[American Journal of Science, Vol. 301, October, 2001, P. 683–726]

MECHANISMS OF FOSSILIZATION OF THE SOFT-BODIED AND LIGHTLY ARMORED FAUNAS OF THE BURGESS SHALE AND OF SOME OTHER CLASSICAL LOCALITIES

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ABSTRACT. **The splendid preservation of the Middle Cambrian Burgess Shale fauna, a fauna of exceptional importance for our understanding of the evolution of life, has not been adequately explained. Preservation of diagenetically altered remnants of the original organic tissues and formation of chlorite/illite coatings and cuticle replacements, both documented in the Burgess Shale fossils though not necessarily occurring together, can be understood as products of the same mechanism of fossilization of soft tissues. It is argued here that this mechanism consists of the following steps: (1) adsorption on structural biopolymers such as chitin, cellulose, and collagens of Fe^{2+} ions released during the oxidation of organic matter by iron(III)-reducing bacteria, (2) inhibition by the adsorbed Fe^{2+} ions of further bacterial decomposition of these biopolymers, which enables them to persist and later become kerogens; (3) in some microenvironments, nucleation of crystals of an iron(II)-rich clay mineral, a berthierine or a ferroan saponite, on the Fe^{2+} ions adsorbed on the preserved biopolymers and growth of such clay-mineral crystals to form a coating on the organic remains and/or to replace parts of the organism. The critical factors in the Burgess Shale-type preservation of Early and Middle Cambrian soft-bodied and lightly armored animals were probably: (1) rapid transport of live or freshly killed organisms into suboxic water, (2) extensive suboxic diagenesis in a sediment of high iron(III)/(organic carbon) ratio, and (3) curtailment of the supply of sulfate ions shortly after the onset of pyritization. The proposed model of early diagenesis that results in Burgess Shale-type fossil preservation critically depends on the availability of steady suboxic depositional environments in open oceanic settings at depths of the order of 100 m in which iron(III)-rich fine-grained sediments, rapidly deposited with the entrained animals by turbidity currents, could accumulate without being disturbed by storm waves and deep currents. Evidence discussed in the present paper suggests that such conditions were common in the Early and Middle Cambrian.**

Adsorption of Fe^{2+} ions on structural biopolymers as a means of protecting organic fossil remains from decomposition by bacterial enzymes is a novel suggestion and needs to be demonstrated by direct experimentation. It is based on the following considerations. First, Fe^{2+} ions are strongly adsorbed on chitin under experimental conditions comparable to those in pore waters of suboxic iron-rich sediments, and while data on Fe^{2+} ion adsorption on collagen and cellulose seem to be lacking, other heavy-metal ions are strongly adsorbed on these biopolymers under appropriate conditions. Second, Fe^{2+} ions bonded with functional groups of chitin, collagen, or cellulose would prevent the very specific configuration and bonding which a biopolymer strand has to achieve within the active-site cleft of the appropriate bacterial enzyme to make enzymatic hydrolysis possible.

Close examination of two other mechanisms recently proposed for Burgess Shale-type preservation of soft tissues shows that they are implausible: preservation by inactivation of extracellular enzymes on clay minerals would require a maladaptive reliance of tissue-decomposing bacteria on free extracellular enzymes, and preservation by attachment of pre-existing clay-mineral particles would require a sequence of physically improbable events.

It is argued here that adsorption of Fe^{2+} ions on structural biopolymers was the first step not only in Burgess Shale-type preservation of soft-bodied and lightly armored fossils but also in the preservation of such fossils by pyritization in Beecher's Trilobite Bed in the Upper Ordovician Frankfort Shale in upstate New York and in the Lower Devonian Hunsrück Slate in Rhineland-Palatinate and in the preservation of

such fossils within siderite concretions in various localities. It was probably the first step in the preservation (obscured by alunitic weathering) of soft-bodied and lightly armored fossils in the Soom Shale of the Cape Province, South Africa, and in the preservation of Ediacaran soft-bodied fossils in the classical localities of the Ediacaran Range of Australia and Mistaken Point, Newfoundland.

1. INTRODUCTION

The marine Burgess Shale Formation of the southern Canadian Rocky Mountains was deposited during the Middle Cambrian at depths of the order of 100 m just off the Cathedral carbonate platform (Fritz, 1971; Aitken and McIlreath, 1981; Collins and Stewart, 1991; Fritz and others, 1991; Fletcher and Collins, 1998), which at the time fringed the north coast of Laurentia (Aitken, 1989) at a latitude of about 20°N (Jurdy, Stefanick, and Scotese, 1995; Dalziel, 1997). The Walcott Quarry Shale Member of the Burgess Shale Formation, near Field, British Columbia, includes a sequence of fine-grained turbidite flows (Piper, 1972), known as the Phyllopod bed, which contains Walcott's (1911a,b, and c, 1912, 1919, 1920) famous Burgess Shale fauna, an assemblage of exceptionally well preserved fossils of soft-bodied and lightly armored animals ("lightly armored" denotes hereinafter animals with hardened integuments that are either not biomineralized or are biomineralized only lightly, like those of decapod crustaceans). Studied systematically over the last 30 yrs by the Cambridge group, this fauna has yielded very important insights into the evolution of the early Metazoa (Whittington, 1971a,b, 1978, 1980, 1985; Conway Morris, 1985, 1986, 1989a, 1998; Briggs and Fortey, 1989; Briggs, Erwin, and Collier, 1994) and is now at the center of a lively debate on the nature of evolution (Gould, 1989; Briggs, Fortey, and Wills, 1992a,b; Foote and Gould, 1992; Lee, 1992; Conway Morris, 1998). Burgess Shale-type faunas have been preserved in a number of Middle Cambrian localities off the Cathedral Escarpment of the northern margin of Laurentia (Collins, Briggs, and Conway Morris, 1983), and there is evidence for world-wide occurrence of such faunas during the Early and Middle Cambrian (Conway Morris, 1989a,b, 1998 p. 116-137).

Various mechanisms have been proposed for the fossilization of the soft-bodied and lightly armored fauna of the Burgess Shale. Walcott (1919, p. 220-221) summed up and interpreted his evidence on fossilization as follows:

> The mucous or gelatinous mass of algae; the spongin and spicules of sponges; the flesh of annelids; the test and body of crustaceans, have all been replaced by a shiny black carbonaceous-appearing siliceous film containing pyrite in various proportions. It is evident that the original organic and inorganic matter was removed by solution and replaced by the black film, the original convexity and relief being lost in the process and by subsequent compression.

Conway Morris (1990) concluded that the fossilization of soft-bodied animals in the Burgess Shale is basically not understood but suggested it may have involved bacterial invasion of the soft bodies, subsequent mineralization of bacteria by iron aluminum silicates, and later diagenetic destruction of bacterial textures; Wollanke and Zimmerle (1990), that the fossilization involved fast and complete embedding of the organisms in the fine-grained, thixotropic smectitic sediment and rapid neoformation of cryptocrystalline silica; Butterfield (1990a, 1995, 1996), who recognized that the "silvery films" of Burgess Shale fossils (sec 3.1) consist of kerogen, attributed the preservation of these films to adsorption and deactivation of tissue-decomposing enzymes on the smectite flakes of the original sediment; Briggs, Erwin, and Collier (1994) suggested that the fossil outlines were preserved by clay minerals that became aligned on the surfaces of the tissues before they decayed completely; Towe (1996), that early injection of fluidized, thixotropic sediment into body cavities followed by gel stabilization preserved reasonably firm impressions of the organisms; Gabbott (1998), that attachment and alignment of clay-mineral particles on the negatively charged surfaces of structural biopolymers of the organisms may have produced the clay-mineral coatings that outline the fossils; Orr, Briggs, and Kear (1998) suggested that either

colloidal or particulate clay minerals accumulated on the decaying tissue or clay minerals precipitated directly onto the tissue where suitable cations were present in solution in the pore waters. Clearly, consensus has not been achieved.

The present paper, written for an interdisciplinary audience by a geochemist who specializes in mechanisms and kinetics of diagenetic reactions, is a critical examination of the large body of published information relevant to the fossilization of the Burgess Shale fauna and flora. The purpose of this work is to find a mechanism of fossilization consistent both with the published evidence on the Burgess Shale and its fossils (soft-bodied or otherwise) and with the physico-chemical framework of early diagenetic reactions that occur in sediments comparable to the original sediments of the Burgess Shale. I have not worked on the Burgess Shale material but have considered all the information on the early diagenetic environment of the Burgess Shale fossils and on their mode of preservation that I could find. This information is scant, but a plausible interpretation does emerge. My only direct contact with the Burgess Shale was a visit to the Walcott Quarry on a rainy and ultimately snowy day, when the creamy color of carbonate laminae exposed on the wet outcrop of the Phyllopod bed reminded me of the siderite of the Hüttenberg deposit in Carinthia and aroused my curiosity regarding the possible role of iron in the preservation of the Burgess Shale fossils.

The paper is organized as follows: (1) introduction, (2) the fossiliferous rocks of the Burgess Shale Formation, (3) the physical nature of the Burgess Shale fossils, (4) the general pattern of bacterial degradation of organic matter in sediments, (5) preservation of structural biopolymers by adsorbed Fe^{2+} ions, (6) application of the proposed mechanism of fossilization to the fauna and flora of the Burgess Shale, with identification of two necessary conditions for Burgess Shale-type preservation, (7) the third condition for the Burgess Shale-type preservation of soft-bodied and lightly armored fauna, identified by comparison with the Hunsrück Slate-type of fossilization of soft-bodied animals, (8) environmental conditions that made possible the occurrence of Burgess Shale-type preservation in Lower and Middle Cambrian environments, (9) the role of adsorption of Fe^{2+} ions on structural biopolymers in some other cases of fossilization of soft-bodied animals, and (10) conclusions. To facilitate the extensive cross-referencing, these sections and their subsections are numbered.

2. THE FOSSILIFEROUS ROCKS OF THE BURGESS SHALE FORMATION

Most Burgess Shale fossils come from two quarries in the Burgess Shale Formation: Walcott's Quarry and Raymond's Quarry. The rocks of the first are assigned to the Walcott Quarry Member, those of the second to the overlying Raymond Quarry Member of that formation (Fletcher and Collins, 1998). In the type locality on the western slope of Fossil Ridge, the beds of both units are subhorizontal: Raymond's Quarry is located about 22 m above Walcott's Quarry (Collins and Stewart, 1991), and each quarry is located only about 10 m from the Cathedral Escarpment, the steep gravity-slide scar that truncated the adjacent carbonate platform, known as the Cathedral Formation (Stewart, Dixon, and Rust, 1993).

The basic published information on the fossiliferous beds of Walcott's and Raymond's quarries is summarized in table 1. Its implications will be discussed later, but four points need to be clarified now.

First, divalent iron is relatively abundant. Iron(II)-rich minerals are conspicuous in Allison and Brett's (1995) mean mineral composition of the Phyllopod bed (table 1): siderite ($FeCO_3$), dolomite, which after equilibration with siderite and calcite at 250°C (sec 6.2) should have a composition $CaMg_{0.34}Fe_{0.66}(CO_3)_2$ (Anovitz and Essene, 1987), and chlorite. Using the above compositions of siderite and dolomite and the composition of trilobite-replacing chlorite reported by Whittington (1980) (see sec 3.3), one finds that siderite contributes 2.0 wt percent of FeO to the mean Phyllopod

TABLE 1

Sedimentology and petrology of fossiliferous beds of the Burgess Shale

Properties	Walcott Quarry Shale Member	Raymond Quarry Shale Member
Sedimentary Successions That Contain the Fossiliferous Beds	"A fairly homogeneous succession of finely laminated, calcareous, silty and graphitic mudstones, typically with a weathered banded-striped appearance ... and interbedded thin limestones near the base" (Fletcher and Collins, 1998, p. 427)	"Essentially a grey, massive, blocky-slaty mudstone succession with pale brown, stripy planar laminae, much less prominently marked than in the Walcott Quarry Shale Member" (Fletcher and Collins, 1998, p. 428)
Detailed Sedimentology of Fossiliferous Beds	The 2.3 m-thick Phyllopod bed is a succession of fine-grained turbidite beds, 10 to 50 mm thick; each complete graded bed consists of a basal calcareous siltstone unit, a set of alternating laminae of mudstone and calcareous siltstone, a set of mudstone laminae that alternate with kerogen-rich laminae, and a top unlaminated mudstone unit; however, many graded beds lack the basal siltstone (Piper, 1972). Many of the laminae "are capped with an organic-rich layer composed of soft-bodied cuticular hash (Allison and Brett, 1995, p. 1080)." There are no trace fossils (Allison and Brett, 1995).	A 2 m-thick succession (Collins and Stewart, 1991) of fine-grained turbidites, in outcrop quite similar to those of the Walcott Quarry, but finer-grained (Allison and Brett, 1995). As in Walcott's Quarry, many of the laminae "are capped with an organic-rich layer composed of soft-bodied cuticular hash" (Allison and Brett, 1995). Trace fossils, such as *Diplocraterion* burrows and *Planolites*-like traces, occur at some levels, but not in layers that contain fossilized soft-bodied animals (Allison and Brett, 1995; Allison, Wignall, and Brett, 1995).
Mineral Composition of Fossiliferous Beds	Mineral composition from X-ray diffractometry of 12 samples spanning 2.0 m, in volume percent (Allison and Brett, 1995): quartz ..... 38.5 calcite ..... 6.6 mica .....40.1 dolomite .... 8.9 chlorite .... 2.5 siderite 3.3	Mineral composition from X-ray diffractometry of 6 samples, in volume percent (Allison and Brett, 1995): quartz ....14.3 carbonates (by mica .....54 difference) ... 12 chlorite ...19.6
Organics, Total Iron, and Pyrite in Fossiliferous Beds	Three fossiliferous samples had total organic carbon ranging from 0.09 to 0.13 wt percent (Butterfield, 1990a). A single wet analysis of a carbonate-poor argillite with kerogen laminae gave FeO, 2.00 wt percent, Fe_2O_3, 0.89 wt percent, and sulfide sulfur, 0.24 wt percent (G. Steiger, quoted by Walcott, 1912). Pyrite content is below detection by X-ray diffractometry (Allison and Brett, 1995).	Pyrite content is below detection by X-ray diffractometry (Allison and Brett, 1995), that is, below 1 wt percent (see text).
Fissility	"In localities where soft-bodied fossils are found (Walcott's quarry, and Raymond's quarry) this graded calcareous siltstone and mudstone tends to split along bedding planes, in contrast to other localities, where the fracture is more irregular and oblique to bedding (Piper, 1972, p. 69-170)".	Laminations in the Raymond Quarry Shale Member are less prone to split parallel to bedding than those in rocks of the Walcott Quarry, except where fossils are common (Fletcher and Collins, 1998).

bed rock, dolomite 2.2 wt percent, and chlorite 0.9 wt percent; this gives a total of 5.1 wt percent FeO, not counting any iron in the illite and the metamorphic white mica, determined together in the analyses of table 1 as "mica." Allison and Brett (1995)

noted that the percentages of different carbonate minerals in the rocks of the Phyllopod bed vary greatly, an observation consistent with Pipers' (1972) description of the graded beds. G. Steiger (quoted by Walcott, 1912), who did a wet chemical analysis of a carbonate-poor Phyllopod bed argillite with kerogen laminae, reported for the rock 2.00 wt percent FeO and 0.89 wt percent Fe_2O_3. The ferric/ferrous ratio is too high for the reported mineral assemblage and may be in serious error (compare Begheijn, 1979), but the total iron, equivalent to 2.80 wt percent FeO, should be reliable.

Second, pyrite content is low. In the case of routine analyses, pyrite content below the detection limit of X-ray diffractometry means less than 1 wt percent of pyrite (K. D. Cowan, personal communication, 2000); with the use of Rietveld method, less than 0.5 wt percent (compare Mumme and others, 1996; Ward, Taylor, and Cohen, 1999). According to Allison and Brett (1995), the pyrite in the rocks of the Phyllopod bed is almost evenly distributed, except for thin pyrite patinas associated with worm-gut traces, but according to S. Conway Morris (personal communication, 1998), lenticular arrays of framboidal pyrite are quite frequent in Burgess Shale rocks. In the Raymond's Quarry rocks "pyrite is predominantly evenly distributed, but is associated with organic matter in some layers. This association includes clustering of framboids around organic flakes and pyritization of organic debris (Allison and Brett, 1995, p. 1081)."

Third, the rocks of the Phyllopod bed are cut across by thin veins, a source of information on the fluids expelled from or circulating through these rocks after the rocks became sufficiently indurated to be fractured, that is, during the late diagenesis and/or very early metamorphism. Apart from a set of late fractures with irregular surfaces coated with carbonates, the only mineralized fractures that cut the Phyllopod bed are parallel veinlets, normal to the bedding, which were cemented with chlorite, reopened and recemented with fine-grained calcite and 'blotches of cupriferous pyrite' (E. S. Larsen, quoted by Walcott, 1912; compare Conway Morris, 1985, pls 1-3, 1998, fig. 16).

Fourth, the growth of large crystals of a white potassium mica within the Phyllopod bed (Piper, 1972; Conway Morris, 1990) indicates that the Burgess Shale underwent very-low-grade, anchizonal metamorphism (Frey, 1987; Merriman, Roberts, and Peacor, 1990; Livi and others, 1997), which implies temperatures in the 200° to 300°C range (Mulis, 1987). According to Butterfield (1996), Ian Harding obtained from (pseudo)vitrinite reflectivity maximum temperatures of 250° to 350°C and from illite crystallinity maximum temperatures of 180° to 280°C and concluded that the Burgess Shale had been exposed to temperatures of 250° to 280°C. R. E. Summons's argument (Towe, 1996) that because his Burgess Shale rock samples contained a fair amount of kerogen but only traces of hydrocarbons, the maximal temperature attained had to be relatively low, is wrong, because the bulk of hydrocarbons would have been expelled with heating to the very low metamorphic temperatures of 250° to 280°C. A crucial aspect of the preservation of Burgess shale fossils is the fact that the Burgess Shale underwent anchimetamorphism without significant shear and thus without developing a cleavage, so that it became an argillite, rather than a slate. The absence of cleavage is clearly reported by Piper (1972, p. 169-170) in his description of organic films in the rocks of the Phyllopod bed and Raymond's Quarry:

> The Phyllopod Bed consists of sharp-based units of calcareous siltstone grading up through alternating laminae into mudstone . . . A similar lithology is found elsewhere in the Stephen Formation . . . However, in localities where soft-bodied fossils are found (Walcott's quarry, and Raymond's quarry 20 m above it), this graded calcareous siltstone and mudstone tends to split along bedding planes, in contrast to other localities, where the fracture is more irregular and oblique to bedding. This bedding-plane fissility in the Phyllopod Bed and the rocks of Raymond's quarry probably results from the many streaks of carbonaceous material, visible in thin section parallel to the bedding, preventing diagenetic clay-mineral bonding between laminae. Such carbonaceous streaks are not known in other developments of the calcareous graded

> siltstone and mudstone. Scanning electron micrographs of the Burgess Shale show only a poor preferred orientation of clay minerals in the bedding plane; this probably resulted from diagenetic growth of clays under conditions of reduced overburden pressure, and may explain why most Stephen Formation lithologies have a poor bedding-plane fissility.

(At that time, the present Burgess Shale Formation was referred to as "the thick Stephen Formation"). According to Piper (1972), it was J. D. Aitken who recognized that the Burgess Shale near the Cathedral Escarpment was protected from significant shear stress by the massive limestones and dolomites of the Cathedral Formation below and to the east and the massive limestones of the Eldon Formation above. In other words, the fossiliferous localities of Burgess Shale were protected by the stress shadow of the Cathedral Escarpment (Conway Morris, 1990). Thus, Burgess Shale fossils were not destroyed by shear, as they would have been farther west, where shales were turned into phyllites.

3. PHYSICAL AND CHEMICAL NATURE OF BURGESS SHALE FOSSILS

3.1. Physical characteristics.—Fossils of Burgess Shale animals typically have the following, extensively documented (Whittington, 1971a and b, 1978, 1980; Conway Morris, 1977, 1985) physical characteristics: (1) The fossils are oriented parallel to bedding surfaces or at low angles to them; they are greatly flattened normal to the bedding plane, and in many cases different parts of the fossil are flattened in different parallel planes that are separated by thin films of shale. (2) When exposed by the splitting of the shale along bedding planes, the fossils commonly also split into parts and counterparts along very smooth fracture surfaces, which may jump, sometimes repeatedly, from one plane of flattening of the fossil to another (for example, Conway Morris, 1985). (3) Both part and counterpart consist of or at least incorporate "silvery films" which show the outer body walls and some inner organs of the soft-bodied and lightly armored animals in exquisite detail; thus the splitting typically proceeds within the "silvery films." (4) The "silvery films" are darker than the rock but are highly reflective when the normal to the fracture plane bisects the angle between the incident and the reflected light; their reflectivity varies greatly from specimen to specimen and may vary greatly over a single part or counterpart, so that, for example, in many cases the gut of a worm is more reflective than the rest of its body (for example, Conway Morris, 1979). In short, Burgess Shale fossils exposed by splitting the rock typically consist of highly reflective films on smooth but not very reflective surfaces of a silicate substrate, like the highly reflective thin films of aluminum on the highly polished but not very reflective surfaces of glass mirrors of modern telescopes. Conway Morris (1990, p. 273) summarized the overall mineralogy of Burgess Shale fossils as follows: "At present the soft parts of fossils are largely composed of silicate films, principally chlorite and potassium micas . . . In terms of the hard parts, those of calcareous organisms are also replaced by similar silicates, although in some cases pyritization has been extensive . . . However, phosphatic species, including the inarticulate brachiopods . . . retain their original composition, while in some cases the sponges retain the siliceous composition of their spicules." Since then, Butterfield (1990a and b, 1996) has shown that many soft-bodied and lightly armored Burgess Shale fossils consist of or at least include remnants of soft tissues transformed into kerogen. The available evidence suggests to me that many Burgess Shale fossils have a dual chemical nature, in that they consist both of exquisitely preserved remnants of the original tissues and of an associated local diagenetic mineralization. The evidence for both aspects is reviewed below.

3.2. Remnants of the original tissues preserved as kerogen.—Remnants of the original tissues of Burgess Shale fossils were discovered by Butterfield (1990a and b, 1996) when he dissolved unsplit rock samples in aqueous solutions of hydrogen fluoride and obtained fragments, 0.1 mm to several millimeters across, of highly reflective thin kerogen films that show the fine detail of the fossilized organisms. Sizeable film

TABLE 2

Organisms from the Burgess Shale and from the Lower to Middle Cambrian shales of the Mount Cap Formation of northwest Canada whose kerogen remains have been isolated and documented

Organisms	Observations and References
cyanobacterium *Marpolia* (fragments of sheaths), leiosphaerid and papillose acritarchs, priapulid *Ottoia* (fragment)	Burgess Shale (Butterfield, 1990a)
jawed polychaetes *Canadia* and *Wiwaxia* (paleae, neurosetae, probable fragments of body-wall cuticle)	Burgess Shale (Butterfield, 1990a,b)
putative pelagic holothurian *Eldonia* (fragments of gut wall)	Burgess Shale (Butterfield, 1996)
Wiwaxia (paleae), different unidentified arthropods (appendages)	Mount Cap Formation (Butterfield, 1994)
trilobites (cuticle fragments), inarticulate brachiopod (periostracum), *Rushtonites*-like small invertebrates (spines), hyolithids (helens, conchs, operculum), chancelloriids (sclerites)	Mount Cap Formation (Butterfield and Nicholas, 1996)

fragments are difficult to obtain from split surfaces because the fossils split along the delicate kerogen films, which adhere to the mineral matrix on both sides (Butterfield, 1990a); however, Butterfield (1996) managed to obtain sizeable film fragments from a split specimen of *Eldonia*. The few Burgess Shale species whose fragments were isolated by the hydrofluoric acid treatment and documented are listed in table 2 together with the species isolated in the same way from the Mount Cap Formation of Northwest Canada, which is of Lower to Middle Cambrian age and shows Burgess Shale-type fossil preservation.

The resistance of the films isolated by Butterfield (1990a and b, 1996) to aqueous solutions of hydrofluoric acid is in itself evidence of their organic nature. Moreover, Butterfield (1996) has obtained the following information on fragments of an *Eldonia* gut that were so isolated: (1) Analysis of isolated gut wall by energy-dispersive X-ray spectrometry gave (wt percent): carbon, 78.0; oxygen, 8.0; but also, because of mineral impurities, aluminum, 1.0; silicon, 10.4; potassium, 1.2; et cetera. (2) X-ray photoelectron spectroscopy (sampling depth of nanometers) of the surface of the reflective layer has shown that its main constituent is organic carbon, much of it in polycondensed benzene rings. (3) Two constituent kerogen layers of the *Eldonia* gut wall were distinguishable: an inner, highly reflective layer and an outer, non-reflective layer. (4) When analyzed by Auger electron spectroscopy (sampling depth of nanometers) with gradual sputtering away of surface atoms, the inner kerogen layer evolved to the composition: carbon, 97.1; oxygen, 1.7; calcium, 1.2 wt percent. (5) Analyzed in the same way, the outer kerogen layer evolved to the composition: carbon, 81.3; nitrogen, 7.0; oxygen, 5.8; phosphorus, 1.4; sulfur, 1.0; potassium, 2.2; calcium, 1.3 wt percent. Butterfield (1996, p. 111) interpreted this difference in chemical composition as due to graphitization that "was limited to *within* the organic-walled structures and did not occur at the more cohesive sediment-organic interface," but a simpler explanation would be that *Eldonia* is actually an annelid and that the highly reflective layer is the originally chitinous gut wall, while the less reflective layer is the originally collagenous body wall (see secs 5.2 and 5.5).

Therefore, it has been shown conclusively that in many cases resistant soft tissues of Burgess Shale organisms have been preserved and converted into kerogen films that show their morphology in exquisite detail. Moreover, kerogen films in the Burgess Shale should be highly reflective compared with their silicate background, for at the onset of anchimetamorphism, vitrinite maximal reflectance in oil is about 3.5 percent (Kish, 1987), which corresponds to maximal reflectances of chitinozoan and graptolite kerogen of about 4.8 percent in oil (Bertrand and Héroux, 1987) or about 16 percent in air, and that is more than three times as high as the reflectances in air of quartz and clay minerals (Ramdohr, 1980, p. 1101-1118). Thus there are sound physical grounds for concluding, as Butterfield (1990a and b, 1996) did, that the "silvery films" of Burgess Shale fossils are all kerogen films.

3.3. Localized diagenetic mineralization as an aspect of fossilization.—Localized diagenetic mineralization was also an aspect of fossilization of some Burgess Shale animals with soft cuticles or with hardened cuticles that were either not mineralized or only lightly mineralized in living animals. The evidence for localized diagenetic mineralization, sparse but unambiguous, consists mainly of local anomalies in major-element contents associated with body outlines and specific organs of Burgess Shale animals exposed on bedding planes (table 3). Note that local anomalies in major-element contents extend not only over the bodies of arthropods *Marella* and *Alalcomenaeus* but also over their appendages, considered to have been originally unmineralized even in trilobites; moreover, such anomalies also extend over the bodies of truly soft-bodied animals such as *Ottoia* and *Eldonia*. In interpreting these anomalies, one needs to keep in mind the sampling depths of the surface-analytical methods used to measure them. In the case of the priapulid *Ottoia*, the observed anomaly could have been caused by a diagenetically altered layer only a few nanometers thick; however, in the cases of the two arthropods and the putative holothurian *Eldonia*, diagenetically altered layers had to be at least a few micrometers thick. The complexity of the observed patterns, that is, the enrichment in aluminum and potassium in some areas, and in silicon, titanium, and sometimes iron, in other areas, can be explained by the partial replacement of an earlier iron(II)-rich chlorite by a potassium mica (presumably phengite), which is documented in table 4 and discussed in section 6.3.

The best evidence for the diagenetic mineralization of Burgess Shale fossils is obtainable by studies of mineralogy and textures of polished cross sections of fossils embedded in the rock. The published evidence of this type, very sparse but very interesting, is summarized in table 4. Note the following:

First, the best-documented cases of diagenetic mineralization of Burgess Shale fossils are the two cases of the replacement of dorsal exoskeletons of the trilobite *Olenoides* by chlorite (table 4). The implications of this replacement, with chlorite crystals cutting right across the complex chitin-protein and calcite layering of these exoskeletons, will be discussed in section 6.3. At this point suffice it to note that Whittington (1980) gives an electron microprobe analysis of the chlorite that replaced the original material of his *Olenoides* exoskeleton. In calculating the structural formula of this chlorite, one can treat all the iron as ferrous iron: this is a reasonable approximation for a mineral in which ferric iron typically does not exceed 15 percent of the total iron even in hematite-rich rocks (Zane, Sassi, and Guidotti, 1998) and which in this case already has a high aluminum content (compare Nelson and Guggenheim, 1993). The resulting structural formula is $Mg_{0.68}Fe^{II}_{1.20}Al_{0.82}Si_{2.75}Al_{1.25}O_{10}(OH)_2Mg_{0.72}Fe^{II}_{1.28}Al(OH)_6$. This chlorite is indeed iron-rich: it is closer to chamosite than to clinochlore.

Second, either the cuticle of Conway Morris's *Eldonia* (table 3) was replaced by crystals of diagenetic clay minerals ultimately replaced by potassium mica, or these crystals grew as a coating on *Eldonia*'s organic remains.

TABLE 3

Burgess Shale fossils exposed on bedding surfaces that have been studied by surface-analytical methods

Surface-Analytical Method and Its Sampling Depth	**Animals and Investigators**	**Observations**
Auger electron spectroscopy; sampling depth of a few nanometers (Hochella, 1990).	priapulid *Ottoia* (R. A. Chappell, reported by Conway Morris, 1977)	Si, Ca contents were higher in the fossil, Al content was lower (for Ca, compare with the first *Eldonia* below).
Electron microprobe analysis; sampling depth of a few micrometers (Goldstein and others, 1992, p, 79-90).	demosponge *Choia* (S. Conway Morris and K. Pye, reported by Conway Morris, 1990)	Siliceous spicules documented by a beckscattered-electron image.
	putative holothurian *Eldonia* (same reference)	Backscattered-electron image of the surface of the fossil shows an aggregate of potassium mica crystals, partially coated with calcite.
	another *Eldonia* (Butterfield, 1996)	In the mineral matrix underlying the reflective kerogen layer of the *Eldonia* body, Al content is higher, while Si and Ca contents are lower, than in the surrounding rock[1].
	primitive arthropod *Marella* (Orr, Briggs, and Kear, 1998)	Over most of the body, including the appendages, Si and Ti contents (correlated), as well as Fe content, are higher than in the surrounding rock, while Al and K contents (correlated) are lower. However, in some organs Al and K contents (correlated) are higher than in the surrounding rock.
	another *Marella* (same reference)	Al and K contents (correlated) are higher in a part of the body than in the surroundings.
	arthropod *Alalcomenaeus*, of uncertain class (same reference)	Over most of the body, including the appendages, Si and Ti (correlated) are higher than in the surrounding rock, but in some parts Al and K (correlated) are higher.

[1]Analysis that was done at the same accelerating voltage as that of the surrounding rock.

Third, in contrast to the above, one cannot see in Butterfield's (1990a, fig. 4) photomicrograph of a cross section of a worm (table 4) any sign of diagenetic mineralization, and N. J. Butterfield (personal communication, 1999) has informed me that there is no indication of localized authigenic mineralization, either replacive or surficial, around that kerogen cuticle.

Thus, the available evidence supports the above suggestion that fossilization in the Burgess Shale can occur both as preservation of resistant organic tissues as kerogen and as localized diagenetic mineralization, and presumably as a combination of both.

TABLE 4

Burgess Shale fossils that have been studied in cross section

Animals	Investigators and Methods of Study	Observations
trilobite *Olenoides serratus*	Whittington (1980), with an electron microprobe.	Dorsal cuticle consisting of minute clay-mineral flakes that are roughly normal to the surface of the cuticle, with illite concentrated on the outside and chlorite on the inside of the cuticle. Pyrite content very low: in the chlorite zone 0.15, in the illite zone 0.34 wt percent.
	S. Conway Morris and K. Pye, with an electron microprobe (reported by Conway Morris, 1990)	Back-scattered electron (BSE) image of a dorsal cuticle, about 100 m thick, is shown in Conway Morris's (1990) figure 2C. The cuticle had been replaced by chlorite; subtle variations in BSE intensity show that chlorite crystals grew at high angles to the cuticle surface and to the fabric of layer silicates in the surrounding matrix. Chlorite was partially replaced by a potassium mica, starting from the outside of the cuticle; mica crystals also grew at high angles to the cuticle surface.
inarticulate brachiopod *Dyctionina*	same as above	BSE image of a *Dyctionina* shell is shown in Conway Morris's (1990) figure 2B. The shell now consists of apparently homogeneous apatite, which has also grown over the periostracum. The periostracum is outlined by blades of potassium mica, oriented tangentially to the original ribbed shell and at varying angles to the layer silicates of the matrix.
an unidentified worm	Butterfield (1990a), under a petrographic microscope	An opaque kerogen cuticle, 10 μm thick, is enveloping a body cavity that is greatly flattened but internally supported by enclosed sediment. There is no localized diagenetic alteration of the sediment that is in contact with the cuticle, inside or outside.

3.4. Ancillary aspects of fossilization that indicate the early diagenetic environment. —Quantitatively unimportant but environmentally significant is the association of small amounts of pyrite, usually in the form of framboids, with many Burgess Shale fossils (Conway Morris, 1986). Pyrite framboids occur as chains on filaments of cyanobacterium *Morania confluens* (Walcott, 1919); pyrite commonly forms coatings on some fossils (Conway Morris, 1985, 1986); pyrite often replaces sponge spicules and dermal layers (Walcott, 1920), partially replaces hard parts of some echinoderms (Conway Morris, 1986) and of some trilobites (Whittington, 1977; Conway Morris, 1986), and in some cases replaces whole trilobites (N. J. Butterfield, personal communication, 1998).

It is also significant for the diagenesis of silicates that although in some cases sponge spicules retained their siliceous composition (Conway Morris, 1990), "sponge spicules and their dermal layers are usually replaced by pyrite or coated with a thin black film (Walcott 1920, p. 265)."

Finally, it is significant that the phosphatic shells of lingulid and dyctinid inarticulate brachiopods are preserved as apatite (Conway Morris, 1990). Note that in the case of Conway Morris's (1990) *Dyctionina* (table 4), most of the shell seems to consist

entirely of apatite, which has even diagenetically overgrown the periostracum, while the periostracum itself was replaced by or provided a substrate for the growth of clay mineral crystals that have been subsequently converted into a potassium mica.

4. THE GENERAL PATTERN OF BACTERIAL DEGRADATION OF ORGANIC MATTER IN SEDIMENTS

If one wants to understand preservation of organic tissues under exceptional conditions, it is reasonable to start by considering the general pattern of bacterial degradation of organic detritus in sediments. The bulk of dissolved organic matter in the water column above both marine and freshwater sediments consists of polymeric, high-molecular-weight compounds that cannot be directly assimilated by bacteria (Chróst, 1991; Hoppe, 1991). The bulk of the organic matter that reaches marine bottom sediments consists of particulate organic matter and of coatings of organic matter that is adsorbed on mineral particles (Meyer-Reil, 1991; Hedges and Keil, 1995). The coatings, which in most shelf and upper-slope sediments contain 0.5 to 1.0 mg C m^{-2}, continue to interact with the dissolved organic matter (Hedges and Keil, 1995). Organic molecules of low molecular weight are being released to the pore water by desorption from the organic coatings and by degradation of particulate organic matter, but they are also continuously being consumed by bacteria; thus the fraction of dissolved organic matter of low molecular weight in the system remains tiny, much smaller than the fraction of dissolved polymeric organic molecules and very much smaller than the fraction of organic matter that is adsorbed on mineral particles (Meyer-Reil, 1991; Hedges and Keil, 1995).

To be taken up by a bacterium, organic molecules have to be transported across the cell membrane by specialized enzymes, and this imposes severe limitations on sizes and structures of directly usable molecules (Chróst, 1991). To be used as a source of food, particulate matter and dissolved polymeric organic matter have to be broken down outside the cell membrane (Chróst, 1991; Meyer-Reil, 1991; Billen, 1991). There is consensus that breakdown of polymeric organic matter, including the constituents of particulate organic matter, is the slow step in the growth of bacteria both within the water column and within the sediment (Billen, 1991; Chróst, 1991; Hoppe, 1991; Meyer-Reil, 1991). Bacteria break down organic matter into directly usable organic molecules by means of extracellular enzymes, which may be divided into *free extracellular enzymes* (those dissolved in the surrounding water) and *ektoenzymes* (those associated with the cell surface). Measurable concentrations of free extracellular enzymes are common in fresh, brackish, and sea water (Chróst, 1991; Smucker and Kim, 1991), but many researchers feel this is due much more to the disintegration of dead bacterial cells than to deliberate excretion of enzymes (Billen, 1991; Chróst, 1991; Meyer-Reil, 1991). Chróst (1991) argued that the most important extracellular enzymes of bacteria are likely to be ektoenzymes because (1) ektoenzymes provide directly usable organic molecules where the producer bacterium can easily use them, but other bacteria cannot, and (2) the activity of ektoenzymes can be regulated by chemical signals from the producer bacterium. This conclusion is supported by Chróst's (1991) finding that in samples from the water column of Plußsee, a naturally eutrophic lake in Holstein, 75 percent of alkaline phosphatase, 85 percent of aminopeptidase, and 89 percent of glucosidase were associated with cell surfaces, while only 17, 4, and 9 percent, respectively, were free extracellular enzymes. It is also supported by Hoppe's (1991) finding that in samples of brackish water from the Kiel Fjord, free bacteria had very much lower specific (that is, per cell) aminopeptidase activities than bacteria attached to suspended organic detritus; this implies that to feed well, bacteria had to be in direct contact with the food source.

It follows, therefore, that preservation of structural and other biopolymers in sediments is likely to occur when enzymatic degradation of these biopolymers along the metabolic pathways commonly used by bacteria is inhibited by the adsorption of

strongly attached ions or molecules from the pore water on the biopolymers. Indeed, one way in which bacterial degradation of soft tissues can be inhibited is well known. It is preservation of soft tissues, especially labile muscle tissues, by adsorption of phosphate ions on the biopolymers of these tissues, followed by precipitation of apatite. Soft tissues preserved by this mechanism, including labile muscle tissues, have been found in many localities, and the process has been duplicated under laboratory conditions (Briggs and others, 1993; Briggs and Kear, 1994; Hof and Briggs, 1997).

It also follows that inactivation of extracellular enzymes by adsorption on smectite flakes, which was suggested by Butterfield (1995) as a possible mechanism of preservation of soft tissues, is not likely to be an effective mechanism of fossilization under natural conditions. We know that free extracellular enzymes are adsorbed on humic substances (Münster and De Haan, 1998) and on organic coatings of mineral particles in marine sediments (Meyer-Reil, 1991). However, marine and freshwater bacteria that live in fine-grained sediments would have developed extracellular enzymes that are not adsorbed on smectites or on the almost ubiquitous organic coatings of clay-mineral flakes, precisely because once adsorbed on such surfaces, bacterial enzymes would be useless. Chróst's (1991) conclusion that extracellular enzymes of the predominantly Gram-negative bacteria of marine and freshwater sediments are mostly either bound to the surfaces of these bacteria or located in their periplasms resolves this problem, for such extracellular enzymes will avoid adsorption on inappropriate natural surfaces.

5. PRESERVATION OF STRUCTURAL BIOPOLYMERS BY ADSORBED Fe^{2+} IONS

5.1. Preservation of bacterial cell walls, capsules, and sheaths.—In trying to understand the fossilization of microorganisms in Precambrian cherts (Hofmann and Schopf, 1983; Knoll, 1985), Ferris, Beveridge, and Fyfe (1986) discovered that in an acid hot-spring setting, cell walls of thermoacidophilic bacteria contained much iron and also were commonly encrusted with silica particles. When Ferris, Beveridge, and Fyfe (1988) attempted to replicate such textures in experiments with *Bacillus subtilis*, they found that high concentrations of dissolved silica alone could not prevent degradation of *B. subtilis* cell walls, but cell walls that were first exposed to dissolved ferric iron adsorbed much iron, retained their structure, and could be preserved by the precipitation of silica. Ferris and coworkers concluded that these bacterial cell walls were preserved because the adsorbed iron inhibited the autolytic (own-cell disintegrating) enzymes of the dead bacteria. Subsequently, Urrutia Mera and Beveridge (1993, 1994) precipitated silicate particles of clay-mineral chemical compositions and morphology on cells of *B. subtilis*. Most importantly, they identified a mechanism of precipitation of silica and silicates on bacterial cell walls that consists of: first, adsorption of heavy-metal ions such as Fe^{2+} and Fe^{3+} on the negatively charged cell walls; and, second, nucleation and growth of silica or silicate crystals on the arrays of adsorbed heavy-metal ions (see also Fortin, Ferris, and Beveridge, 1997). Adsorption of ferrous iron followed by precipitation of clay minerals, first a gel-like chamositic phase and then a crystalline kaolinitic phase, was also observed to occur on bacteria in the solute-rich waters of Rio Solimões, Brazil (Konhauser and others, 1993) (the chemical composition of endmember chamosite is $Fe^{II}_3Si_3AlO_{10}(OH)_2.Fe^{II}_2Al(OH)_6$, that of kaolinite is $Al_2Si_2O_5(OH)_4$). Bacterial remains can also be mineralized by iron(III)-rich clay minerals under certain sea-bottom conditions: some submarine white-smoker chimneys contain accumulations of microscopic tubes that correspond in form and in size to cyanobacterial sheaths but consist of fine multiply-folded sheets of nontronite (Köhler, Singer, and Stoffers, 1994), a smectite of composition that can be approximated by the formula $(Na, \frac{1}{2}\ Ca)_xFe^{III}_2Si_{4-x}Al_xO_{10}(OH)_2$, where $x \approx 0.30$. Nontronite has either replaced cyanobacterial sheaths or grown on them.

Are structural polymers of bacterial cell walls the only structural biopolymers that can be stabilized by adsorption of ferrous or ferric ions and subsequent precipitation of

silicate minerals? Or can other structural biopolymers, such as the polysaccharides chitin and cellulose and the structural proteins collagens, also be preserved by such a mechanism under appropriate conditions? I shall address this question using chitin as the test-case, because, first, the mechanism of enzymatic degradation of chitin has been studied extensively, and, second, chitin fibrils in a protein matrix form the integuments of Recent arthropods and priapulids and the tough gut linings of Recent annelids (Jeuniaux, 1982), and such integuments and gut linings are splendidly preserved in the Burgess Shale fauna (Whittington, 1985; Briggs, Erwin, and Collier, 1994).

5.2. Mechanisms of bacterial degradation of chitin and the effect of Fe^{2+} ions adsorbed on chitin on the rate of such degradation.—Under normal marine conditions, the chitin that reaches the sea bottom is rapidly degraded by chitinolytic bacteria (Gooday, 1990a). As is the case with most particulate organic matter deposited on the sea bottom, decomposition of chitin under aerobic and dysaerobic conditions is rapid and thorough (Hedges and Keil, 1995). In contrast, decomposition under anaerobic conditions is slower and much more selective, so that certain types of organic molecules can be selectively preserved (Hedges and Keil, 1995). Degradation of chitin is achieved by enzymatic hydrolysis, that is, cutting of covalent bonds of the chitin backbone by the appropriate enzymes, bacterial chitinases (Gooday, 1990b). Because bacteria cannot ingest the chitin fibers, these fibers have to be cut into manageable fragments outside the bacteria. This is done by endochitinases, which cut the glycosidic bonds that bind the repeating *N*-acetyl-D-glucosamine units within the interior of the chitin molecule and/or by exochitinases, which cut off the terminal *N*-acetyl-D-glucosamine groups of chitin molecules (Gooday, 1990b). Extracellular chitinases do occur in the water column as free chitinases (Smucker and Kim, 1991) and therefore must also occur as free chitinases in pore waters of fresh sediments, but in sediments free chitinases are likely to be adsorbed within the organic coatings on mineral particles (Wetzel, 1991). However, in accordance with Chróst's (1991) argument for the dominance of ektoenzymes among the bacterial extracellular enzymes (sec 4), most bacterial extracellular chitinases are likely to be ektochitinases, whether they cut the glycosidic bonds that bind the repeating *N*-acetyl-D-glucosamine units within the interior of the chitin molecule (ekto-endochitinases) or cut off the terminal *N*-acetyl-D-glucosamine groups (ekto-exochitinases). Ektochitinases are not lost to adsorption on mineral particles or on the organic coatings of mineral particles, but to use them, bacteria have to be in direct contact with chitinous substrates. Indeed, Gooday (1990a) provides several SEM images of chitinolytic bacteria attached to their chitin-rich substrates.

As exemplified by the exochitinase of the bacterium *Serratia marcescens* (Perrakis and others, 1994), chitinases are globular proteins with active-site clefts in which a chitin strand has to fit properly if it is to assume the transition-state conformation that makes possible rapid cutting of one of its glycosidic bonds. As shown by a study of the chitinase/lysozyme of *Hevea brasiliensis* (rubber-tree), which belongs to the same class as the exochitinase of *S. marcescens*, the fit involves a series of very specific hydrogen bonds and van der Waals interactions between the appropriate functional groups of the enzyme and of the chitin (Terwisscha van Scheltinga and others, 1995).

At pH values close to 7, chitin strongly adsorbs heavy-metal ions such as Fe^{2+} and Cu^{2+} from seawater: when Muzzarelli and Tubertini (1969) added 4.0 g/l of finely dispersed chitin to seawater that had concentrations of both Fe^{2+} and Cu^{2+} raised to 0.44 mmol/l, at pH 7 and 20°C, they found that the chitin adsorbed 100 percent of the dissolved Fe^{2+} and 80 percent of the dissolved Cu^{2+}. Each Cu^{2+} ion adsorbed on chitin is bonded with nitrogen atoms of amino groups and with oxygen atoms of both hydroxyl and acetyl groups (Ershov and others, 1992); when adsorbed on chitin, the slightly larger Fe^{2+} ion must be bonded with the same groups. If the concentration of

Fe^{2+} ions in the pore water of the sediment is high enough to load chitin with adsorbed Fe^{2+} ions, the relevant functional groups of bacterial chitinases will not be able to achieve the requisite coordination with the chitin strands and cut their glycosidic bonds; in other words, bacterial decomposition of chitin will be inhibited. This is of interest because under favorable conditions, bacterial reduction of ferric iron can result in Fe^{2+} concentrations in pore waters of sediments as high as 0.5 to 0.7 mmol/l (Aller, Mackin, and Cox, 1986), comparable to those in Muzzarelli and Tubertini's (1969) experiments.

5.3. Environmental conditions that make possible relatively Fe^{2+}-rich pore waters.—Early diagenetic conditions that can give relatively high Fe^{2+} concentrations in pore waters of marine sediments are suboxic conditions in fine-grained marine sediments that are rich both in organic matter and in ferric iron. *Suboxic conditions,* in the sense of Froehlich and coworkers (1979), are operationally defined as the conditions under which the redox potential of the pore water is low enough for the bacterial dissimilatory reduction of dissolved nitrate and of manganese(IV) and iron(III) oxyhydroxides but is not low enough for bacterial reduction of sulfate ions (Froehlich and others, 1979; Berner, 1981; Coleman, 1985, Curtis, 1985). *Dissimilatory reduction of iron(III)* is the use of iron(III) as the external electron acceptor in bacterial metabolism (Lovley and Phillips, 1986, 1987, 1988; Lovley, 1991), in other words, it is the coupling of the oxidation of organic carbon or H_2 with the reduction of Fe(III) (Nealson and Saffarini, 1994). An example of dissimilatory iron(III) reduction particularly relevant here is the reaction

$$CH_2O + 4Fe(OH)_3 \rightarrow HCO_3^- + 4Fe^{2+} + 7OH^- + 3H_2O, \qquad (1)$$

where CH_2O symbolically represents organic matter when this reaction is carried out by bacteria. Dissimilatory iron(III) reduction can be carried out in sediments by a wide range of bacteria (Fredrickson and Gorby, 1996), of which some are specialized iron-reducing bacteria (Lovley and Phillips, 1988) and some are sulfate-reducers that are using the energetically more favorable iron(III) reduction pathway as long as iron(III) is available (Lovley and others, 1993; Coleman and others, 1993).

The terms *oxic*, *suboxic*, and *anoxic conditions* have been used by different authors in different ways; in the present paper they will be used in accordance with the operational definitions of Froehlich and others (1979), given in table 5. Concentrations of dissolved oxygen at the boundaries between these conditions according to Allison, Wignall, and Brett (1995), whose dysoxic conditions correspond to an oxygen-depleted range of oxic conditions in the sense of Froehlich and coworkers, are also given in that table. The upper limit of suboxic conditions appears to be somewhat lower than Allison, Wignall, and Brett's 0.2 ml O_2/l: in the oxygen-minimum layers of cold deep oceanic waters, zooplankton biomasses are significantly reduced below 0.15 ml O_2/l, a threshold below which at least partial use of anaerobic metabolism seems to be required (Childress and Seibel, 1998), and Devol (1978) found that aerobic respiration of bacteria in the Saanich Inlet ended at 0.09 to 0.17 ml O_2/l, while that of bacteria from the Costa Rica Dome area of the East Pacific oxygen-minimum layer ended at 0.05 to 0.13 ml O_2/l. As O_2 concentration declines further and becomes too low to measure, one can judge its decline by the increase in the concentration of dissolved H_2, which is an important reaction intermediate in bacterial consortia. In experiments done in the dark, at 20°C and 0.1 MPa, with freshwater sediments of Potomac River, Lovley and Goodwin (1988) found that during bacterial dissimilatory reduction of nitrate and of Mn(IV), the concentration of dissolved H_2 was lower than 0.05 nmol/l, but during bacterial dissimilatory reduction of Fe(III) the concentration of dissolved H_2 was equal to 0.2 nmol/l, and during bacterial dissimilatory reduction of sulfate it was as high as 1.0 nmol /l.

TABLE 5

Terminology for redox conditions in seawater and pore waters of Froehlich and others (1979), used in the present paper, compared with that of Allison, Wignall, and Brett (1995)

Terminology of Froehlich and Others (1979)	**Terminology of Allison, Wignall, and Brett (1995)**
Oxic Conditions: Concentration of dissolved O_2 is sufficiently high for aerobic metabolism of at least bacteria.	**Oxic Conditions**: Concentration of dissolved O_2 ranges from equilibrium with atmospheric oxygen down to 1.0 ml/l. **Dysoxic Conditions**: Concentration of dissolved O_2 ranges from 0.2 to 1.0 ml/l.
Suboxic Conditions: Concentration of dissolved oxygen and the redox potential are too low for aerobic metabolism, but too high for the bacterial reduction of sulfate. This is the redox range within which some bacteria carry out dissimilatory reduction of nitrate, manganese(IV), and iron(III).	**Suboxic Conditions**: Concentration of dissolved O_2 is between 0 and 0.2 ml/l; nitrate is being reduced to nitrite.
Anoxic Conditions: Concentration of dissolved oxygen and the redox potential are so low that bacterial reduction of dissolved sulfate occurs where sulfate is present, as in seawater.	**Anoxic Conditions**: Concentration of dissolved O_2 is 0 ml/l.

Note: Since Kaiho (1994) introduced the terms oxic, dysoxic, suboxic, and anoxic into foraminifer literature, foraminifer specialists have also been using these terms; however, they have inverted the order of dysoxic and suboxic and use the term dysoxic to denote O_2 concentrations between 0.1 and 0.3 ml/l and suboxic to denote O_2 concentrations between 0.3 and 1.5 ml/l. Besides having priority, the geochemist's usage is more consistent with the general usage of dys- and sub-, because while the literal translation of dysoxic can be either 'unoxygenated' or 'poorly oxygenated', that of suboxic is unambiguously 'below the oxygenated range'.

It is obvious that dissimilatory reduction of iron(III) requires both reactive organic matter and reactive iron(III), but it is not so obvious what qualifies as reactive organic matter or reactive iron(III) in a given situation. As already mentioned, organic substances in sediments consist mostly of particulate organic matter and of organic polymers adsorbed on mineral grains. To model realistically organic diagenesis in sediments under both oxic and anoxic conditions, Westrich and Berner (1984) had to divide the organic matter in sediments into a highly reactive fraction, a less-reactive fraction, and a fraction essentially non-reactive on the time scale of early diagenesis. Hedges and Keil (1995) have shown that there is actually a continuous spectrum of reactivities of organic substances in sediments. Where iron(III) is present in sediments, it occurs mostly in mineral particles or in coatings of amorphous iron(III) hydroxides or of iron(III) oxyhydroxides on mineral particles, for at the near-neutral pH values of most sediment pore waters the concentration of dissolved Fe^{3+} ions is very low (Stumm and Morgan, 1981, p. 238-249). Amorphous iron(III) hydroxides can rapidly dissolve to provide iron-reducing bacteria with Fe^{3+} ions, but the crystalline FeO(OH) polymorphs dissolve much less rapidly, and Fe_2O_3 dissolves very slowly. Because the rate of dissimilatory iron(III) reduction varies with the reactivity of the source of iron(III)

(Lovley and Phillips, 1988; Lovley, 1991; Nealson and Saffarini, 1994), this reactivity is a critical factor in marine sediments in which dissimilatory iron(III) reduction competes with the dissimilatory sulfate reduction. If Fe^{3+} ions are readily available, dissimilatory bacterial iron(III) reduction, which uses a more efficient terminal electron acceptor than the competing dissimilatory sulfate reduction, proceeds at concentrations of reaction intermediates, such as molecular hydrogen, that are too low for the dissimilatory bacterial sulfate reduction (Lovley and Phillips, 1986, 1987, 1988; Lovley, 1991; Lovley and others, 1993; Nealson and Saffarini, 1994; Fredrickson and Gorby, 1996).

Having a lower charge and being larger than Fe^{3+} ions, Fe^{2+} ions produced by dissimilatory iron(III) reduction (eq 1) are much more soluble at the near-neutral pH values of sediment pore waters (Stumm and Morgan, 1981, p. 264-268), so they can readily diffuse through the pore water and reach structural biopolymers. Structural biopolymers, being relatively resistant (refractory, recalcitrant) forms of organic matter (Kristensen, Aller, and Aller, 1991), will outlast most other constituents of animal and plant tissues. Their anionic functional groups will attract Fe^{2+} ions from the solution, and as long as Fe^{2+} ions remain adsorbed on these groups, structural biopolymers will be protected from enzymatic decay.

5.4. Nucleation and growth of iron(II)-rich layer silicates on preserved organics.—If a fine-grained siliciclastic sediment originally contained significant amounts of both reactive iron(III) hydroxides and reactive organic matter, then during the early diagenesis under suboxic conditions Fe^{2+} ions will tend to accumulate in the pore water and at anionic sites on interfaces between the aqueous solution and solid particles, including the anionic sites on biopolymers. Ultimately the solution will become supersaturated with respect to iron(II)-rich minerals, first iron(II)-rich clay minerals such as berthierine or ferroan saponite, and then siderite ($FeCO_3$) (Coleman, 1985; Aller, Mackin, and Cox, 1986; Curtis, 1987; Taylor and Curtis, 1995).

As we have seen in the case of bacterial cell walls, regular two-dimensional arrays of Fe^{2+} ions adsorbed on the anionic functional groups of structural biopolymers can provide templates for the nucleation of iron(II)-rich minerals; that is, given an adequate supersaturation with respect to an iron(II)-rich mineral, anions of these minerals can bond to the adsorbed Fe^{2+} ions, then more Fe^{2+} ions can bond to these anions, and so on, until a crystallite of critical size has formed. Thus if there is an adequate supply of both organic matter and iron(III) hydroxide, not only is chitin partially protected by adsorbed Fe^{2+} ions, but also an iron(II)-rich clay mineral such as berthierine or ferroan saponite may nucleate on the arrays of Fe^{2+} ions adsorbed on the chitin. A similar process, nucleation of heavy-metal oxyhydroxides, has been observed to occur on mollusk-shell detritus in some deep-sea settings (Poulicek, Machiroux, and Toussaint, 1986). *Berthierine*, a clay mineral of composition such as $(Fe^{II}, Mg)_{3-x}(Fe^{III},Al)_ySi_{2-z}Al_zO_5(OH)_4$, with $y = x + z < 1$ and with more iron(II) than magnesium, is suggested here as one possible early diagenetic iron(II)-rich silicate, because it is a common diagenetic silicate in iron(II)-rich sediments (Taylor and Curtis, 1995). However, if the concentration of dissolved silica in the pore water is relatively high because of the presence of amorphous silica, smectites, or volcanic glass, another iron(II)-rich clay mineral, *ferroan saponite*, of composition

$$(Na,K)_v(Ca,Mg)_w(Fe^{II},Mg)_{3-x}(Fe^{III},Al)_ySi_{4-z}Al_zO_{10}(OH)_2$$

$$\text{with } v + 2w = x + z - y < 0.40$$

and with more iron(II) than magnesium (Kohyama, Shimoda, and Sudo, 1973; Aja, Rosenberg, and Kittrick, 1991) could precipitate instead.

As in the case of mineralization of bacterial cell walls, berthierine and ferroan saponite that nucleated on the preserved biopolymers would grow into the available

space. This space could be the original pore space, or space created by the decay of organic matter of the cuticle and dissolution of the enclosed biominerals, for dissimilative reduction of iron(III) coupled with formation of ferrous saponite, with the silica derived from sponge spicules and aluminum from kaolinite, releases hydrogen ions,

$$\begin{aligned}&12Fe(OH)_{3\,(amorph.)} + 13.20SiO_{2\,(amorph.)} + 0.70Al_2Si_2O_5(OH)_{4\,(kaol)}\\&\quad + 3CH_2O_{(org.\,matter)} + 1.40Na^+_{(aq)}\\&\quad = 4Na_{0.35}Fe^{II}_3Si_{3.65}Al_{0.35}O_{10}(OH)_{2\,(sapon)}\\&\quad + 4.40H^+_{(aq)} + 3HCO^-_{3\,(aq)} + 14.70H_2O_{(l)} \qquad (2)\end{aligned}$$

If calcite is present in the same microenvironment, it would tend to dissolve,

$$CaCO_{3\,(calcite)} + H^+_{(aq)} = Ca^{2+}_{(aq)} + HCO^-_{3\,(aq)}, \qquad (3)$$

and this would create space for the growing iron(II)-rich clay minerals.

Precipitation of iron-rich clay minerals can occur rather rapidly. In the experiments of Michalopoulos and Aller (1995), done with iron-rich anoxic marine sediments of the Amazon delta at 28°C, smectitic clay minerals of average composition $K_{0.48}Na_{0.02}Al_{1.63}Fe^{II}{}_{0.45}Mg_{0.20}Ti_{0.02}Si_{3.24}Al_{0.76}O_{10}(OH,F,Cl)_2$ precipitated within 12 to 36 months on substrates that occur naturally in such sediments. I could not find any data on half-lives of structural biopolymers decaying under suboxic conditions in iron(III)-rich sediments. However, pieces of squid-pen chitin-protein that were exposed within a 20 μm nylon mesh to the seawater of the Hareness Inlet, Scotland, had a half-life of 3.1 months in that much more challenging, oxic environment (Gooday, 1990a), while burrow-lining tubes of sea anemones *Ceriantheopsis americanus*, made of a silk-like protein, were decaying in oxic seawater, anoxic seawater, and anoxic sediment with half-lives of 11, 20, and 38 months, respectively (Kristensen, Aller, and Aller, 1991).

Growth of clay minerals on biopolymers should protect these biopolymers from decay: small organic molecules adsorbed on mineral surfaces are protected to a greater or lesser extent from bacterial decomposition (Gordon and Millero, 1985), because, being already bonded to their mineral substrate, they do not react readily with bacterial enzymes. However, preservation of organic tissues by the attachment of pre-existing clay-mineral particles on them (Gabbott, 1998; Orr, Briggs, and Kear, 1998) is unlikely for the following reason. To be well protected from enzymatic hydrolysis, an adsorbed organic polymer needs to be bonded to its substrate at numerous functional groups: if large loops of polymer backbone are sticking into the aqueous solution, they can be readily attacked. To give such protection to an organized array of structural biopolymers, a clay-mineral particle needs to be attached to this array across a surface that fits the surface configuration of that array, with the surface ions of the clay-mineral particle matching the appropriate surface functional groups of the biopolymer array. Such a match is relatively easily attainable when a clay-mineral crystallite nucleates, helped by the electrostatic field of the adsorbed heavy-metal ions, on the surface of a biopolymer array. However, the probability of a suspended clay-mineral particle (1) having the correct surface configuration and (2) docking on the biopolymer array in the right orientation is extremely low.

5.5. Preservation of structural polysaccharides and collagen.—Although developed with regard to chitin, the foregoing arguments on the effect of metal-ion adsorption on the enzymatic hydrolysis of biopolymers are quite general, and one would expect them to apply to bacterial degradation of other structural biopolymers on which Fe^{2+} ions are strongly adsorbed: as long as large numbers of Fe^{2+} ions are adsorbed on their carboxyl, hydroxyl, phosphate, and/or amine groups, these biopolymers should also

be protected from enzymatic hydrolysis. Enzymatic hydrolysis of the structural polysaccharides of macroalgae, such as cellulose, requires very specific interactions between their functional groups and those of the active sites of the appropriate enzymes (Wilson and others, 1995). It is known that at near-neutral pH values, Cu^{2+}, Zn^{2+}, Cd^{2+}, and Pb^{2+} ions are adsorbed on the closely spaced hydroxyl groups of cellulose (Farrah and Pickering, 1978). In view of the already discussed similarities between the properties of Cu^{2+} and Fe^{2+} ions, it is certain that Fe^{2+} ions would also be adsorbed. The presence of Fe^{2+} ions would prevent the very specific set of interactions between the functional groups of cellulose and of the enzyme required for the cutting of a cellulose strand.

The structural polymers of chordates, echinoderms, and body walls of annelids are proteins, mainly collagens (Jeuniaux, 1982). Collagen fibers consist of arrays of rod-shaped tropocollagen molecules, each of which consists of three strands in a characteristic triple-helical conformation (van der Rest and Garrone, 1990). These triple helices incorporate numerous hydroxyproline residues, whose arrays of hydroxyl groups are sufficiently dense to create hydration sheaths around the helices (Bella and others, 1994). Enzymatic hydrolysis of the triple helices of tropocollagen molecules entails sets of very specific interactions between the functional groups of one strand of the helix and the functional groups of the active site of the enzyme (Perona and others, 1997). Adsorption of large numbers of Fe^{2+} ions on the functional groups of the collagen strand in question would make the required pattern of interactions impossible.

Although there is no experimental evidence to show that Fe^{2+} ions adsorbed on collagen inhibit enzymatic hydrolysis of collagen, support for this mechanism comes from investigations of an analogous process, iron tanning of leather. Iron tanning has not been studied much because it gives leathers that are inferior to the widely used chrome-tanned leathers. Chrome tanning, which among other things protects leather from enzymatic degradation, is based on cross-linking of collagen fibers by Cr^{3+} complexes in which terminal Cr^{3+} ions are complexed by functional groups of the collagen (Brown, Dudley, and Elsetinow, 1997; Fennen, 1998; Brown, 1999; Gayatri and others, 1999). Iron tanning is an analogous process in which cross-linking is accomplished by Fe^{3+} complexes; when the iron is introduced as the relatively mobile Fe^{2+} ions that are subsequently transformed into Fe^{3+} ions, the resulting leathers contain 2 to 3 percent of iron and have a feel similar to that of chrome-tanned leathers (Tonigold, Hein, and Heidemann, 1990). It is reasonable to conclude that although the larger and lower-charge Fe^{2+} ions would be adsorbed on collagen less strongly than Fe^{3+} ions, enzymatic hydrolysis of collagen is likely to be inhibited by the adsorbed Fe^{2+} ions as long as an Fe^{2+} concentration of the order of 0.1 mmol/l is maintained in the ambient aqueous solution.

6. Application of the proposed mechanism of fossilization to the fossiliferous beds of the Burgess Shale: depositional environment, original sediment, and diagenesis

6.1. Depositional environment.—The fine-grained turbidites of the Walcott Quarry Member and Raymond Quarry Member of the Burgess Shale Formation were deposited at the north- to northwest-facing passive margin of the Laurentian craton, at the latitude of about 20°N (Jurdy, Stefanick, and Scotese, 1995; Dalziel, 1997), off the Cathedral carbonate platform and on the open-ocean bottom, at depths of the order of 100 m (Fritz, 1971; Aitken and McIlreath, 1981; Collins and Stewart, 1991; Fritz and others, 1991; Fletcher and Collins, 1998).

The mineral composition of the rocks of the Phyllopod bed (table 1) indicates that the turbidity currents bypassed the carbonate platform, flowing through submarine canyons and then spreading in fans at the base of the Cathedral Escarpment

(Piper, 1972). The 10 to 50 mm thick fine-grained turbidite beds of the Phyllopod bed (table 1) would in their original loose state have been about 50 to 250 mm thick (compare Rieke and Chilingarian, 1974, p. 31-86). Each turbidite bed (consisting, when complete, of laminated siltstone followed by parallel-laminated siltstone-mudstone that is itself followed by non-laminated mudstone) was deposited from a single decelerating turbidity current laden with silt and clay (compare Carey and Roy, 1985; Piper and Stow, 1991). The entrained animals, seaweeds, and cyanobacterial colonies were brought in by the turbidity current and dropped with the rest of the sediment. Significantly, none of the animals, not even the burrowers, shows any sign of attempted escape; consequently, Whittington (1971a, 1985), Conway Morris (1990), Briggs, Erwin, and Collier (1994) all concluded that the animals were stunned or dead on arrival. The simplest explanation of such a fate of the entrained animals is that the environment was suboxic or anoxic; the high iron(II) content and low pyrite content (table 1) suggest that the conditions were suboxic.

The case for suboxia or anoxia is reinforced by the lack of trace fossils, such as tracks or burrows, even at the tops of the laminated turbidite beds of the Phyllopod bed (table 1). Considering the fact that these rocks were quarried with the express purpose of studying their fossils, this observation is highly significant. By the Middle Cambrian there was ample evidence for shallow burrowers on the same shelf of the Laurentian craton (Droser and Bottjer, 1988), and the Burgess Shale fauna itself includes a number of burrowers. Given the open-sea location, just off the shelf edge, the simplest interpretation of the lack of burrowing is that conditions were quasi-anaerobic or anaerobic in the sense of Bottjer and Savrda (1993), that is, the bottom water contained too little dissolved oxygen for macro- and meiofauna. In other words, the lack of trace fossils also suggests that the conditions at the bottom of the water column were permanently suboxic or worse.

The depositional environment of the even finer-grained turbidites of the Raymond Quarry member (table 1) underwent significant fluctuations throughout their deposition: at times the redox potential of Raymond Quarry sediments was so high that burrowers lived in the sediment; at other times it was so low that there were no burrowers, and consequently the sediment remained laminated. The conditions under which soft-bodied and lightly armored animals were preserved were those in which there was no burrowing and little pyritization (Allison and Brett, 1995). Therefore, the depositional environment of the fossiliferous beds of the Raymond Quarry Member also appears to have been suboxic.

6.2. The original composition and the diagenetic history of the fossiliferous beds.—Allison and Brett's (1995) mean mineral composition, in volume percent, of the argillites of the Phyllopod bed of the Burgess Shale (table 1) is quartz 38.5, illite and low-grade-metamorphic white K-mica (determined together as 'mica') 40.1, chlorite 2.5, calcite 6.6, dolomite 8.9, and siderite 3.3. We need to infer from this mineral composition both the mineral composition of the original sediments and the diagenetic and metamorphic history of these rocks.

Changes in bulk inorganic chemistry of mudrocks with deep burial diagenesis are a controversial topic. Hower and others (1976), who studied cuttings of Oligocene to Miocene shales of the Texas Gulf Coast from a well near Galveston over a depth interval of 1.2 to 5.5 km, concluded that with burial, the deepest samples lost significant amounts of H_2O, CaO, Na_2O, and CO_2. Similarly, Land and others (1997), who studied cuttings of Oligocene to Miocene shales from a well near Corpus Christi over a depth interval of 2.1 to 5.5 km, concluded that with burial, the deepest samples lost significant amounts of $CaCO_3$, mineral-bound H_2O, and SiO_2, additional Ca and Sr, light rare-earth elements, Fe, and Li, and gained K_2O and Rb. However, in these rocks it is difficult to disentangle changes in bulk chemistry with depth that are due to

deep diagenesis from those due to differences in the compositions of the original sediments. It is clear that significant export of ionic and molecular species dissolved in pore water occurs with the compaction and diagenesis of mudrocks (for example, Füchtbauer, 1961; Emery, Smalley, and Oxtoby, 1993), but because of the low solubilities of most inorganic constituents of the rock in the pore water, the percentage changes in the contents of these constituents in the rock that can be carried out by expelling pore water are miniscule. There is, however, the possibility of changes in bulk chemical and mineral composition caused by waters circulating through the fractured shale, a possibility raised by Land and others (1997). In the case of the Burgess Shale one has to consider such changes seriously, because deep diagenetic waters have caused the second, late-diagenetic stage of dolomitization of the nearby rim of the Cathedral Formation carbonate platform (Yao and Demicco, 1997). Whether these waters also caused changes in the argillites can be judged from the mineralized fractures (veinlets) in the argillites of the Phyllopod bed (sec 2). According to E. S. Larsen (*in* Walcott, 1912) these fractures form two sets: (1) a set of parallel veinlets, normal to the bedding, which were cemented with chlorite, re-opened, and re-cemented with fine-grained calcite and nests of cupriferous pyrite, and (2) a set of late fractures with irregular surfaces coated with carbonates, of no interest here. The mineral assemblage of the veinlets of the first set is a reflection of the mineral assemblage of the host rocks, and there is no sign of alteration along the fracture walls; thus these veinlets are dehydration veins in the sense of Coombs (1993). The expelled aqueous solutions were at first supersaturated with respect to chlorite; then, presumably because of a pressure drop, they became supersaturated with respect to calcite and pyrite. Thus the aqueous solutions expelled from the compacting mudrocks were rich in $Si(OH)_4$, Ca^{2+}, Mg^{2+}, Fe^{2+}, HCO_3^-, and HS^-; however, the contents of all these species in the pore water being small in comparison with the contents of the corresponding constituents of the enclosing argillite, only the content of H_2O in the Burgess Shale was changed significantly.

Regarding changes in mineralogy with deep burial, Hower and others (1976) concluded that the main reaction that took place with the deep burial of Texas Gulf Coast shales was

$$\text{smectite} + \text{potassium feldspar} + \text{detrital mica} = \text{illite} + \text{chlorite} + \text{quartz} \quad (4)$$

and that dissolution of calcite with the loss of calcium and CO_2 was also important. Land and others (1997) concluded that the following changes occurred with the deep burial of Texas Gulf Coast mudrocks: (1) the percentages of detrital calcite, kaolinite, potassium feldspar, calcic plagioclase, and muscovite decreased, (2) the percentage of detrital quartz did not change significantly, (3) the percentages of chlorite and albite increased, and (4) mixed-layer illite-smectites continuously transformed from smectite-richer to illite-richer compositions. With further burial, illite-rich smectite would have been transformed into illite (compare Wang, Frey, and Stern, 1996).

It follows that with deep burial, most smectite present in the original sediments of the fossiliferous Burgess Shale beds would have been converted into illite (as shown below, a minor fraction was converted into chlorite). However, there remains the possibility that the original sediments of the fossiliferous Burgess Shale beds contained a large fraction of detrital illite. To find whether this was the case, we can turn to the relation between tectonics and sedimentation. Detrital illite ultimately comes from erosion of shales, argillites, and slates exposed in young mountain belts (Chamley, 1989, p. 163-192; Pujos, Latouche, and Maillet, 1996; Debrabant, Lopez, and Chamley, 1997). At the time of the Burgess Shale deposition, the relevant margin of the Laurentian craton had not been subjected to mountain building for about 1.3 Ga (Hoffman and Bowring, 1984; Hoffman, 1989; Fritz and others, 1991; Dalziel, dalla

Salda, and Gahagan, 1994; Cecile, Morrow, and Williams, 1997). Therefore, there was no source for a significant fraction of detrital illite in the original sediment. Moreover, we know that on the opposite side of the continent, at comparable southern paleolatitudes, smectite was produced by the weathering of red-bed deposits of the Appalachian Basin from the Ordovician to the Permian (Mora and Driese, 1999). It follows that the present abundances of illite and white mica largely reflect the original abundance of smectite derived from the weathering of the rocks of the Canadian Shield and that the sediment that gave rise to the mineral assemblage of table 1 consisted mainly of smectite, quartz, and biogenic calcite, presumably with minor potassium feldspar (eq 4).

The present contents of siderite, ferroan dolomite, and chlorite, which together amount to 14.7 volume percent of the average rock of the Phyllopod bed, indicate that extensive bacterial oxidation of organic matter on the iron(III)-reducing pathway has taken place. Both siderite and early-diagenetic precursors of iron(II)-rich chlorite, such as berthierine and ferroan saponite (Hillier, Fallick, and Mater, 1996; Bettison-Varga and Mackinnon, 1997), are strictly diagenetic constituents of Phanerozoic sedimentary rocks, products of oxidation of organic matter on the iron(III)-reducing pathway (Coleman, 1985; Aller, Mackin, and Cox, 1986; Curtis, 1987; Taylor and Curtis, 1995). The original dolomite presumably crystallized during the early diagenesis as rather pure $CaMg(CO_3)_2$ (Kelts and McKenzie, 1982; Baker and Burns, 1985), but with increasing temperature, this dolomite would have reacted increasingly with some of the original calcite and some of the original siderite to produce the present ferroan dolomite (Anovitz and Essene, 1987). Correcting for that reaction, one obtains for the carbonate minerals at the end of the early diagenetic stage 9.7 volume percent $CaCO_3$, 3.0 percent $CaMg(CO_3)_2$, and 6.0 percent $FeCO_3$.

The observed amounts of iron-rich chlorite, siderite, and ferroan dolomite imply a significant amount of iron in the original sediment of the fossiliferous beds of the Burgess Shale. Released by weathering under an atmosphere comparable to today's and transported only a short distance from the continent, this iron would have been transported primarily as iron(III) hydroxide adsorbed on smectite particles brought into the sea by rivers (Froehlich and others, 1979; Aller, Mackin, and Cox, 1986; Lovley and Phillips, 1986, 1987; Lovley, 1991; Hedges and Keil, 1995; Debrabant, Lopez, and Chamley, 1997). The estimated mean iron(II) content in the argillite of the Phyllopod bed is 4.0 wt percent (sec 2); to produce this amount of iron(II) by the reduction of iron(III) hydroxide according to eq (1), an amount of organic carbon equal to 0.21 wt percent of the present argillite had to be oxidized into carbonate. Precipitation of ferroan saponite instead of berthierine would have required a relatively high concentration of dissolved silica (compare Aja, Rosenberg, and Kitrick, 1991), obtainable by dissolution of some of the original iron-poor smectite and of siliceous spicules of demosponges other than *Vauxia* and of hexactinellid sponges (Walcott, 1920; Rigby, 1986; Conway Morris, 1990; Briggs, Erwin, and Collier, 1995, p. 64-87).

During the deep diagenesis, the already discussed transformation of iron-poor smectite into illite (see also Wang, Frey, and Stern, 1996) and of iron-rich smectite (ferroan saponite) into chlorite (Hillier, Fallick, and Mater, 1996; Bettison-Varga and Mackinnon, 1997) took place, as well as continued equilibration of carbonate minerals.

With the even deeper burial, very-low-grade metamorphism occurred. Illite-smectite became illite (compare Wang, Frey, and Stern, 1996). The partial replacement of chlorite by white K-mica, described in section 3.3, suggests metamorphism at a low metamorphic temperature but relatively high pressure, resulting in formation of phengite (a somewhat magnesian and ferroan white mica) by a reaction similar to Massonne and Schreyer's (1987)

$$\text{chlorite} + \text{K-feldspar} = \text{phengite} + \text{phlogopite} + \text{quartz} + H_2O. \qquad (5)$$

6.3. Preservation of biopolymer tissues and diagenetic mineralization of Burgess Shale fossils.—As shown in section 3.2, some of the cuticles, tough gut linings, and other biopolymer tissues of Burgess Shale organisms were demonstrably preserved as kerogen (table 2), and the "silvery films" documented in photographs of many more Burgess Shale organisms are plausibly interpreted as organic remains transformed into kerogen. Numerous chitinous arthropod cuticles and annelid gut walls were preserved (for example, Briggs, Erwin, and Collier, 1994), as well as collagenous body walls of the chordate *Pikaia*, echinoderms, and annelids (Whittington, 1985; Briggs, Erwin, and Collier, 1994), polysaccharid cell walls of seaweeds (Walcott, 1919; Whittington, 1985; Briggs, Erwin, and Collier, 1994), and sheaths of the cyanobacterium *Marpolia* (Whittington, 1985; Briggs, Erwin, and Collier, 1994). These remains were preserved in suboxic, Fe^{2+}-rich pore waters of the Burgess Shale sediment by the mechanism outlined in sections 5.2, 5.3, and 5.5. The gradual transformation of the residual chitin, collagen, and polysaccharide into kerogen with deep burial would have been analogous to the transformation of preserved structural biopolymers of microalgal outer walls into kerogen with deep burial (Derenne and others, 1991).

Preservation of biopolymer tissues in the fossiliferous beds of the Burgess Shale was not always accompanied by diagenetic mineralization, for there is no such mineralization around Butterfield's (1990a) worm cuticle (table 4). However, in a number of cases diagenetic mineralization either accompanied the preservation of biopolymer tissues or replaced such tissues (tables 3 and 4). The general mechanism of such diagenetic mineralization of organic remains by suboxic, Fe^{2+}-rich pore waters (sec 5.4) is applied here to the documented cases of such mineralization in the Burgess Shale.

Mineral replacements of dorsal exoskeletons of the trilobite *Olenoides* (table 4) are considered first, because: (1) diagenetic mineralization of soft-bodied and lightly armored animals cannot be understood in isolation from that of other organisms and from the diagenesis of the sediment; (2) replacements of *Olenoides* exoskeletons are the best-documented cases of diagenetic mineralization of Burgess Shale fossils; and (3) even the dorsal exoskeletons of trilobites, though mineralized more heavily than their crustacean analogues, contained a significant fraction of organic matter. The last assertion is supported by the following arguments. First, plastic deformation of trilobite exoskeletons subjected to predator attack (Nedin, 1999) suggests relatively high contents of biopolymers in them. Second, the commonly dark color of fossilized trilobite exoskeletons, which tends to be comparable to the colors of ostracod and inarticulate brachiopod shells and darker than those of bivalve, snail, and articulate brachiopod shells (H. M. Steele-Petrovich, personal communication, 1999), suggests significant concentrations of organic matter: many ostracod shells and shells of phosphatic articulate brachiopods have high contents of organic matter (Maddocks, 1992; Williams, 1997), and, unlike calcite and apatite, kerogen turns dark with heating. Third, hard cuticles of recent arthropods generally consist of a very thin waxy epicuticle, a thin and thinly layered exocuticle that is hardened by quinone tanning, and a thick and thickly laminated but pliable endocuticle, with both the exocuticle and the endocuticle made up of plywood-like interstratifications of laminae that consist of parallel bundles of chitin-protein fibers in a protein matrix (Roer and Dillaman, 1984; Neville, 1998; Fahrenbach, 1999; Farley, 1999). Among the decapod crustaceans, both the exocuticle and the endocuticle are also impregnated with low-magnesium calcite, the exocuticle moderately, the endocuticle heavily except for a thin membranous layer at its base (Roer and Dillaman, 1984; Giraud-Guille, 1984). Similarly, dorsal cuticles of exceptionally well preserved trilobites show a thin organic epicuticle, a thin and finely laminated exocuticle, a thick and thickly laminated endocuticle, and a thin and finely laminated inner layer, with both the exocuticle and the endocuticle consisting of

interstratified laminae containing bundles of organic fibers and laminae of low-magnesium calcite (Mutwei, 1981; Wilmot and Fallick, 1989; Dalingwater and others, 1991; Whittington and Wilmot, 1997).

In the documented replacements of dorsal exoskeletal cuticles of trilobites in the Burgess Shale, the cuticles were replaced by aggregates of platy chlorite crystals oriented at high angles to the cuticle surface (table 4). Because the late-diagenetic chlorite crystals would have inherited the orientations of their predecessors, the original berthierine or ferroan saponite (Bettison-Varga and Mackinnon, 1997), the original berthierine or ferroan saponite crystals had grown right across the plywood-like interstratification of chitin-protein layers and across the low-magnesium calcite crystals that had grown on these layers, which means that the organic matrix was decaying and the calcite crystals were dissolving. Clay minerals such as berthierine and saponite form platy crystals because they grow much faster parallel to their basal planes than normal to their basal planes. If numerous, densely packed, tiny clay-mineral crystals initially formed on the surface of the cuticle, due to rapid nucleation at high supersaturation, the ultimate extents of their growth would be strongly dependent on their crystallographic orientations: those crystals whose basal planes were nearly orthogonal to the cuticle surface could continue growing in one lateral direction until they reached the opposite surface of the cuticle or encountered crystals growing from that opposite surface, while those crystals not so oriented would stop growing as soon as they impinged in all lateral directions on the neighboring clay-mineral crystals. The final product of such growth is an array of lath-shaped crystals that are nearly orthogonal to their substrate, a texture that differs from the textures of smectite and chlorite coatings on sandstone grains (for example, Hillier, Fallick, and Mater, 1996) only in that it was generated by replacement of the decaying organic constituents and of calcite that was dissolving according to eqs (2) and (3).

While preservation of originally calcified dorsal exoskeletons of trilobites is common in many settings, preservation of trilobite appendages or of most of the lightly-built arthropods found in the Burgess Shale is not; the cuticles of trilobite appendages and of most non-trilobite arthropods of the Burgess Shale had presumably been hardened by quinone tanning but not heavily biomineralized. Thus it is highly significant that diagenetic mineralization of the arthropods *Marella* and *Alalcomenaeus* (table 3) extends over their whole bodies, including the appendages. The variability of major-element ratios within this mineralization (table 3) is readily explainable by the sequence of replacements discussed in the previous section, but without cross sections further interpretation is impossible. S. Conway Morris and K. Pye's observation of illitic mineralization of a specimen of the putative holothurian *Eldonia* (table 3), a truly soft-bodied animal, is also highly significant.

Phosphatic shells of Recent discinid and lingulid inarticulate brachiopods consist of granules of carbonate fluorapatite (4-8 nm across), chitinous strands, and fibrillar collagens, all within a matrix of glucosaminoglycans, with up to 50 wt percent of the laminated shell consisting of the listed organics (Williams, 1997). The complex organic structure of Conway Morris's (1990) *Dyctionina* shell (table 4) seems to have been entirely replaced by apatite, which even overgrew its periostracum. Tangential nucleation of the presumably iron(II)-rich clay minerals on the *Dyctionina* periostracum, which were ultimately converted into a potassium mica, is analogous to that often observed on bacterial cell walls (Konhauser and Urrutia, 1999). Note that the preservation of phosphatic brachiopod shells rules out a two-step mechanism of fossilization of the organic remains that would have consisted of an initial replacement of organic tissues by apatite and a later replacement of apatite by silicates. Note also that the depositional setting of the Burgess Shale (sec 6.2) was different from settings that favor phosphatization (sec 8.3).

With deep burial, the original platy crystals of berthierine or ferroan saponite were transformed into platy crystals of chlorite of the same orientation (compare Bettison-Varga and Mackinnon, 1997). Finally, during anchimetamorphism, partial replacement of chlorite by phengitic (somewhat magnesian and ferroan) white micas took place (Massonne and Schreyer, 1987; Livi and others, 1997), starting at the interface between the chloritic fossil and the illite-rich matrix. If the iron(III)-reducing bacteria were as small as those isolated by Lovley and Phillips (1988) from the Potomac River Estuary (1-2 μm long and 0.2-0.5 μm in diameter), their remains may not be recognizable after the very-low-grade metamorphism.

Note that, as discussed in sections 5.2 to 5.5, there are two obvious conditions for the preservation of animal and algal remains on the described reaction pathway. The first is rapid attainment of suboxic conditions, so that the damage done by the relatively indiscriminate decay under oxic conditions is avoided. The second is presence of sufficient reactive iron(III) in the sediment for suboxic conditions with a high concentration of Fe^{2+} ions in the pore water; this is required for protection of the structural biopolymers of cuticles, gut linings, et cetera by adsorbed Fe^{2+} ions and, where local sediment composition is favorable, growth of iron(II)-rich clay minerals on them. The third condition will become obvious when another, related type of fossil preservation is examined in the next section.

7. THE THIRD CONDITION FOR THE BURGESS SHALE-TYPE PRESERVATION OF SOFT-BODIED AND LIGHTLY ARMORED FAUNA, IDENTIFIED BY COMPARISON WITH THE HUNSRÜCK SLATE-TYPE FOSSILIZATION OF SOFT-BODIED ANIMALS

The conditions for Burgess Shale-type preservation of soft-bodied and lightly armored fauna can be clarified by comparison with the preservation of animal morphology by the replacement of soft tissues with pyrite, herein referred to as the Hunsrück Slate-type of fossilization. Pyritization of animal remains occurs by a two-step process: first, oxidation of organic matter by sulfate-reducing bacteria,

$$SO_4^{2-} + 2CH_2O \rightarrow HS^- + HCO_3^- + H_2CO_3 \quad (6)$$

and, second, precipitation of the produced sulfide ions by reaction with dissolved Fe^{2+} ions,

$$2HS^- + Fe^{2+} = FeS_2 \quad (7)$$

(Goldhaber and others, 1977; Raiswell and others, 1993). Two well-studied examples of such preservation are Beecher's Trilobite Bed in upstate New York and Hunsrück Slate near Bundenbach and Gemünden in Rheinland-Palatinate (hereinafter: the Hunsrück Slate). Beecher's Trilobite Bed contains many well-preserved specimens of *Triarthrus eatoni*, complete with appendages (Beecher, 1902; Raymond, 1920; Briggs, Bottrell, and Raiswell, 1991). In the Hunsrück Slate fossils are rare, but they include trilobites and other arthropods, fish, ophiuroids, and orthoconic and goniatitic cephalopods, all with pyritized soft tissues (Stuermer, 1970; Stürmer and Bergström, 1973; Bergström, 1990; Briggs and others, 1996; Bartels, Briggs, and Brassel, 1998). Hunsrück Slate fossils studied by scanning electron microscopy show replacement textures consisting of euhedral to subhedral pyrite crystals, a few micrometers across, which enclose scattered pyrite framboids (Briggs and others, 1996). As in the Burgess Shale, there is no evidence of preservation of soft tissues by phosphatization in either Beecher's Trilobite Bed or Hunsrück Slate.

Fossiliferous beds of the Burgess Shale (Phyllopod bed), Beecher's Trilobite Bed, and Hunsrück Slate are compared in table 6. It is notable that all these beds (1) are parts of laminated successions of fine-grained marine turbidites, deposited at depths of

TABLE 6

Fossiliferous beds of the Burgess Shale (Phyllopod Bed), Beecher's Trilobite Bed of the Frankfort Shale (Upper Ordovician), and Hunsrück Slate (Lower Devonian)

Properties	Phyllopod Bed of the Burgess Shale	Beecher's Trilobite Bed of the Frankfort Shale near Rome, New York	Fossiliferous Hunsrück Slate Beds near Bundenbach and Gemünden, Rhineland-Palatinate
Sedimentary Successions Containing Fossiliferous Beds	Fine-grained marine turbidites, "a fairly homogeneous succession of finely laminated, calcareous, silty and graphitic mudstones" (Fletcher and Collins, 1998). Having undergone anchizonal metamorphism without developing slaty cleavage (see text), they are actually argillites.	A thick succession of fine-grained marine turbidite beds (Cisne, 1973; Briggs, Bottrell, and Raiswell, 1991).	A thick succession of mostly fine-grained marine turbidites. Have undergone upper-anchizone or lowest greenschist-facies metamorphism (Briggs and others, 1996), with vitrinite reflectances $R_{o\,max}$ from 5.9 to 6.7 percent (Ecke and others, 1985). Slaty cleavage is commonly subparallel to the bedding, so the fossils are largely unaffected (Bergström, 1990; Briggs and others, 1996).
Detailed Sedimentology of Fossiliferous Beds	A sequence of fine-grained turbidite beds, 10-50 mm thick; each complete bed consists of a basal calcareous siltstone unit, alternating laminae of mudstone and calcareous siltstone, alternating mudstone and kerogen-rich laminae, and unlaminated mudstone (Piper, 1972)	A graded turbidite siltstone bed, about 40 mm thick, lying on a scoured mudstone bed with remnants of burrows (Cisne, 1973; Briggs, Bottrel, and Raiswell, 1991). Well-preserved trilobites lie 7 to 10 mm above its base, parallel to the bedding plane and strongly aligned by the current, as many facing up as facing down (Beecher, 1902; Raymond, 1920; Cisne, 1973; Briggs, Bottrell, and Raiswell, 1991).	The original sediments were generally laminated, with few traces of infaumal burrowers, but an abundant epifauna of surface-dwelling arthropods has left a variety of traces on the bedding surfaces and there are also constructed burrows of infaunal animals that obtained food and oxygen from the surface, of which *Chondrites* is common (Briggs and others, 1996; Sutcliffe, Briggs, and Bartels, 1999).
Organics, Iron, and Pyrite in Fossiliferous Beds	Organic carbon contents measured by Butterfield (1990a) in 3 samples, 0.09 to 0.13 wt percent. Mean total iron corresponding to the mean mineral composition obtained by Allison and Brett (1995) from 12 samples is 4.0 wt percent. G. Steiger (in Walcott, 1912) obtained for one carbonate-poor sample 2.2 wt percent of total iron and 0.24 wt percent of sulfide sulfur. Pyrite contents below the detection limit of X-ray diffractometry (Allison and Brett, 1995).	In a 200 mm-thick sequence of fine-grained turbidite beds, with Beecher's Trilobite Bed in the middle, Briggs, Botrell, and Raiswell (1991) found high total iron content (5.31 ± 0.44 wt percent, Raiswell, 1997), low total organic carbon (0.02-0.20 wt percent), and low total sulfur content (not reported, but degrees of pyritization range from 0.10 to 0.45).	Briggs and others (1996) found (a) high total iron (5.72 ± 0.29 wt percent in slate that is adjacent to pyritized fossils, 5.44 ± 0.20 wt percent in a reference block with a pyrite lens, and 5.21 ± 0.37 wt percent in slate that is adjacent to unpyritized fossils from other Hunsrück Slate localities); (b) low total organic carbon (0.33 ± 0.05 wt percent near pyritized fossils, 0.34 ± 0.06 wt percent in the reference block); and (c) low total sulfur (0.17 ± 0.06 wt percent in samples adjacent to pyritized fossils, 0.23 ± 0.05 wt percent in the reference block).
Sulfur Isotopic Composition in Fossiliferous Beds	No data.	$\delta^{34}S$ values (relative to CDT): early framboidal pyrite, -20 to -15 permil; pyrite that coats or replaces trilobite exoskeletons, -3 to +21 permil; pyrite that coats or replaces trilobite limbs, +10 to +27 permil (Briggs, Botrell, and Raiswell, 1991).	$\delta^{34}S$ values (relative to CDT): pyritized fissils, +8.0 ± 9.3 permil, and slate adjacent to them, -12.0 ± 11.6 permil; pyrite associated with unpyritized fosils from other localities, -6.3 ± 7.1 permil, and slate adjacent to these fossils, -7.9 ± 9.5 permil (Briggs and others, 1996).

the order of hundred meters, and (2) have relatively high iron contents and much lower contents of both total organic carbon and total sulfur.

There was a difference in the availability of oxygen in the bottom water of the Phyllopod bed, on the one hand, and the bottom waters of Beecher's Trilobite Bed

and the fossiliferous beds of the Hunsrück Slate, on the other. Bottom water above the Phyllopod bed was definitely suboxic or worse, for there are no burrows or tracks at the tops of turbidite beds, and burrowers brought in with the sediment made no attempt to escape. Beecher's Trilobite Bed was deposited on a scoured mudstone bed that had been burrowed (Cisne, 1973), so bottom water was oxic before deposition of the bed. Tracks and constructed burrows were found in a number of fragments of Hunsrück Slate beds (Sutcliffe, Briggs, and Bartels, 1999), but the relation between these fragments and the fragments with fossils is unknown, and oxygen concentration in the bottom water may have fluctuated as it did in the Raymond Quarry Member of the Burgess Shale, in which soft-bodied and lightly armored fossils are not preserved in burrowed beds (table 1).

The availability of oxygen in the bottom water overlying Beecher's Trilobite Bed and the fossiliferous beds of Hunsrück Slate has been estimated from the degree of pyritization (DOP) of these rocks, defined as the content of pyrite iron divided by the sum of the content of pyrite iron and the content of HCl-soluble iron (which is potentially reactive to H_2S). From the DOP values summarized in table 6, Briggs, Botrell, and Raiswell (1991) concluded that Beecher's Trilobite Bed (table 6) was overlain by well-oxygenated bottom water, and Briggs and others (1996) concluded the same about fossiliferous Hunsrück Slate beds. There can be little doubt that very low DOP values would also be obtained for the argillites of the Phyllopod bed, possibly leading to the same conclusion. However, there is a problem in applying Raiswell and coworkers' (1988) DOP < 0.42 criterion for sediments deposited under well-oxygenated bottom water to the laminated fine-grained turbidites considered here. Raiswell and others (1988) established that DOP was less than 0.42 in sediments deposited under well-oxygenated bottom water by measuring DOP values of fine-grained siliciclastics that had been largely homogenized by bioturbation and had preserved abundant trace fossils and local body fossils. The difference in textures between bioturbated and laminated rocks should not affect the competition between aerobic bacterial degradation and bacterial degradation on the sulfate-reducing pathway, because extensive degradation by both these processes requires diffusion of their terminal electron acceptors, O_2 and SO_4^{2-} respectively, into the sediment from the bottom water. In the first approximation (neglecting the very low concentration of these acceptors at the sites of decay), the flux of each of these electron acceptors is proportional to the product of its diffusion coefficient and its bottom-water concentration; because the bottom-water concentration of SO_4^{2-} is constant, it is the bottom-water concentration of O_2 that determines whether aerobic or sulfate-reducing bacteria will be more successful. However, when competition with bacterial degradation on the iron(III)-reducing pathway is also considered, the situation is changed, for its terminal electron acceptor, iron(III) hydroxide, is distributed throughout the sediment. If deposition is so fast that diffusional transport of SO_4^{2-} from the bottom water is severely curtailed, bacterial degradation of organic matter on the iron(III)-reducing pathway is favored as long as there is plenty of iron(III) hydroxide in the sediment; in other words, as the deposition rate increases, DOP tends toward zero whether oxygen concentration in the bottom water is high or low. Therefore, in the case of laminated, fine-grained, *iron-rich* marine turbidites, whether they retained their laminae because the bottom water could not maintain a fauna or because successive turbidite beds were being deposited too fast for recolonization, low DOP is not a reliable indicator of well-oxygenated bottom water.

Indeed, sulfur isotopic analyses of sulfides in Beecher's Trilobite Bed and in fossiliferous Hunsrück Slate beds, given in table 6 as deviations from the Cañon Diablo troilite standard, indicate that supply of SO_4^{2-} ions to the sediment was cut off relatively early. Briggs, Botrell, and Raiswell (1991) recognized from their sulfur isotope ratios

that when the early framboidal pyrite precipitated in Beecher's Trilobite Bed (at high supersaturations, compare Wang and Morse, 1996), the system was open to bottom-water sulfate, but sulfide ions incorporated into the pyrite that coated and replaced trilobite cuticles were derived from a dwindling supply of pore-water sulfate. Therefore, Briggs, Botrell, and Raiswell concluded that the exceptional preservation of trilobites in Beecher's Trilobite Bed resulted from the rapid burial of dead trilobites in a sediment rich in reactive iron but poor in organics, in which seawater SO_4^{2-} ions diffusing toward the trilobite carcasses enabled sulfate-reducing bacteria to oxidize the reactive organic matter of these remains, but the sulfide produced reacted promptly with the abundant Fe^{2+} ions of the pore water and pyrite precipitated right on the organic remains. Similarly, Briggs and others (1996) concluded that pyritization of fossils in the original sediment of Hunsrück Slate proceeded after the inflow of sulfate from the bottom water was cut off, because $\delta^{34}S$ values of pyritized fossils are much higher than those of the pyrite dispersed in the slate surrounding the pyritized fossils, those of the pyrite in the slate surrounding unpyritized fossils from other localities, and those of the pyrite associated with unpyritized fossils. Their final conclusion, based on the pyrite precipitation model of Raiswell and others (1993), was:

> A combination of two factors is critical to soft-tissue preservation, rapid burial, and sediment chemistry. Carcasses must be buried rapidly to avoid breakdown by benthic scavengers under oxic conditions. The surrounding sediment must contain (1) low concentrations of available organic matter (hence pyrite formation is organic matter-limited, and residual dissolved iron and sulfate can migrate to the decay site) and (2) unusually high concentration of iron that is reactive toward dissolved sulfide, permitting rapid and efficient pyritization of the soft tissue (Briggs and others, 1996, p. 657-658).

Raiswell (1997) pointed out that early-diagenetic pyritization of calcium carbonate shells requires that enough CO_2 be generated to cause undersaturation with respect to the calcium carbonate of these shells; this condition, he concluded, is satisfied when sediments are subjected to relatively slight sulfate reduction. Pyritization of calcified trilobite dorsal exoskeletons implies that this condition was also satisfied during the early diagenesis of the fossiliferous beds of the Hunsrück Slate.

Both Beecher's Trilobite Bed and the fossiliferous Hunsrück Slate beds appear to have had molar ratios between the reactive iron(III) and the organic carbon in the sediment higher than four, so that bacterial oxidation of organic matter on the iron(III)-reducing pathway proceeded for a long time. This maintained high concentrations of dissolved Fe^{2+} ions in the suboxic pore waters and therefore also high surface concentrations of adsorbed Fe^{2+} on the structural biopolymers of animal cuticles and tough gut linings, which protected these biopolymers. By the time the supply of iron(III) was depleted and bacterial oxidation of organic matter on the sulfate-reducing pathway became competitive (sec 5.3), there was little organic matter left outside the animal remains. Because of the high initial concentration of Fe^{2+} ions in the pore water, pyritization took place right on the structural biopolymers of the dead fauna (eq 7). As dissolved Fe^{2+} ions were consumed, and their concentration declined, Fe^{2+} ions that had been adsorbed on structural biopolymers were increasingly desorbed from them; this left the biopolymers unprotected and enabled the bacteria to degrade them.

Early diagenesis of fossiliferous Burgess Shale beds was similar to those of Beecher's Trilobite Bed and of fossiliferous Hunsrück Slate beds in that it proceeded in a relatively iron(III)-rich sediment overlain by seawater, that some precipitation of pyrite did occur, and that pyrite precipitation was terminated because rapid accumulation of overlying sediments cut off the diffusive supply of dissolved sulfate. The difference is that in the fossiliferous Burgess Shale beds the diffusive supply of sulfate was terminated so early that organic biopolymers were extensively preserved and were at most lightly coated with pyrite.

Therefore, the third condition for the Burgess Shale type of fossil preservation is that the diffusive supply of dissolved sulfate from the overlying seawater be cut off before extensive pyritization can occur, so that structural polymers of animal cuticles and of tough gut linings are left protected by the adsorbed Fe^{2+} ions to evolve into kerogen with or without growth of iron(II)-rich silicates around them.

8. Environmental conditions that made possible the occurrence of Burgess shale-type preservation in Lower and Middle Cambrian environments

8.1. Translation of geochemical conditions into oceanographic conditions.—Why was Burgess Shale-type preservation of soft-bodied and lightly armored animals relatively common in the Lower and Middle Cambrian and so rare afterward? To answer this question, one needs to translate the already stated geochemical conditions for Burgess Shale-type preservation into oceanographic conditions that would allow this type of early diagenesis in an open-marine setting such as that of the Burgess Shale. The first geochemical condition is avoidance of the relatively indiscriminate oxic decay of the animals' tissues; in an open-sea setting, this requires (A) rapid transport of the animals, live or freshly killed, by a fine-grained turbidity current into (B) a deeper setting with suboxic bottom water, which (C) is not exposed to a current that could winnow the sediment. The second geochemical condition is that early diagenesis occur under steady suboxic conditions with a relatively high concentration of Fe^{2+} ions in the pore water; this requires that (D) the sediment contains an adequate amount of reactive iron(III), that is, iron(III) hydroxide, and (E) the sediment is protected from mechanical disturbances that could expose it to oxic water, that is, it lies below the wave base of even great storms. The third geochemical condition, termination of the diffusive transport of sulfate from the water column to the sediment before extensive pyritization could occur, requires (F) rapid burial of the fossiliferous bed under a thick cover of subsequent turbidites.

8.2. Settings in which steady suboxic conditions occur on the present-day ocean bottom.—Steady suboxic conditions seem to occur on the present ocean bottom only where the innermost zones (most depleted in oxygen) of some oxygen-minimum layers of low- to middle-latitude oceans impinge on the continental slopes and seamounts; elsewhere, suboxic conditions on the sea bottom are transient states on the way to anoxia (Diaz and Rosenberg, 1995). Development of oxygen-minimum layers in the present global ocean has been quantitatively explained by Shaffer and Sarmiento (1995) and Shaffer (1996), who treated them with a model consisting of a shallow high-latitude surface layer (in part covered by ice), high-latitude deep ocean water, low- to middle-latitude surface layer, and low- to middle-latitude deep ocean water (the last modelled with continuous resolution). Using realistic physical and biogeochemical processes with carefully constrained parameters and calibrating the physical aspects of the model with the observed temperature and ^{14}C profiles, they predicted profiles of dissolved oxygen and phosphate (now definitely known to be the limiting nutrient over most of the ocean, see Tyrell, 1999) that are in impressive agreement with the mean observed profiles for different ocean basins. These authors showed that as the cold, turbulent, high-latitude surface water, with 7.4 ml/l of dissolved oxygen (close to saturation with respect to atmospheric oxygen) and 1.4 μmol/kg of dissolved phosphate (a high value possible because at high latitudes new production of organic matter is limited by the available light), sinks to become high-latitude deep ocean water, its mean O_2 concentration is reduced to about 65 percent of its original value by the decay of sinking detrital organic matter. This deep ocean water is carried by thermohaline circulation toward the low latitudes, and on the way it is exposed to the rain of organic detritus from the middle- to low-latitude surface layer. Because the sinking organic matter decays exponentially with depth, it reduces O_2 concentration most dramatically in the upper part of the deep ocean water, at depths of a few

hundreds of meters, thus creating the oxygen-minimum layer. Conversely, the concentration of dissolved phosphate, very low in the middle- to low-latitude surface ocean water, rapidly increases with depth until it reaches a maximum in that layer because of the combined contributions of the original dissolved phosphate of the deep oceanic water and the phosphate released by the decay of organic matter.

Oxygen depletions in these layers can be very pronounced even when averaged over broad oceanic regions: North Pacific Ocean has a mean O_2 concentration at the oxygen minimum as low as 0.96 ml/l, and North Indian Ocean as low as 0.53 ml/l (Shaffer, 1996). Where the flux of organic detritus is very high, that is, where the dissolved phosphate of upwelling oxygen-minimum waters generates a very high organic productivity in the surface layer and a large flux of organic detritus into the deep ocean water, severe oxygen depletion can occur, with extensive suboxic and even anoxic conditions. Thus, for example, off the Peru coast, bacterial reduction of nitrate (compare sec 5.3) is widespread in the upper part of the oxygen-minimum layer (Codispoti, 1981), while along some stretches of the Peru coast, suboxic conditions start within 80 m from the ocean surface, and O_2 concentrations below 0.11 ml/l extend over depth intervals of hundreds of meters (Arthur, Dean, and Laarkamp, 1998). These conditions are comparable to those postulated in section 6.1 for the depositional environment of the fine-grained turbidites of the Burgess Shale, but the high current velocities along these stretches of the Peru coast prevent deposition of muddy sediments (Arthur, Dean, and Laarkamp, 1998).

Because of the relatively high concentrations of dissolved phosphate within oxygen-minimum layers (which according to Shaffer, 1989, could exceed 2 mmol/l), where these layers impinge on the continental slope in areas of slow sedimentation, phosphate from the bottom water and from the decaying organic matter and fluoride from the bottom water react with calcite of the sediment to produce the accumulations of carbonate fluorapatite that are known as phosphorites (Froehlich and others, 1979; Van Cappellen and Berner, 1988; Krajewski and others, 1994; Glenn and others, 1994). This is an important indirect indicator of suboxic conditions within past open-ocean settings.

8.3 Development of suboxic conditions in the past.—Under the present regime of thermohaline circulation, generally thought to be driven by the cooling of oceanic high-latitude surface waters, the extent and intensity of suboxic conditions are controlled by the intensity of the deep thermohaline circulation, by the new organic production of the high-latitude surface waters, and by the new organic production of low- to middle-latitude surface waters (Sarmiento, Herbert, and Toggweiler, 1988; Shaffer, 1989, 1996; Herbert and Sarmiento, 1991). The thermohaline circulation is coupled with the equator-to-pole thermal gradient and is also controlled by the distribution of the continents, the influx of fresh water into high-latitude regions, et cetera (Herbert and Sarmiento, 1991; Seidov and Haupt, 1997; Poulsen and others, 1998). When, in modeling, one increases the flux of decaying organic matter at middle to low latitudes, suboxic conditions develop at the oxygen minimum and spread upward and downward from it, and then anoxic conditions develop at the oxygen minimum and spread upward and downward within the suboxic zone (Shaffer, 1989); thus at times of ocean-wide anoxia, widespread development of suboxic conditions above and below the anoxic layer is to be expected. The increase of new organic production within the high-latitude shallow ocean water to the limit allowed by the present supply of phosphate would result in widespread anoxia in the oceans (Shaffer, 1996). Intensification of the thermohaline circulation would result in the spread of suboxic conditions and in the extreme cases anoxia, while intensification of convective mixing of high-latitude surface and deep water would have the opposite effect (Herbert and Sarmiento, 1991).

The extents and intensities of suboxic and anoxic conditions in the Lower Paleozoic may also have been influenced by contributions to the thermohaline circulation from warm, saline waters that were sinking because of evaporative concentration over the then extensive shelf and marginal seas (Brass, Southam, and Peterson, 1982; Southam, Peterson, and Brass, 1982). Today there are such contributions from the Red Sea and the Persian Gulf (You, 1997), but they are insignificant on the global scale; however, they may have been significant at times when there were extensive shelf and marginal seas in the zones of net evaporation, as, for example, in the Middle and Upper Cretaceous (Poulsen and others, 1998). In any case, judging from what we know about the Cretaceous to Recent dynamics of the global ocean, suboxic conditions could have been widespread within oxygen minimum layers of Lower and Middle Cambrian oceans.

8.4. Evidence for widespread suboxic and anoxic conditions in the Lower and Middle Cambrian.—Several lines of evidence suggest that suboxic conditions prevailed in the depositional environments of the upper continental slope during much of the Early and Middle Cambrian. First, there is extensive evidence for the worldwide occurrence of black shales and therefore anoxia during the Early and Middle Cambrian (Brasier, 1980, 1992; Thickpenny and Leggett, 1987); in fact, black shales indicative of anoxia were widespread throughout the Early Paleozoic (Berry and Wilde, 1978). Moreover, as pointed out in section 8.3, Shaffer's (1989) model of oxygen-minimum layers predicts that development of anoxia in the open oceans is accompanied by widespread development of suboxic conditions. Second, extensive formation of phosphorites, which are indicative of widespread phosphate-rich suboxic waters, occurred during the Lower and Middle Cambrian (Brasier, 1980, 1992; Cook and Shergold, 1984; Cook, 1992). Third, there is isotope geochemical evidence for repeated episodes of mass mortality in the Lower and Middle Cambrian seas, extending well into the Upper Cambrian, which have been interpreted as consequences of mixing of well-oxygenated water masses with anoxic deep water masses (Ripperdan and others, 1992; Saltzman and others, 1995; Saltzman, Runnegar, and Lohman, 1998; Perfetta, Shelton, and Stitt, 1999).

Finally, there is paleontological evidence for impingement of suboxic water on the continental slopes during the Lower and Middle Cambrian. Ocean bottom exposed to suboxic water of oxygen-minimum layers supports at most a meager benthic meiofauna and no benthic macrofauna (Diaz and Rosenberg, 1995), so its potential for fossilization of local fauna is very low. However, the scarcity of burrowing in Lower and Middle Cambrian sediments of the continental slope and continental rise is in sharp contrast with the worldwide abundance of trace fossils in shallow-water siliciclastics of the same age (Seilacher, 1974; Crimes, 1974, 1987, 1992). Moreover, the Lower and Middle Cambrian shallow-water trace fossils included a number of ichnogenera that in the Ordovician colonized deep-water environments (Crimes and Anderson, 1985; Hofmann and Patel, 1989; Crimes, 1992). It is utterly implausible that the spread of the trace-producing fauna into adjacent *unoccupied* deep-water niches would take some 70 my. Crimes (1974) suggested that the delay in colonization of deep oceans by trace-forming fauna may have been due to inadequate supplies of organic detritus within the muds of the early deep-sea floor, but the above-mentioned wide extent of Cambrian black shales contradicts that hypothesis. Thus Crimes's (1974) alternative suggestion, that the delay in colonization of deep-sea bottoms by trace-making fauna was the result of a low oxygen concentration in the deep sea, seems to be unavoidable.

8.5. Evidence for uncommonly iron-rich fine-grained siliciclastics in the Cambrian and Ordovician.—The critical difference between the fine-grained siliciclastics of Early and Middle Cambrian continental-slope environments and those of better-understood, later, oxygen-depleted environments, such as that at the Cenomanian-Turonian bound-

ary (Schlanger and others, 1987; Arthur, Schlanger, and Jenkyns, 1987; Arthur, Dean, and Pratt, 1988), may be in their curiously high content of reactive iron. Reactive iron in sediments and sedimentary rocks is operationally defined as pyrite iron plus iron that is readily extractable from the sediment or ground sedimentary rock in a concentrated HCl aqueous solution (either within one minute in boiling 12M HCl solution or within 24 hrs in room-temperature 1M HCl solution); in shales, that would be iron in pyrite and in carbonates, in part iron in sheet silicates, but not iron in magnetite or in well-crystallized hematite (compare Berner, 1970; Haese and others, 1997). Raiswell and Berner (1986) and Raiswell and Al-Biatty (1989) have studied a series of shale samples of different ages whose original sediment was deposited under oxic conditions (recognized by the presence of benthic fossils and/or burrowing); following their usage, these shales are hereinafter referred to as normal marine shales. In a set of 226 samples of Cambrian, Ordovician, and a few Silurian normal marine shales analyzed by Raiswell and Al-Biatty (1989), organic carbon content ranged from 0.1 to 3.7 wt percent, the content of reactive iron ranged from 0.7 to 8.8 wt percent, and there was a pronounced positive correlation between the two contents. In contrast, in Raiswell and Al-Biatty's set of 102 samples of Devonian, Carboniferous, Jurassic, and Cretaceous normal marine shales, organic carbon content ranged from 0.1 to 10.4 wt percent, while reactive iron content, after an initial increase with the increasing organic carbon content, remained in the range of 1 to 3 wt percent. The original organic carbon contents of Raiswell and Al-Biatty's Cambrian to Silurian shales would not have been significantly decreased by oxidation on the iron(III)-reducing pathway, because it takes only 0.054 g of organic carbon to reduce 1 g of iron(III) (see eq 1). However, it follows from the stoichiometry of pyrite and from eq 8,

$$2CH_2O_{(org.\ matter)} + SO^{2-}_{4\,(aq)} = 2HCO^{-}_{3\,(aq)} + H_2S_{(aq)} \qquad (8)$$

that it takes 0.915 g of organic carbon to produce 1 g of pyrite iron. Thus Raiswell and Al-Biatty's (1989) iron-rich and highly pyritized Cambrian and Ordovician shales (compare also Raiswell and Berner, 1986) were derived from muddy sediments whose organic carbon contents were comparable to those of later muddy sediments, but whose contents of reactive iron were anomalously high.

Raiswell and Al-Biatty (1989) could not tell whether their Cambrian and Ordovician shales were diagenetically enriched in iron derived from adjacent sediments, or their original muddy sediments were exceptionally rich in reactive iron. For the latter case they envisaged iron being derived from deep lateritic weathering, like that of Aller, Mackin, and Cox's (1986) iron-rich inner-shelf muds off the Amazon River mouth, or from terrestrial volcanic debris; both would be capable of providing large fluxes of reactive iron to the sea at times when siliciclastic fluxes were suppressed. However, extensive diffusion of iron into shales would itself require close interstratification of these shales with iron-rich sediments or volcanics, so that in the absence of widespread volcanic activity such iron enrichment would also require large fluxes of iron from weathering. The exceptionally high iron abundance in Raiswell and Al-Biatty's Cambrian and Ordovician shales does not stand in isolation: Van Houten and Purucker (1984), Van Houten and Arthur (1989), and Young (1989) have found that glauconitic sediments were very abundant on Middle and Upper Cambrian and Early Ordovician continental shelves, oolitic ironstones (iron oxide- and chamosite-rich) were very abundant on Ordovician and Devonian continental shelves, and all these iron-rich sediments were stratigraphically associated with black shales. The above authors all agree that the iron-rich continental-shelf sediments were deposited at times of transgressions, when high sealevels reduced the rate of erosion of silicate rocks, and the invading seas mobilized iron-rich weathering products that had accumulated on the invaded lowlands. However, comparison with Jurassic and Cretaceous sedimentary

sequences shows that the difference between Raiswell and Al-Biatty's (1989) Cambrian and Ordovician shales and their later equivalents cannot be due only to a difference in the extent of transgressions.

Today, an estimated 78 percent of the flux of iron from the weathering land masses to the oceans is transported by rivers, the remainder by wind (Duce and Tindale, 1991). The iron carried to the oceans by rivers is overwhelmingly particulate (Duce and Tindale, 1991); some of it is carried in the bed load (as sand-sized mafic clasts), but most of it is carried in the suspended load, as iron hydroxide coatings on clay-mineral particles or as colloidal iron hydroxide particles stabilized by adsorbed organics (Sholkovitz, 1976; Boyle, Edmond, and Sholkovitz, 1977; Lisitsyn, 1978, p. 204-210). Deposition of that iron occurs in a highly non-uniform way, most of it in estuaries and deltas or downcurrent from them (Lisitsyn, 1978, fig. 62). Thus while Raiswell and Al-Biatty's (1989) iron-rich Cambrian and Ordovician shales indicate ready availability of iron in near-continental settings in which Burgess Shale-type fossil preservation was occurring, it is not clear whether they reflect a pattern of iron deposition in the oceans that was significantly different from today's. If they do, the difference is likely to be due to a qualitative difference between the weathering of Cambrian and Ordovician land masses, with their thin and rootless covers of liverworths, hornworths, mosses, and lichens (Shear, 1991; Gray, 1993) and Devonian and later land masses, with their thick covers of vascular plants equipped with deep roots and mycorrhizae and capable of much greater production of organic ligands capable of mobilizing iron (Shear, 1991; Gray, 1993; Berner, 1992, 1997; Taylor and Osborn, 1996).

9. The role of adsorption of Fe^{2+} ions on structural biopolymers in some other cases of fossilization of soft-bodied and lightly armored animals

9.1. The Soom Shale.—There are interesting similarities and some intriguing differences between the Burgess Shale-type preservation and the preservation of soft-bodied and lightly armored fauna in the Upper Ordovician Soom Shale of the Cape Province of South Africa, recently studied in considerable detail by Gabbott (1998). The Soom Shale is a black shale, seldom thicker than 15 m, lying on tillites and covered by a thin-bedded argillaceous siltstone; the contact with the tillites is in part gradual, in part intercalated, therefore the original sediments were deposited in cold, not very deep water (Theron, Rickards, and Aldridge, 1990). Gabbott's (1998) analyzed samples of the Soom Shale consist mainly of quartz and illite, with chlorite and pyrite and with less common apatite and alunite-crandallite solid solutions (alunite is $KAl_3(SO_4)_2(OH)_6$; crandallite is $CaAl_3(PO_4)_2(OH)_5$).

Fossil preservation in the Soom Shale is similar to that in the Burgess Shale in two respects: (1) some refractory organic remains are preserved as kerogen (acritarchs, spores, chitinozoans, and an enigmatic needle-shaped fossil), (2) eurypterid and some trilobite cuticles, ostracod shells, and some chitinozoan tests were replaced by illite (Gabbott, 1998). However, fossil preservation in the Soom Shale differs from the preservation in the Burgess Shale in three respects: (1) In the Soom Shale illite also replaces some apatitic shells of inarticulate brachiopods (which are preserved as apatite in the Burgess Shale), some apatitic conodont elements, and in places even conodont muscle tissue (Gabbott, 1998), which must have first been replaced by apatite (compare Briggs and Kear, 1994). (2) In the Soom Shale the originally aragonitic shells of orthocone nautiloids, the originally calcitic exoskeletons of trilobites, and the residual apatite parts of inarticulate brachiopods and conodont elements were dissolved, leaving molds (Gabbott, 1998), though remnants of apatitic conodont elements are occasionally preserved (Gabbott, Aldridge, and Theron, 1995). (3) In the Soom Shale alunite-crandallite often accompanies or substitutes for illite

(Gabbott, 1998); this suggests replacement of illite by alunite-crandallite (see below), but the textures have not been documented.

Gabbott (1998) interpreted the alunite-crandallite of the Soom Shale as a product of early diagenesis, formed under unusually acid conditions on the sea bottom. The requisite sea-bottom conditions would be bizarre, because precipitation of alunite requires high concentrations of both potassium and sulfate ions, such as are typically encountered in shallow hydrothermal alteration of granitic rocks by originally H_2S-rich water vapor (Hemley and others, 1969).

The analyzed samples of Soom Shale were core samples, hand specimens, and fossil-bearing hand specimens from the Sandfontein Farm and the Keurbos Farm. Gabott notes:

> Sediments analyzed show a variation in the degree of weathering. Least weathered are the core samples, but even these sometimes show pervasive shear zones and split easily into discs; therefore, they may have been altered to some degree from an original early diagenetic mineralogy by contact with meteoric waters. Sediment samples from Sandfontein have been similarly affected, and in addition, have been subjected to surface weathering processes, including those induced by percolating meteoric waters. The least pristine samples are from Keurbos, which, in addition to exhumation, have been subjected to deep Neogene weathering and alteration by extensive shear-zone fluids (Gabbott, 1998, p. 638).

Alunite is known to form as a product of weathering of pyrite-rich shales in a dry climate, where oxidation of pyrite produces sulfuric acid, low humidity prevents excessive dilution of the resulting acid, so that pore waters are sulfate-rich, and potassium is being released by dissolution of illite in these waters (Thiry and others, 1995). The climatic setting of Soom Shale outcrops fits incipient weathering of that type, and release of calcium by the dissolution of calcite and apatite and release of phosphate by the dissolution of apatite explain the precipitation of alunite-crandallite solid solutions instead of pure alunite.

When weathering is taken into consideration, Gabbott's (1998) evidence on the Soom Shale and its fossils is consistent with early diagenesis under suboxic conditions, with the high concentration of Fe^{2+} ions protecting structural biopolymers from decay and iron(II)-rich smectites nucleating on the organic remains and replacing different shells, followed by pyritization that led to early loss of iron from the originally iron(II)-rich replacive smectites. However, phosphatization of calcitic and aragonitic shells shows that the bottom water was much richer in phosphate than the bottom water of Burgess Shale sediments, and pyritization may have proceeded much farther in the original sediments of the Soom Shale than in those of the Burgess Shale.

9.2. Fossilization of soft-bodied and lightly armored animals and of plants within siderite concretions.—One can reasonably infer from the arguments on the effect of adsorbed Fe^{2+} ions on the bacterial decay of structural biopolymers (secs 5.2, 5.3, and 5.5) that adsorbed Fe^{2+} ions played a crucial role in the fossilization of soft-bodied and lightly armored animals and of plants in siderite concretions. An example of such preservation is the Pennsylvanian Mazon Creek Fauna of the Francis Creek Shale Member, Carbondale Formation, northeastern Illinois, deposited partly in laminated muds of freshwater environments (Braidwood fauna) and partly in alternating mud and silt laminae of a brackish estuarine environment dominated by diurnal tides (Essex fauna; Baird and others, 1985, 1986; Kuecher, Woodland, and Broadhurst, 1990). Siderite concretions grew around the animal and plant remains by precipitation of siderite within the pore spaces of the mud or laminated mud and silt (Baird and others, 1985, 1986; Kuecher, Woodland, and Broadhurst, 1990). The physical nature of the animal fossils has been described as follows:

> Essex soft-bodied animals, including medusae, siphonophores, the problematic organism *Tullimonstrum gregarium* . . . , molted shrimp, numerous polychaetes, and the larval fish *Esconichthys apopyris* are preserved as flattened composite impressions; these appear as light-colored areas against a background of darker siderite. The jellyfish *Essexella asherae* ("the blob") often displays a thin film of dark gray-green microcrystalline pyrite on the impression surface, which further

> accentuates this fossil. Other blobs served as planar surfaces for precipitation of sphalerite or kaolinite, which typically obscures detail. Bivalves, gastropods, and chitons are typically moldic; shell molds and voids within shells not filled with sediment often contain sphalerite, calcite, or kaolinite. However, many of these spaces are found unfilled. Shrimp (particularly unmolted *Belotelson magister*), the cycloid crustacean *Cyclus americanus,* rare scorpions, an echiuroid worm *Coprinoscolex ellogimus,* and several polychaetes display thin surficial films of variably degraded organic cuticle (Baird and others, 1986, p. 276).

In other words, siderite precipitated around animal remains, but it did not replace either the structural biopolymers of invertebrate cuticles and of fish skin, which in these Fe^{2+}-rich pore waters had to be stabilized by adsorption of Fe^{2+} ions, nor calcium carbonate shells. The latter means that the pore waters were saturated with respect to calcite, which is not always the case in environments of formation of siderite concretions (Allison and Pye, 1994). Precipitation of siderite without precipitation of iron-rich clay minerals implies a starting silicate mineral assemblage that is stable in contact with the Fe^{2+}-rich pore waters. The survival of siderite and lack of pyrite in the estuarine sediments that contained the Essex fauna imply lack of diffusive transport of sulfate ions into the sediment, presumably due to rapid sedimentation and to the relatively low sulfate concentration in the brackish water of the tide-dominated estuary.

9.3. Did iron(III) reduction play a role in the preservation of Ediacaran soft-bodied Fossils? —Wollanke and Zimmerle (1990) observed that in general unusually rich fossil deposits tend to contain or to have contained volcanic ash or smectites, an association that they attributed to the rheological properties of smectite-rich sediments. However, this association may instead be due to volcanic ash and smectite-rich sediments providing reactive iron(III) for the early organic diagenesis on the iron(III)-reducing pathway. The common occurrence of amorphous iron(III) hydroxides adsorbed on smectites and their effective use in dissimilatory iron(III) reduction were discussed in section 5.3. It should be also noted that volcanic glass itself is a reactive source of ferric iron: mean Fe_2O_3 contents of common volcanic rocks in Le Maitre's (1976) compilation of chemical analyses range from 1.48 wt percent for rhyolite to 3.79 wt percent for basalt, and this iron can be readily leached from fine fragments of such rocks (Berger, Schott, and Loubet, 1987). Thus Wollanke and Zimmerle's generalization could reflect the role of adsorbed Fe^{2+} ions in the initial stage of fossilization.

A particularly interesting case is that of the soft-bodied Ediacaran fossils (Glaessner, 1984). In their classical locality, the Ediacara Range of South Australia, these fossils occur within the Ediacara Member of the Rawnsley Quartzite, in a tide-dominated lagoonal sequence of sandstone beds with thin siltstone seams (Jenkins, Ford, and Gehling, 1983). Wade (1968) has shown that in the Ediacara Range these fossils generally occur as casts and molds at siltstone seams and that, therefore, the animal carcasses had to last long enough for their relief to be fixed by early diagenesis of the overlying and/or underlying sand. During the Tertiary, rocks of the Ediacara Member in the Ediacara Range were subjected to deep weathering (Jenkins, Ford, and Gehling, 1983), so that the siltstone seams have been eroded almost entirely from the outcrops, and the mineral composition of the sandstone has been drastically altered. However, in core samples of Ediacara Member sandstones, quartz framework grains, both cemented and uncemented, are coated with iron(III) oxide or oxyhydroxide (Wade, 1968). If the sands in the lagoon had been coated with iron(III) hydroxides, the associated silts should also have been, which again indicates an association between the temporary preservation of soft-bodied animals and the presence of iron(III) hydroxides.

The circumstances are much clearer in the case of the Ediacaran fossils of Mistaken Point, Newfoundland, which I have examined *in situ.* There, Ediacaran fossils occur within a sequence of turbidite beds that now grade from graywacke to argillite; they occur as casts on the ripple-marked top of a graded turbidite bed, covered by about 10 mm of tuff (Misra, 1969). Simple coincidence of the occurrence of tuff, which

is most conspicuous in the gray turbidite sequence because of its creamy weathering, and the occurrence of fossils of soft-bodied animals, which appear not to occur in the rest of the sequence, is implausible. Like the analogous casts/molds in the Ediacara Range (Wade, 1968, fig. 20), the casts of soft-bodied organisms at the Mistaken Point required temporary preservation of these organisms until the molds in the overlying sand were stabilized by very early diagenesis; only then could the plastic flow of the underlying mud fill the molds. The creamy weathering of the tuff indicates formation of iron(III) oxyhydroxides and therefore betrays a certain abundance of iron. Therefore, one can conclude that temporary preservation of Mistaken Point fossils was achieved by adsorption of Fe^{2+} ions derived by suboxic diagenesis from the iron(III)-rich volcanic glass of the tuff.

Ediacaran oceans were stratified, with deep anoxic waters (Kaufman, Jacobsen, and Knoll, 1993; Logan and others, 1995; Canfield and Teske, 1996; Kimura and others, 1997; Shields and others, 1997, 1999). According to Cook (1990), there was a major phosphate deposition peak in the Ediacaran Period, not nearly as high as the phosphate deposition peak at the Precambrian-Cambrian transition, but comparable to that at the end of the Early Cambrian. Therefore, one wonders whether the worldwide preservation of Ediacaran faunas is related to an encroachment of suboxic waters on the continental shelves (see sec 8.2).

10. CONCLUSIONS

Preservation of diagenetically altered remnants of the original organic tissues and formation of chlorite/illite coatings and cuticle replacements, both documented in the Burgess Shale fossils, can be understood as products of the same mechanism of fossilization of soft tissues and hardened cuticles. This mechanism consists of: (1) adsorption on structural biopolymers, such as chitin, cellulose, and collagens, of Fe^{2+} ions released during the oxidation of organic matter by iron(III)-reducing bacteria; (2) the resulting inhibition, by the adsorbed Fe^{2+} ions, of further bacterial hydrolysis of these biopolymers, which preserves these biopolymers until they become kerogens; (3) in some microenvironments, nucleation of crystals of an iron(II)-rich clay mineral, a berthierine or a ferroan saponite, on the arrays of Fe^{2+} ions that are adsorbed on the preserved biopolymer and growth of such clay-mineral crystals to form a coating on the organic remains and/or to replace parts of the organism.

Adsorption of Fe^{2+} ions on structural biopolymers as a means of protecting organic fossil remains from decomposition by bacterial enzymes is a novel suggestion and needs to be demonstrated by direct experimentation. This suggestion is supported by two considerations. The first is that strong adsorption of Fe^{2+} ions on chitin has been shown to occur at bulk water chemistry, Fe^{2+} concentration, and pH comparable to those in pore waters of suboxic iron-rich sediments, and while data on the adsorption of Fe^{2+} ions on collagen and cellulose seem to be lacking, other heavy-metal ions are strongly adsorbed on these biopolymers under appropriate conditions. The second consideration is that Fe^{2+} ions bonded with functional groups of chitin, collagen, or cellulose would prevent the very specific configuration and bonding that a biopolymer strand has to achieve within the active-site cleft of the appropriate bacterial enzyme to make enzymatic hydrolysis possible.

Close examination of two other mechanisms recently proposed for Burgess Shale-type preservation of soft tissues shows that they are implausible. Preservation of soft tissues by inactivation of extracellular enzymes on clay minerals would require an unlikely, maladaptive reliance of bacteria on free extracellular enzymes. Preservation of soft tissues by attachment of pre-existing clay-mineral particles onto them would require a sequence of highly improbable events: precise dockings of particles with contact-surface configurations and charge distributions that match those of the surface of biopolymer arrays that form cuticles, gut linings, et cetera.

The critical factors in the Burgess Shale-type preservation of Early and Middle Cambrian soft-bodied and lightly armored animals and seaweeds were probably as follows: (1) Dumping of these organisms, still alive or freshly killed, by turbidity currents into the suboxic moderately deep water of Early and Middle Cambrian oceans, which enabled them to avoid the relatively indiscriminate oxic decomposition. (2) The long stage of decomposition of most of the organic remains on the iron(III)-reducing pathway, made possible by the abundance of reactive iron(III) hydroxides and by the steadily suboxic early-diagenetic environment, during which the relatively resistant structural biopolymers of cuticles, tough gut linings, et cetera were protected from enzymatic hydrolysis by the adsorbed Fe^{2+} ions. (3) The very early curtailment of diffusive supply of sulfate to the fossil-bearing beds of the Burgess Shale, which occurred before precipitation of pyrite could deplete the dissolved and adsorbed Fe^{2+} ions, so that the structural polymers of cuticles and tough gut linings were left protected by the adsorbed Fe^{2+} ions.

The sediments of Beecher's Trilobite Bed and of the Hunsrück Slate near Bundenbach and Gemünden that contain pyritized soft-bodied animals were also rich in reactive iron(III) and relatively poor in organic matter, so that high concentrations of dissolved Fe^{2+} ions were maintained in the suboxic pore waters until localized sulfate reduction started (Briggs, Botrell, and Raiswell, 1991; Briggs and others, 1996). Structural biopolymers of the soft-bodied animals of these sediments were protected by adsorbed Fe^{2+} ions until the sulfide ions produced by sulfate-reducing bacteria scavenged the Fe^{2+} ions and pyritized the organic remains.

The proposed model of early diagenesis that results in Burgess Shale-type fossil preservation depends critically on the availability of steady suboxic depositional environments in an open oceanic setting, at depths of the order of hundreds of meters, in which iron(III)-rich fine-grained sediments, rapidly deposited with the entrained animals by turbidity currents, could accumulate without being disturbed by storm waves and deep currents. Evidence discussed in the present paper suggests that such conditions were common in the Early and Middle Cambrian.

When the deep alunitic weathering to which fossiliferous outcrops and core samples of the Upper Ordovician Soom Shale were exposed is taken into account, Gabbott's (1998) evidence on the preservation of soft-bodied fossils in the Soom Shale is consistent with a Burgess Shale-type early diagenesis under suboxic conditions.

Obviously, Fe^{2+} ions adsorbed on structural biopolymers of cuticles and the like play a crucial role in the fossilization of soft-bodied and lightly armored animals within siderite concretions. Fe^{2+} ions adsorbed on structural biopolymers of cuticles probably also played a crucial role in the fossilization of the enigmatic Ediacaran soft-bodied organisms in the classical localities of the Ediacara Range of South Australia and at Mistaken Point in Newfoundland.

ACKNOWLEDGMENTS

I thank Dr. Miriam Steele-Petrovich for convincing me to write this paper, advising me in matters paleontological, and patiently helping me present my arguments in a way appropriate for a multidisciplinary audience. I thank Professor Colin Barker, Dr. Gary E. Jenneman, and Mr. Christopher R. M. McFarlane for their helpful comments on the first draft and Professor Robert C. Aller, Dr. Nicholas J. Butterfield, and Professor Simon Conway Morris for their constructive criticism of the first, short version of this paper. I am particularly indebted to Dr. Butterfield for carefully reviewing the second version, raising further questions, and making clear to me the nature of some of the evidence. I also thank Mr. Roger H. Box for the use of a computer at a critical time and the management of Phillips Petroleum Company for the permission to publish the original note.

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