite framboids from mudstones of various ages suggest formation in freshly deposited muds of soupy consistency (O'Brien and Slatt 1990; Bennett et al. 1991; O'Brien 1995). Moreover, bioturbation features suggest that Chattanooga Shale surface muds were soft and soupy (Lobza and Schieber 1999), a condition that most likely was typical for many other Upper Devonian

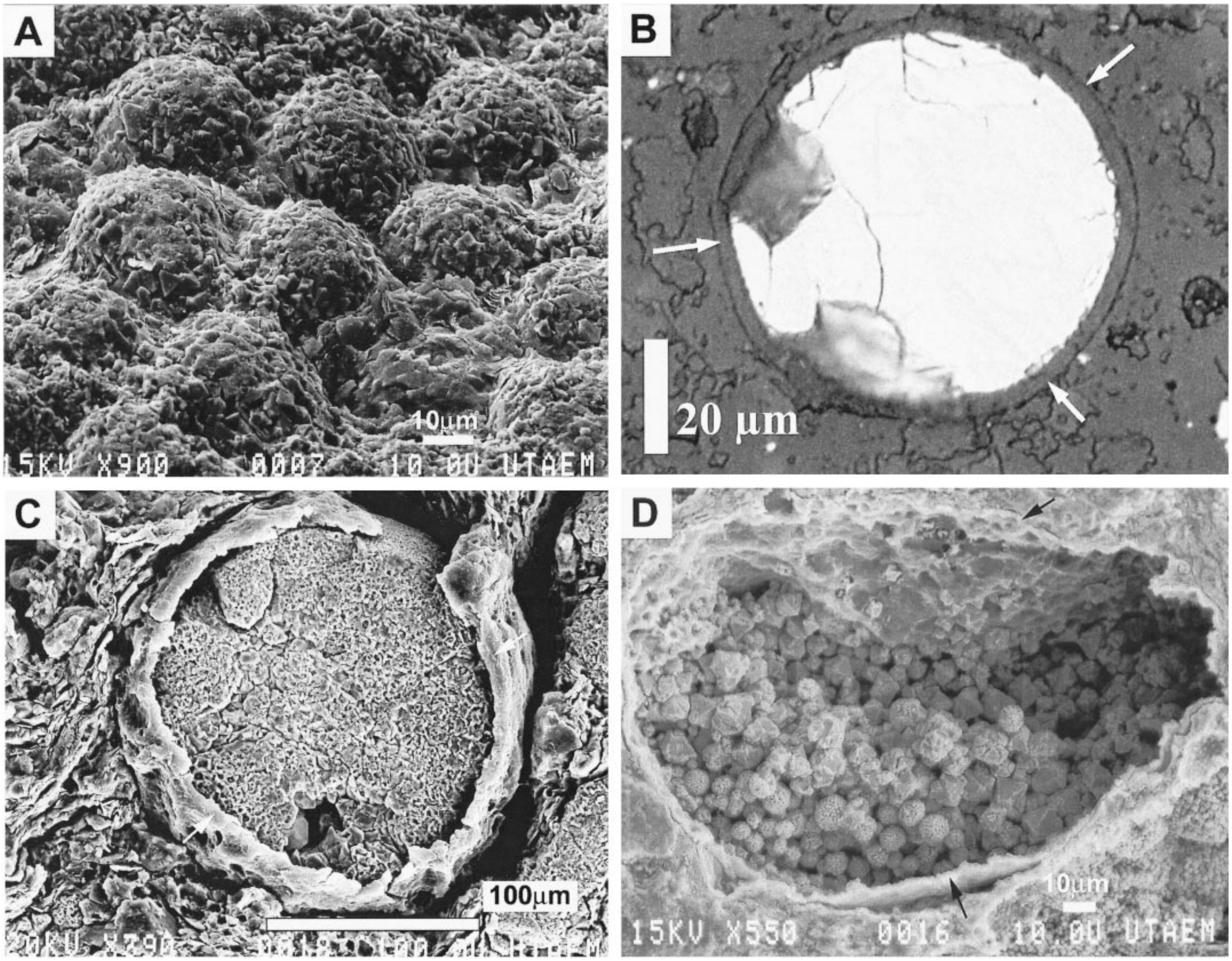

FIG. 8.—**A)** SEM close-up of bumpy surface, showing that this type of surface consists of closely packed framboids with intervening pyrite cement. This image also attests to the general observation that framboids are for the most part of the same size throughout a given cyst (see captions for Figs. 3A and 7A). **B)** Photomicrograph (reflected light) of polished thin-section view of pyrite sphere in shale matrix. The section has not been etched, thus framboids are not visible. Arrows point out the organic wall of the *Tasmanites* cyst. **C)** SEM photo of pyrite sphere in lag deposit. Sample was ground flat and slightly etched. The enclosing cyst wall is still intact (white arrows), and shows that the pyrite sphere originated as a *Tasmanites* cyst fill in underlying shales. Part of the outer surface of the cyst is exposed and shows surface textures comparable to *Tasmanites* elsewhere (Winslow 1962; Tappan 1980). **D)** SEM photo of pyrite half-sphere in lag deposit. Sample was ground flat and slightly etched. The enclosing cyst wall is still intact (black arrows), and shows that the pyrite half-sphere originated as a *Tasmanites* cyst fill in underlying shales. Because post-framboid cementation was not strong, part of the cyst fill fell out after etching. The framboid fill is clearly visible, as well as the fairly uniform framboid size, and the ''upwards'' grain size increase of pyrite cement.

mudstones of the eastern U.S. The very shallow depth of formation indicated by textural features is in good agreement with studies of modern sedimentary pyrite formation that indicate that most pyrite forms in the uppermost few centimeters of the sediment (Berner 1970; Canfield et al. 1992). Studies of modern sediments also show that pyrite framboid formation is a consequence of greigite formation under mildly reducing conditions, and occurs at the redox interface that separates waters with dissolved oxygen from those with dissolved sulfide (Wilkin and Barnes 1997).

By comparison with what we know about framboid formation in modern sediments, the framboidal pyrite in the pyrite spheres and related grains studied here should also have formed very early in diagenesis, in an essentially unconsolidated soupy sediment. Given that *Tasmanites* cysts are thin-walled and most likely were soft and flexible at the time of deposition (Tappan 1980), we can expect these fragile structures to be flattened by compaction, a view borne out by ubiquitous collapsed cysts in many petrographic examinations of these shales (e.g., O'Brien and Slatt 1990; Schieber 1998, 1999).

In view of this fragility, the fact that we observe pyrite spheres at all is good evidence of very early diagenetic pyrite formation, essentially in absence of any overburden. Because cysts are so liable to collapse, their fills most likely formed in the uppermost few centimeters to decimeters of a low-density, water-rich sediment. Many of the pyrite spheres show smooth exteriors (Figs. 3A, 3B, 3C, 7A, 7B), rather than a bumpy surface (Fig. 7D, 8A) that would result from pressing framboidal fills and cyst walls together. This observation indicates that even the somewhat later diagenetic pyrite cementation between framboids typically took place under minimal sediment cover. When we do observe bumpy surfaces, they tend to occur together with other features suggestive of compression, such as wrinkled surfaces and compressed (shortened) cysts (Fig. 7D; scenario 3 in Fig. 13).

In modern pyrite-generating environments, early diagenetic pyrite is usu-

FIG. 9.—Scours at base of pyritic lag deposit. The scours are filled with pyrite spheres.

ally of very small grain size (20 μm or less; Canfield et al. 1992), whereas larger pyrite grains are thought to reflect additional pyrite production during deeper burial of the sediment (Canfield and Raiswell 1991). In that context, the comparatively large pyrite spheres found in the Devonian shales of this study, while undeniably early diagenetic on textural grounds, are an unusual form of early diagenetic pyrite formation. The size of these grains, as well as their *in situ* abundance (e.g., Fig. 5) suggests that there was much more reactive iron (grain coatings of iron oxides and oxyhydroxides; Carroll 1958) in the system than observed in studies of pyrite formation in modern sediments (Canfield and Raiswell 1991; Canfield et al. 1992). Explaining this ''anomaly'' is beyond the scope of this study, but raises a number of intriguing questions for future research. For example, could the iron supply be related to (1) a supply of terrigenous grains with unusually thick iron oxide and oxyhydroxide coatings (a climate effect?), (2) the slow sedimentation rates of these black shales, or (3) the possibility of iron enrichment from accumulation of large quantities of planktonic organisms (Van Leeuwe et al. 1997).

One might initially think that the presence of half-spheres indicates that compression may have partially flattened spheres prior to or during pyrite formation. We argue, however, that half spheres do not indicate early compression. The smooth concave surfaces that are typical for half spheres (Fig. 3B) indicate that post-framboid pyrite cementation (the fill between framboids) occurred prior to any compression. Had it not been so, we should expect bumpy surfaces, such as seen in polar regions of wrinkled spheres (Fig. 7D). Rather than an indication of early compression, half spheres more likely are an indication of insufficient early diagenetic pyrite formation (scenario 2, Fig. 13). Cysts were partially filled and cemented with pyrite at the same shallow depth as other (spherical) cyst fills, and when the cyst was gradually buried, the part that had not been filled with pyrite collapsed and was flattened onto the upper surface of the half-spheres (Fig. 8D). Hollow spheres formed when more cementation along the cyst margins was possible before burial (Figs. 4A, 13). In cases of very slow burial they were able to completely fill with pyrite and form spheres with unequal distribution of framboids (Fig. 7A) or ''filled'' half spheres (Fig. 13). When compression became too large prior to filling of the central cavity, the ''roof'' of the cavity collapsed and led to formation of a ''collapsed'' hollow sphere (Figs. 4B, 13).

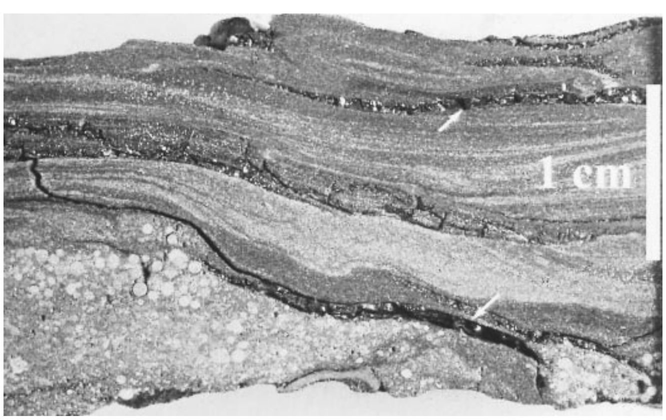

FIG. 10.—A lag deposit that contains lenses of pyrite spheres in the base, and cross-laminated sand with carbonized wood (white arrows) in the upper part.

Additional evidence for very shallow and early formation of pyritic cyst fills comes from a prior study of silica-filled *Tasmanites* cysts in the Chattanooga Shale (Schieber 1996). Spherical cyst fills of chalcedony and quartz occur in phosphate nodules of the Chattanooga Shale, and judging from differential compaction around these nodules, they had formed in uncompacted, freshly deposited mud. Phosphate nodules in modern sediments typically form within 10–20 cm of the sediment–water interface (Blatt 1992; Burnett 1977). Chattanooga Shale phosphate nodules also contain spherical pyritic cyst fills (Schieber 1996) with the same textural properties as described in this paper. A close temporal coincidence or overlap between pyrite and silica deposition in *Tasmanites* cysts is also indicated by intergrowth and coprecipitation of silica and pyrite in these cysts (Schieber 1996), and by silica cement within pyritic cyst fills described in this study (Fig. 12).

DISCUSSION

Baird and Brett (1991) interpreted pyritic lags in Devonian strata of the northeastern U.S. as evidence for anoxic waters above the seabed. Internal waves, moving along the pycnocline boundary, were thought to be responsible for seabed erosion and lag formation. Simple reworking by surface waves was considered unlikely, because under such shallow and energetic

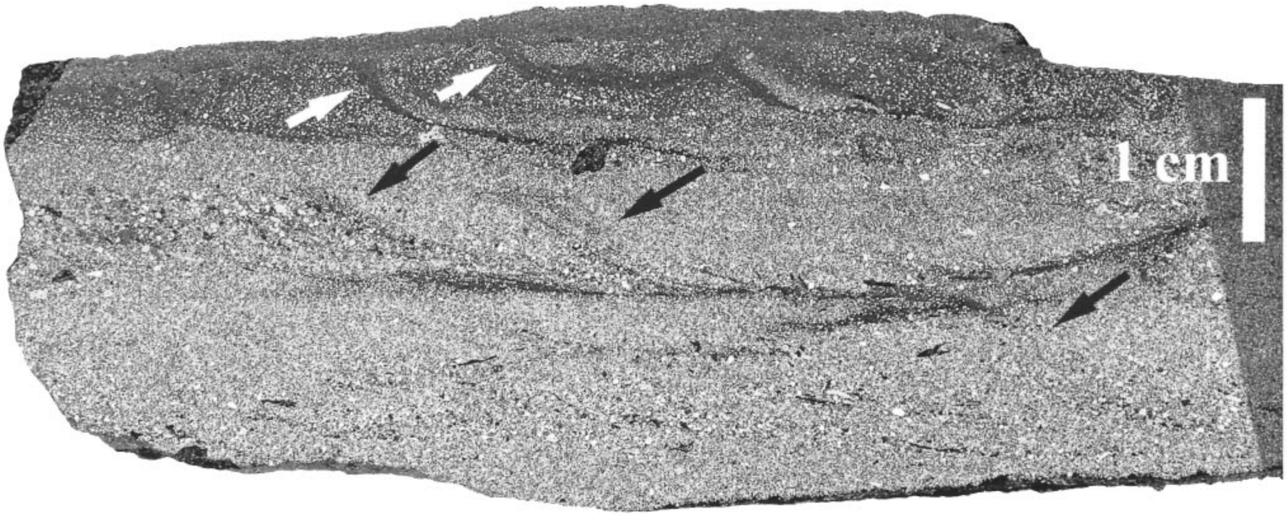

FIG. 11.—A ripple cross-laminated lag deposit that consists mainly of pyrite spheres. Black arrows point out foreset laminae, white arrows point out ove rturned foresets, probably due to current drag.

conditions the bottom waters would have been at least somewhat oxygenated, a condition thought detrimental to the survival of exhumed pyrite grains.

In contrast, recognition of widespread erosional features and storm deposits in the Chattanooga Shale of the southeastern U.S. led Schieber (1994, 1998) to believe that these black shales record shallow-water conditions above storm wave base. Surface productivity rather than anoxic bottom waters was considered the main factor for black shale formation. Nonetheless, pyritic lag deposits, similar to those observed by Baird and Brett (1991), were also found in the Chattanooga Shale (Schieber 1998).

The main reason for Baird and Brett (1991) to require anoxic bottom waters in their model was the position of the ''zebra'' facies within an anoxic basin model (''down slope'' of dysoxic gray mudstones), and the belief that this was a necessary condition to preserve exhumed pyrite grains. Experiments by Morse (1991), however, show that pyrite grains of the size considered here can survive quite well for extended periods on an oxygenated seafloor. Furthermore, in a case of high surface productivity it is likely that between episodes of storm reworking the seafloor was covered with a blanket of loose organic detritus. This detritus may have consisted of a mixture of plankton, terrigenous organic matter, and biosediment aggregates (Bennett et al. 1991). Bacterial decomposition of this surface material should have rendered its interstitial waters dysoxic or even anoxic, thus shielding pyritic lag deposits from oxygenation by overlying seawater.

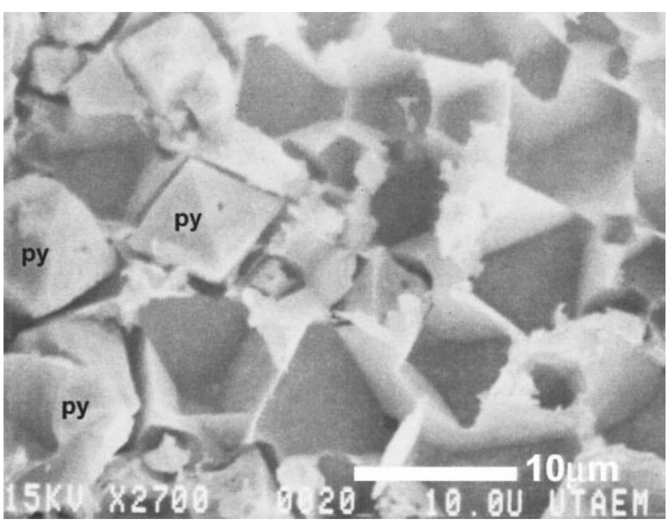

FIG. 12.—SEM photo that shows quartz cement between pyrite grains in a pyrite sphere. The lighter-colored areas are quartz, and the darker areas are mostly the former sites of pyrite grains that were removed by prolonged etching with HNO_3. Presence of quartz was verified with energy dispersive X-ray analyzer. A few pyrite grains (marked py) are still lodged in their quartz ''sockets''.

That conditions were not as forbiddingly anoxic as initially presumed (Rhoads and Morse 1971; Robl and Barron 1988) is also indicated by the morphology of the pyrite grains themselves. Under fully anoxic conditions, when there is an excess of hydrogen sulfide, pyrite tends to be disseminated evenly as small grains, because all the iron that is released from terrigenous grains is immediately precipitated. Under oxic bottom waters, the sediment is often anoxic, but is typically non-sulfidic in the surface layer (Berner 1981) and allows localized pyrite accumulation. While it has long been assumed that the sulfide in the surface layer is oxidized to sulfate by downward diffusion of oxygen, it appears that in modern sediments bacterial decay of organic matter is so efficient at removing oxygen from pore waters that there is little chance for sulfide oxidation (Canfield and Raiswell 1991; Canfield et al. 1992). Instead, it appears that reactive iron minerals, mainly iron oxyhydroxide coatings on terrigenous grains, are the controlling factor. These coatings are a ready source of easily solubilized iron, and keep pore waters free of H_2S through pyrite formation (Canfield and Raiswell 1991; Canfield et al. 1992). Because iron can migrate through the sediment under the ensuing combination of anoxic and non-sulfidic conditions, localized pyrite accumulation in anaerobic microenvironments of decaying organic matter is possible (Brett and Allison 1998). In reducing mudstones with macrofossils this is often manifested by the presence of pyrite steinkerns. *Tasmanites* cysts represent localized concentrations of organic matter, and in a way, their pyrite fills can also be considered a kind of steinkern. Their formation in a mudstone does require migration of substantial quantities of iron to the cyst cavities, which would be impossible to achieve in a mudstone that is simultaneously anoxic and sulfidic. For reasons above, it appears therefore quite possible that pyritic lags with pyrite spheres formed in shallow water during seafloor reworking by storms, and did not require anoxic bottom waters and internal waves for their formation. Considering that these grains are as large as 0.9 mm, twice as dense as quartz, and associated with bone fragments up to 20 mm in size, the flow velocities at the seabed should have been on the order of 1 m/s or more (Harms et al. 1982; Boggs 1987).

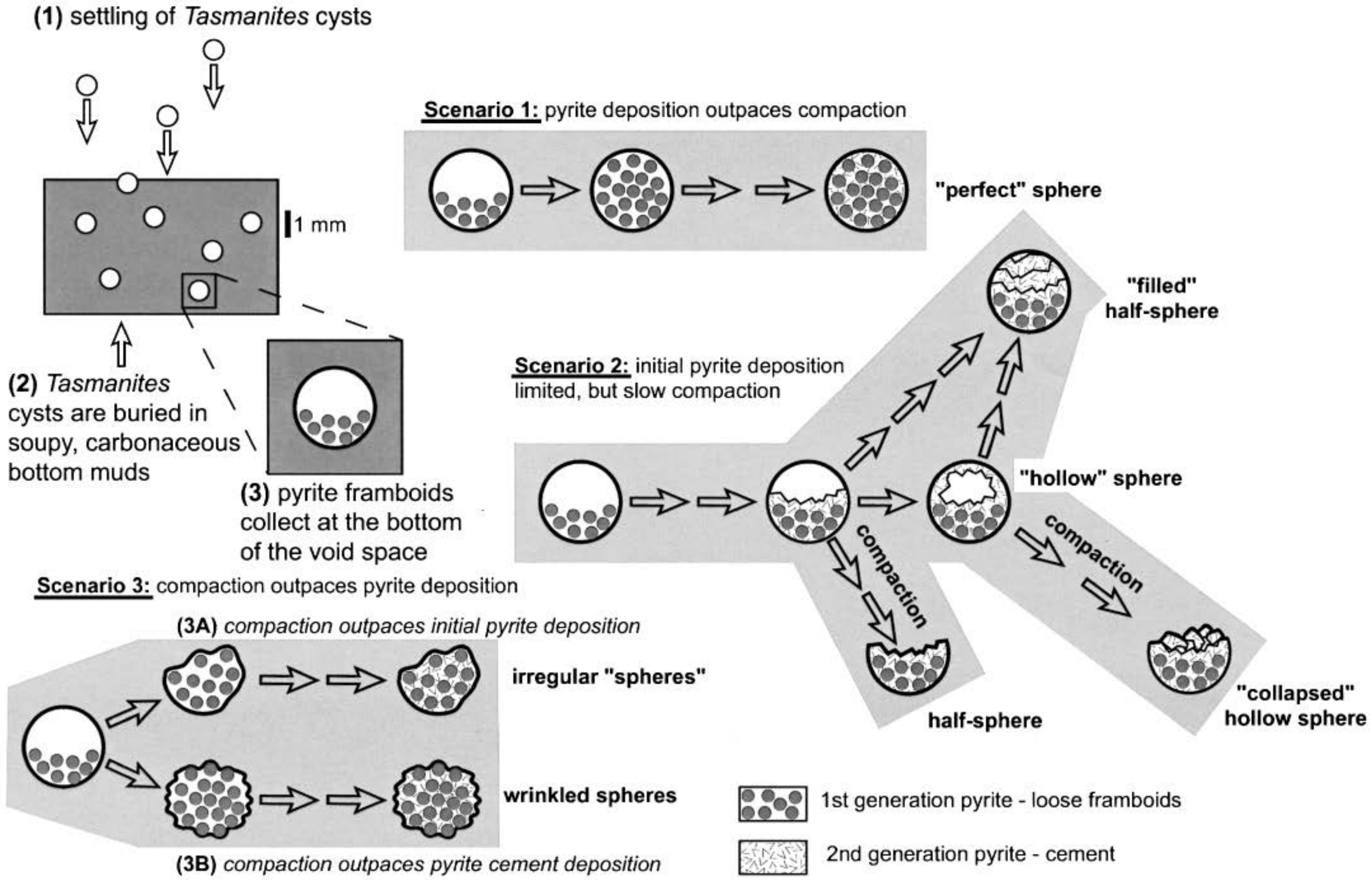

FIG. 13.—Summary of the envisioned formation of pyrite spheres and related pyrite morphologies. Formation of pyrite framboids in *Tasmanites* cysts begins shortly after the cysts have been incorporated into the reducing bottom muds. Depending on the speed of pyrite formation, several scenarios can be envisioned. (1) When pyrite framboid formation and subsequent cementation occur before noticeable compaction of the sediment occurs, perfect spheres result. (2) When initial pyrite formation is slow in comparison to scenario 1, the cysts may be only partially filled with pyrite framboids and cement. Upon compaction this leads to formation of half spheres. If sedimentation rates are very small, however, the cysts may gradually fill in with pyrite cement and form hollow spheres, and may even become completely filled with cement and show asymmetrical distribution of framboids (geopetal feature). Should compaction occur before complete fill, these hollow spheres may be crushed and form ''collapsed'' hollow spheres. (3) In cases where sedimentation rates are comparatively large, compaction outpaces deposition. In the case that the cyst does not become filled completely with framboids prior to onset of compaction, an ''irregular'' sphere results (3A). On the other hand, if the cyst does become filled with framboids prior to compaction, and cementation occurs after compaction, a wrinkled sphere results (3B).

Pyritic cyst fills are much more readily observed in distal mudstone successions, a circumstance that points towards low sedimentation rates as a factor that favors formation of the observed pyrite spheres and pyritic lag deposits. Slow sedimentation rates would have allowed *Tasmanites* cysts to remain close to the sediment surface in the sulfate reduction zone (Brett and Allison 1998) for a long time period, thus avoiding cyst collapse and allowing enough time for iron migration and pyrite deposition (Fig. 13). Partially collapsed cysts on first approximation indicate that pyrite deposition was outpaced by sedimentation and burial. Yet, half-spheres show evidence only of compaction by way of a collapsed upper part, whereas the partial pyrite fill of the lower part shows no signs of compaction (Fig. 3B). If compaction had affected the lower part we might for example expect to see lens-shaped rather than concavo-convex half spheres, or we might expect to see that framboids are more closely packed than in fully developed spheres. The absence of such features suggests that the incomplete fill is more likely a consequence of a limited iron supply than of more rapid burial and compaction (Fig. 13). This interpretation is supported by the observation that where *in situ* half-spheres are found in given shale horizons, they are the dominant form of cyst pyrite, whereas pyrite spheres are rare or absent.

A remaining question is, why in the New York occurrences half spheres are commonly found directly beneath black shale bands in ''zebra'' facies. The answer is probably a geochemical one, related to anoxic but non-sulfidic conditions as discussed above. If the gray shales were turbiditic, as suggested by Broadhead et al. (1982), they would have been initially non-reducing (oxic). Following burial under a thin blanket of organic-rich mud, H_2S would have diffused downwards and could have either been ''buffered'' by the reactive iron content of the sediment (Canfield and Raiswell 1991; Canfield et al. 1992), or alternatively it could have been ''buffered'' by the oxygen in the pore waters. In either case, the gray shales would have become temporarily non-oxic as well as non-sulfidic in the vicinity of the black–gray contact. This would have allowed iron migration to algal cysts with localized production of H_2S. Eventually, when the buffer capacity of the gray mud was exhausted, continued H_2S emanations from the overlying black mud layer would have would have rendered the gray mud layer sulfidic, thus ending iron migration. This scenario agrees with textural observations (see preceding paragraph) that suggest iron limitation as the cause of limited pyrite deposition and half-sphere formation (scenario 2, Fig. 13).

Pyrite spheres as described here are not unique to Devonian black shales. Comparable pyrite textures have for example been illustrated by Love (1971) from the Silurian of Wales, and have been referred to as polyframboids. Other examples occur in the Mid-Proterozoic Belt Series of Montana (Schieber 1985), the Cambrian of Belgium (Love 1971), the Early Ordovician Powers Steps Formation of Newfoundland (Ranger 1979; Schieber, unpublished data), and the Triassic ''Rogenpyrit'' of Germany (Fabricius 1961). Finally, aggregates of framboids, irregular as well as spherical in shape, have been described from modern sediments by various authors (Bertolin et al. 1995; Bailey and Blackson 1984; Bailey, personal communication 1998). Several of these are clearly framboid accumulations in cavities of organic remains (Kato 1967; Love 1969; Bailey and Blackson 1984). Pending pyrite cementation, they represent potential pyrite spheres that could be reworked into lags as described from the Devonian sediments of this study. Future study of recent sediments may well reveal polyframboids forming in algal cysts and comparable organic particles, as well as various stages of pyrite cementation of these aggregates. Thus, there is a good chance that pyrite spheres as described here may also contribute to the better understanding of other mudstone successions in the sedimentary record.

CONCLUSION

Sand-size pyrite spheres, half-spheres, and related grains observed in lag deposits of Upper Devonian shales of the eastern U.S. originally formed as early diagenetic infills of *Tasmanites* cysts. Textural features as well as comparisons with modern sediments suggest that pyrite deposition in *Tasmanites* cysts occurred in the uppermost few centimeters to decimeters of the sediment column, within water-rich, soupy muds.

The pyrite spheres and associated grains constitute a population of sand-size particles that were produced *in situ* rather than being brought in from a source outside of the depositional basin. They are an intrabasinal component. Such pyrite grains are indicative of reducing sediments, but not necessarily of a reducing water column. Concentration of pyrite spheres into lags suggests vigorous wave and/or current activity, and most likely indicates comparatively shallow water. Observations from the Chattanooga Shale suggest that these lags may actually have formed during storm wave scour (at a water depth of tens of meters; Schieber 1994, 1998) rather than through internal wave impingement as envisioned by Baird and Brett (1991). As such, the presence of pyrite sphere lags in distal mudstone successions may be an indicator of shallower water, such as found for example on submarine swells or in areas of nutrient upwelling in shelf settings.

Pyrite sphere concentrations are a type of iron placer, requiring variable removal and winnowing of older sediment. They should be useful as tracers for identification of sequence boundaries, lowstand system tracts, and flooding surfaces associated with eustatic events in distal mudstone facies. Moreover, bedding-plane occurrences of shale-enclosed half spheres should be useful as geopetal indicators in structurally disturbed sections.

The fact that comparable pyrite grains can be found in sediments that range in age from the Precambrian to the Holocene suggests that early diagenetic pyrite spheres as described here are much more common in the sedimentary record than currently presumed. As such, understanding the significance of pyrite spheres in the Devonian mudstones studied here is likely to have future applications in mudstone successions throughout the sedimentary record.

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