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FOSSILS TO FERTILIZER: TAPHONOMIC IMPLICATIONS OF URANIUM ROLL FRONTS

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ABSTRACT

Wyoming is famous for its deep structural basins containing both abundant vertebrate fossils and uranium-ore deposits in the form of roll fronts. Research conducted in The Breaks, an area of badlands in the northeastern corner of the Hanna Basin, south-central Wyoming, shows that these two disparate phenomena have an important relationship. Vertebrate bones and teeth, composed of bioapatite, are chemically stable under most diagenetic conditions. The chemical changes that occur at the leading edge of a propagating roll front, however, are capable of eliminating these fossils. This happens as pyrite is oxidized, which releases sulfuric acid to the ground water. Sulfuric acid reacts vigorously with apatite, releasing soluble phosphate. Phosphate liberated from the dissolved bones and teeth provides a valuable, often limiting, nutrient to plants or lichens once the roll front is exposed on the ground surface. In The Breaks, bedrock permeability is the most important factor controlling the distribution of roll fronts and, therefore, also of vertebrate fossils. Thus, patterns of roll-front distribution, observed from differing lithologic characteristics or floral assemblages growing on the rock, might provide a useful prospecting tool for paleontologists.

INTRODUCTION

In this paper, I discuss field relationships between roll fronts and vertebrate fossils in The Breaks in south-central Wyoming (Fig. 1), and I propose a simple geochemical model for the interaction between vertebrate fossils and roll fronts. The pattern of geochemical alteration in The Breaks is essentially identical to that observed in areas affected by uranium roll-front deposits in other Tertiary basins in Wyoming (Davis, 1969; Granger and Warren, 1974; Harris and King, 1993; Higgins, 1999). Vertebrate fossils appear to be preserved only in parts of The Breaks that are unaltered by roll fronts.

Wyoming is noted for its abundant vertebrate fossils as well as for its common uranium roll-front-type deposits. Vertebrate fossils and roll-front deposits are both common in the deep structural basins that define the Wyoming landscape. The basins formed concurrently with major deeply rooted mountain uplifts during the Laramide Orogeny (Late Cretaceous–Early Paleogene), resulting in the majority of mountain ranges currently present today in Wyoming (Knight, 1951; Hansen, 1986; Lillegraven and Snoke, 1996).

The Hanna Basin lies in south-central Wyoming (Fig. 1) and is filled with nearly 12,000 m of Late Cretaceous–Paleocene sediments. At the top of this succession lies the Cretaceous–Paleocene Ferris and Hanna formations, which together are approximately 5530 m thick (Lillegraven and Snoke, 1996). These formations have yielded numerous vertebrate fossils, which have been described elsewhere (Eberle and Lillegraven, 1998; Higgins, 2000, 2003).

In the northeastern corner of the Hanna Basin lie outcrops of the Hanna Formation in an area of badlands known as The Breaks (Fig. 1). Within this ~3500 m section, Higgins (2000, 2003) described a Paleocene mammalian fauna from 136 different localities restricted to 550 m near the middle of the section (termed the VFBZ: vertebrate-fossil-bearing zone) Detailed analysis of the fauna indicates that this section brackets the boundary between the Torrejonian and Tiffanian North American Land Mammal Ages (Higgins, 2000, 2003).

Higgins (2000, 2003) noted that while vertebrate-fossil-bearing localities are abundant in the VFBZ, such localities are essentially nonexistent outside the VFBZ. The general lithology and depositional style above and below the VFBZ are very similar to that of the VFBZ (Lillegraven and Snoke, 1996; Higgins 2000, 2003), suggesting that the depositional environments were similarly conducive to vertebrate-fossil deposition and preservation both inside and outside the VFBZ. Differential diagenetic alteration between vertebrate-fossil-bearing and vertebrate-fossil-barren strata is apparent (Lillegraven and Snoke, 1996; Higgins, 1999). Sideritic concretions and bleached, weakly lithified sandstones are common where vertebrate fossils are lacking, apparently, whereas strongly carbonate-cemented sandstones are present where vertebrate fossils may be found.

ROLL-FRONT RECOGNITION AND CHEMISTRY OF FOSSIL DESTRUCTION

Roll fronts exposed on the Earth's surface preserve mineral suites indicative of reduction-oxidation (redox) reactions occurring between anoxic (reducing) groundwaters deep below the Earth's surface and oxic (oxidizing) groundwaters passing through the rock (Fig. 2). Roll fronts typically form tongue-shaped zones of altered host rock with a sharp and distinct boundary with unaltered rock. The immediate area where oxidizing waters contact reducing waters is termed the redox interface (Fig. 2). Uranium roll fronts are divisible into several zones, defined by the oxidation state of uranium and the assemblage of certain minerals. There are five general divisions, from unaltered to fully altered rock: unaltered rock, protore zone, ore zone, limonite zone, and hematite zone (Davis, 1969; Fig. 2). Uranium, in the form of uraninite (UO_2), is at its greatest concentration directly in front of the redox boundary, in the ore zone (Davis, 1969).

Figure 3 illustrates one of the most obvious examples of a roll front in the Hanna Formation. This outcrop includes a fossil locality (University of Wyoming locality V-90102) preserved in unaltered rock adjacent to and at the same stratigraphic level as altered rocks. Within the VFBZ, sandstone and conglomerate not altered by roll fronts are characterized as thin bedded, yellowish in color, and cemented by calcite. Conglomerate that contains vertebrate fossils is always unaltered by roll fronts. Altered sandstone and conglomerate are characterized by being more massive and blocky, bleached in color, and poorly cemented. Sideritic concretions, often secondarily oxidized, are a common feature of alteration in finer-grained rocks.

Common components of unaltered rocks in Laramide basins include pyrite (FeS_2) and calcite ($CaCO_3$; Granger and Warren, 1974). At the redox interface, sulfur in pyrite is oxidized to sulfate, and calcite is dissolved. Reduced, or ferrous, iron (Fe^{2+}) remains to combine with carbonate liberated from calcite to form siderite ($FeCO_3$). As oxidation continues, the Fe^{2+} of siderite is also oxidized, and various Fe oxides are

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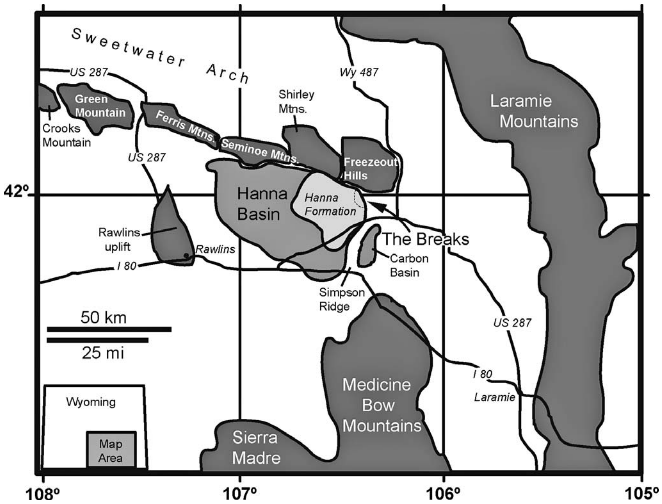

FIGURE 1—Location map of the Hanna Basin and The Breaks.

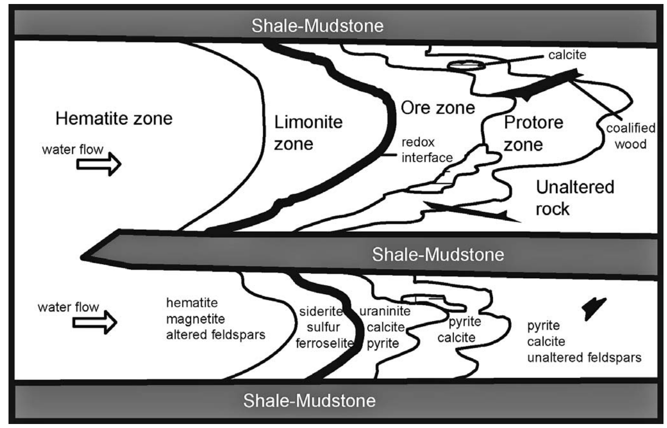

FIGURE 2—Schematic diagram of a typical roll front. Adapted from Davis (1969) and Granger and Warren (1974).

formed. Overall, the reactions occurring at the redox interface of roll fronts may be summarized as the conversion of pyrite and calcite, via oxidation of pyrite, into gypsum and siderite. Sulfuric acid is produced in this reaction:

$$CaCO_3 + FeS_2 + 3.5O_2 + 3H_2O \rightarrow CaSO_4{\cdot}2H_2O\downarrow \text{ (gypsum)} + FeCO_3\downarrow + H_2SO_4 \text{ (sulfuric acid)} \quad (1)$$

Vertebrate bones and teeth are composed of a mineral that falls into the group generally termed apatite. The actual mineral composition of bones and teeth is variable within a single animal and also changes with diagenetic processes. For this reason, I refer to the mineral of bones and teeth as bioapatite. In living animals, bioapatite is most often similar to the mineral dahllite ($Ca_{10}(PO_4,CO_3)_6(OH)_2$). During fossilization, fluorine substitutes for the hydroxyl group, resulting a bulk compositional change toward francolite ($Ca_{10}(PO_4,CO_3)_6(OH,F)_2$). The presence of vertebrate fossils only in rocks not altered by roll fronts in The Breaks suggests that reactions occurring during the progression of roll fronts encourage the dissolution of fossil bone and tooth minerals.

Francolite is commonly present in phosphate rocks used to make fertilizers. The phosphate must be released from apatite into a soluble form accessible to plants. The simplified reaction for this from Toy and Walsh (1987, p. 79) is

$$2Ca_5(PO_4)_3F + 7H_2SO_4 + 3H_2O \rightarrow 7CaSO_4 + 3Ca(H_2PO_4)_2{\cdot}H_2O + 2HF \quad (2)$$

This highly exothermic reaction of apatite with sulfuric acid yields the mineral anhydrite ($CaSO_4$), soluble monocalcium phosphate ($Ca(H_2PO_4)_2{\cdot}H_2O$), and hydrogen fluoride (HF). The hydrogen fluoride leaves the system, often as a gas or as SiF_4, the product of the reaction of HF and silica. Anhydrite and monocalcium phosphate are then ground and bagged as fertilizer (Toy and Walsh, 1987).

If bioapatite (as dahllite) were entered into equation (1) as a constituent of unaltered rocks, the hypothesized reaction occurring in sediments caused by the passage of roll fronts in The Breaks is

$$7CaCO_3 + 12FeS_2 + 2Ca_{10}(PO_4, CO_3)_6(OH)_2 + 43.5O_2 + 55H_2O \rightarrow 12FeCO_3 + 24CaSO_4{\cdot}2H_2O + 3Ca(H_2PO_4)_2 + CO_2 \quad (3)$$

Apatite is dissolved by sulfuric acid formed during the oxidation of pyrite. This equation is somewhat unrealistic, however, because free oxygen never actually reaches the redox interface in roll fronts (Granger and Warren, 1974). Sulfuric acid, however, is produced at the redox interface following a series of reactions. Free oxygen is used up at the contact between the hematite and limonite zones to produce ferric thiosulfate and

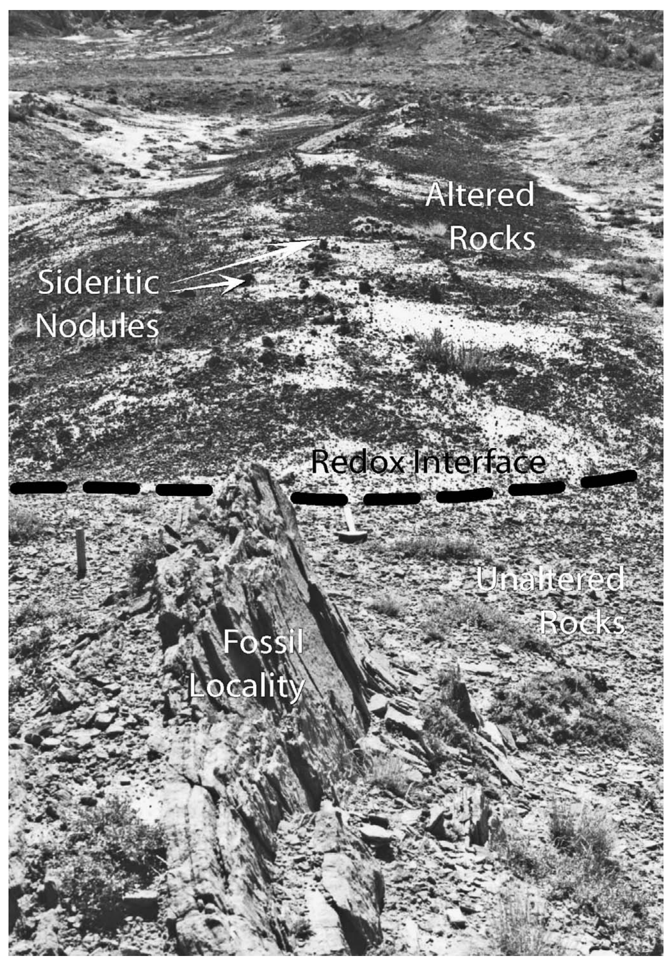

FIGURE 3—A roll front in The Breaks. Thin-bedded rocks in the foreground are University of Wyoming vertebrate locality V-90102. The redox interface of a roll front, marked by dashed lines, when active progressed toward the photographer. Dark pebbles lie on bleached soil of altered rock behind the redox interface. These pebbles are remnants of sideritic concretions that have crumbled to form a loose rock hash.

TABLE 1—Porosity and permeability measurements for sandstone samples collected throughout The Breaks. Measurements were made by Core Lab Incorporated in Carrollton, Texas.

Sample number	Strat level (m)	Relation to VFBZ	Reacts to acid	Sandstone grain size	Porosity (%)	Klinkenberg permeability (md)	Air permeability (md)
PH-237		outside	N	fine	23.2	212	216
PH-238		outside	N	medium	24.3	2657	2691
PH-239	975	within	N	fine	19.8	14.1	15.9
PH-240	972	within	Y	fine	18.9	48.8	51.1
PH-241	1052	within	N	medium	19.1	9.11	11
PH-242	1058	within	N	fine	18	3.33	4.39
PH-243	1059	within	Y	medium	5.13	0.13	0.181
PH-244	1242	within	N	fine	21.5	123	127
PH-245	1241	within	Y	medium	19.5	33.4	36
PH-246	1401	within	Y	medium	29.7	0.006	0.013
PH-247	1489	within	Y	medium	3.67	0.0004	0.001
PH-248	1492	within	Y	coarse	5.75	1.03	1.26
PH-249	1618	outside	Y	fine	4.38	1.27	1.82
PH-250	1616	outside	N	fine	16	1.13	1.48
PH-251	1795	outside	Y	medium	22.7	521	525
PH-252	1794	outside	N	medium	24.3	1912	1941
PH-253	1881	outside	Y	medium	5.81	0.024	0.043
PH-254	1879	outside	N	fine	24.1	149	163

bicarbonate in solution (Granger and Warren, 1974). At the redox interface, thiosulfate reacts with Fe^{2+} in pyrite, resulting in the precipitation of siderite and the production of sulfuric acid (Granger and Warren, 1974). Sulfuric acid produced in this reaction probably would be sufficient locally to eliminate any nearby bones and teeth.

Unaltered rock is characterized by the presence of abundant organic material, calcite, and bioapatite. Altered rock lacks organics and bioapatite but has siderite—which may further oxidize to iron oxide minerals (like hematite). This pattern is essentially identical to that present in sediments found in caves in Greece, France, and Israel, where researchers are using geochemistry to distinguish between those rocks from which bioapatite fossils have been dissolved during diagenesis and those in which bioapatite fossils were never deposited in the first place (Weiner et al., 1993, 2002; Karkanas et al., 1999, 2000, 2002; Berna et al., 2004). The basic pattern in cave deposits shows that the presence of calcite is indicative of unaltered or only slightly altered rocks. If calcite were present in the sediment, bones in the sediment would also still be preserved. If calcite were missing, yet authigenic dahllite were present, bones would still be present, as dahllite and bioapatite are essentially the same mineral. Any sediment that lacks both calcite and dahllite would not preserve bones but would potentially possess other phosphate minerals more insoluble than dahllite (Weiner et al., 1993; Karkanas et al., 1999).

Another important characteristic of roll fronts is the loss of organic matter during alteration (Davis, 1969; Granger and Warren, 1974). Oxidation of pyrite and organic matter early in roll-front alteration uses up most or all the oxidizing ferric thiosulfate in solution, resulting in reducing conditions. Under such conditions, Fe^{2+} is mobile and recombines with carbonate from dissolved calcite to form characteristic sideritic concretions. Once all the organic material or pyrite has been oxidized, the siderite may oxidize to hematite (see Karkanas et al., 2000).

It is evident from the above discussion that, while uranium may be a component of roll-front deposits, it does not directly participate in the alteration reactions that result in the suite of minerals that define roll-front morphology. Uranium is simply mobilized and mineralized with changing redox conditions (Granger and Warren, 1974). The crucial component is the oxidation of pyrite to produce the sulfuric acid that dissolves bioapatite. Furthermore, even the presence of pyrite may not be necessary, as the oxidation of organic matter and dissolution of calcite may be sufficient to create a chemical environment that will dissolve bioapatite (Karkanas et al., 2000).

LITHOLOGIC CONTROL ON ROLL-FRONT DISTRIBUTION

Porosity and permeability of rock in the Hanna Formation appears to be the single most important control on the distribution of roll fronts in The Breaks. In general, rock in the VFBZ is finer grained and less permeable to movement of groundwater than rock outside of the VFBZ (Table 1). Rocks of low permeability would slow or stop the progression of roll-fronts, thereby preserving any fossils contained within (Fig. 4; permeability is plotted on the right side of the drawing). Although the vertebrate localities are typically in relatively porous rock like conglomerate, mudstone and claystone enveloping the coarser lenses act as a shield to roll-front progression.

To further test the above hypothesis, porosity and permeability in 18 sandstone samples collected throughout The Breaks (Table 1) were measured (by Core Lab, Inc., in Carrollton, Texas); only rocks of similar lithology and alteration state were compared to eliminate the possibility that rocks may be more permeable because of alteration by roll fronts rather than because of original lithological differences. The measurements show, in general, statistically significant increases in permeability in sandstone outside the VFBZ as well as increased permeability of rocks clearly altered by roll fronts (Higgins, 1999). Subtle changes in sediment size and source, due to tectonic activity, climatic variation, or both during deposition, are most likely responsible for the observed differences in permeability.

Phosphate is an important nutrient for all organisms, including lichens. It is noteworthy that lichens grow abundantly on the present surface of the VFBZ, especially on soils formed from altered rock, resulting in a greenish appearance of strata of the VFBZ when observed from a distance. Lichens are present, but not nearly so abundant, on rock above and below the VFBZ, most of which is heavily altered. The pattern of lichen growth in The Breaks suggests a scenario in which phosphate released by roll-front activity outside the VFBZ was swept away by groundwater flow from these more permeable rocks and is no longer available for plant or lichen consumption. Within the VFBZ, lower permeability resulted in the preservation of some vertebrate fossils, and, where alteration did occur, phosphate remained close to where it was liberated from fossils.

ORIGIN OF THE PRE-ROLL-FRONT MINERAL SUITE

The redox reactions responsible for the destruction of vertebrate fossils are dependent on the presence of pyrite in the rock. Pyrite in sediments

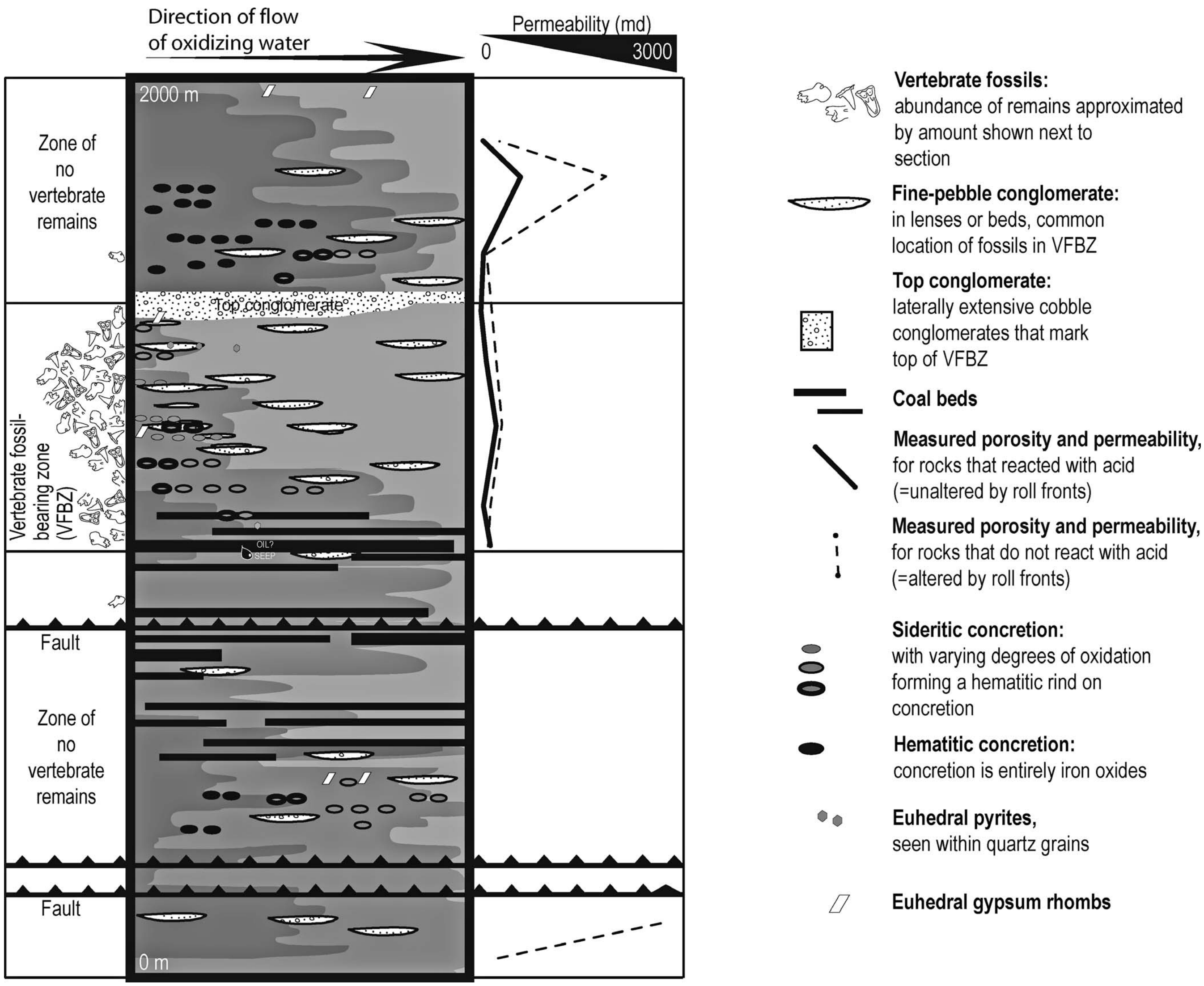

FIGURE 4—Schematic diagram of lower 2000 m of the Hanna Formation exposed in The Breaks, from the base to the base of the lower of two lacustrine units in the Hanna Formation. Measured rock permeability (millidarcies [md], Klinkenberg corrected) is plotted on the right side of the diagram for rocks that react with acid (solid line) and rocks that do not react with acid (dashed line).

forms commonly under anoxic conditions, often owing to the activity of sulfate-reducing bacteria in environments with abundant organic matter (Wilkin and Barnes, 1997; Machel, 2001). Deposition of the Hanna Formation (Fig. 5) occurred very rapidly, at an average of about 0.23 mm per year (Lillegraven and Snoke, 1996; Higgins, 2003). Soils, where identifiable, are only very poorly developed. Thick coaly and carbonaceous layers are present, especially above and below the VFBZ. As deposition occurred, marshy and highly organic layers were rapidly buried and cut off from atmospheric oxygen. The utilization of gypsum and other organics in the sediment by sulfate-reducing bacteria resulted in the mineralization of pyrite (Fig. 6). Sulfate reduction continued until biological activity ceased, either because temperatures exceeded ~125–145°C (Machel, 2001) or perhaps because some important nutrient, such as sulfate itself, was exhausted in the environment.

SUMMARY AND CONCLUSIONS

Field evidence in The Breaks suggests that reactions occurring at the redox interface of uranium roll fronts can eliminate vertebrate fossils from rock. In this paper, I propose a mechanism for the elimination of apatite-based vertebrate teeth and bone. This mechanism is dependent upon the oxidation of pyrite to form sulfuric acid, which then dissolves the fossils. Rocks of lower permeability in the Hanna Formation restrict the flow of oxidizing water, slowing or stopping roll-front progression and resulting in the preservation of vertebrate fossils.

Recognition of roll-front alteration in the deep Laramide basins of Wyoming and Montana will be of great help to the numerous vertebrate paleontologists actively pursuing research in those areas. When time is limited, a paleontologist might focus fieldwork in areas clearly unaltered by roll fronts, thereby maximizing the possibility of finding new vertebrate fossils.

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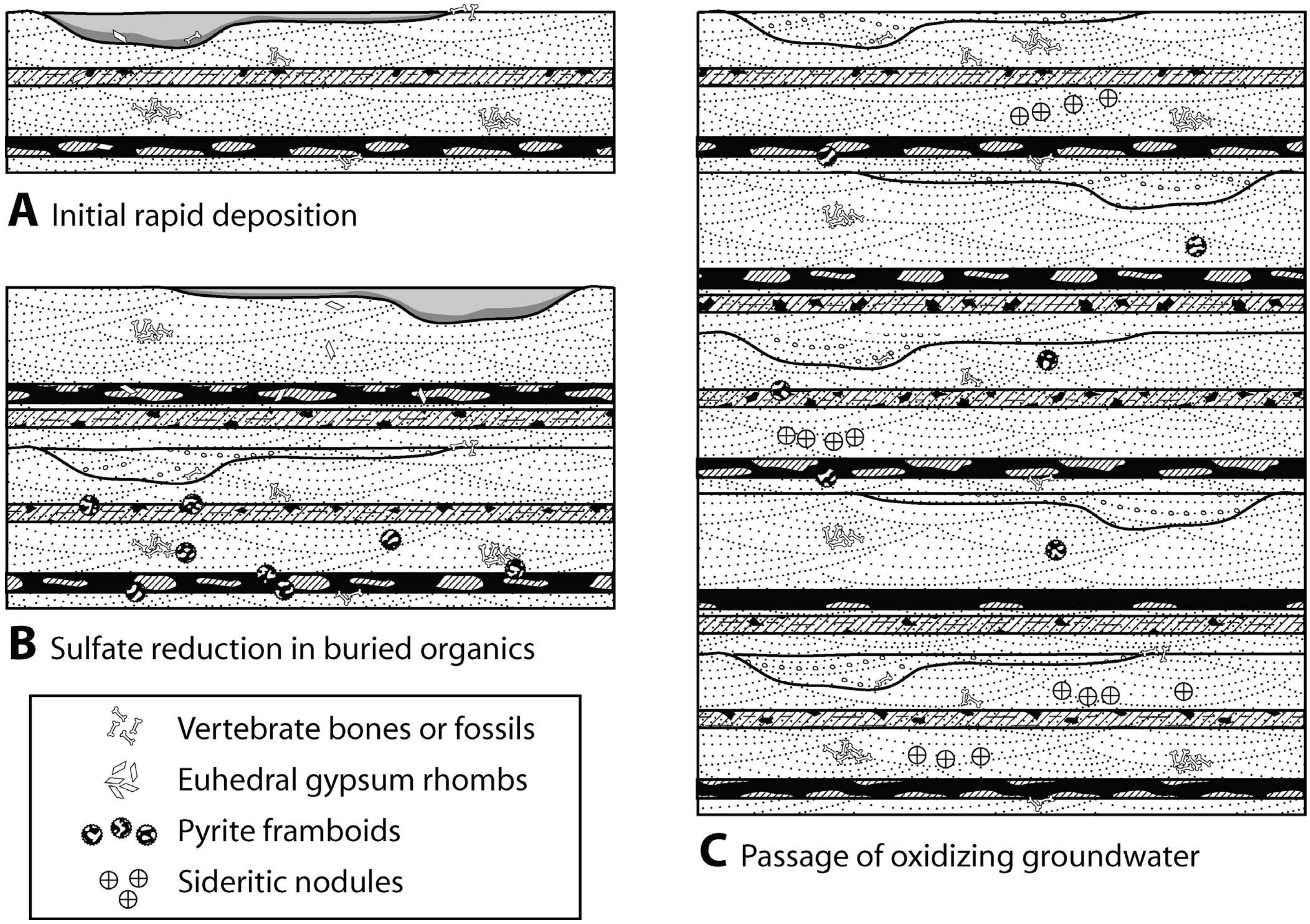

FIGURE 5—Cartoon depositional and diagenetic history of the Hanna Formation. A) Initial deposition of sediments in a rapidly subsiding basin. Shallow, sediment-laden streams deposit materials on floodplains and organic-rich boggy areas. Gypsum precipitates. B) Organic materials are rapidly buried and cut off from atmospheric oxygen. Sulfate-reducing bacteria use sulfate from gypsum. The resulting sulfide is incorporated into pyrite framboids. C) After burial and lithification, rocks bearing vertebrate fossils, pyrite framboids, and organic-rich units are altered by uranium roll fronts, resulting in the loss of vertebrate fossils and pyrite and the appearance of sideritic concretions.

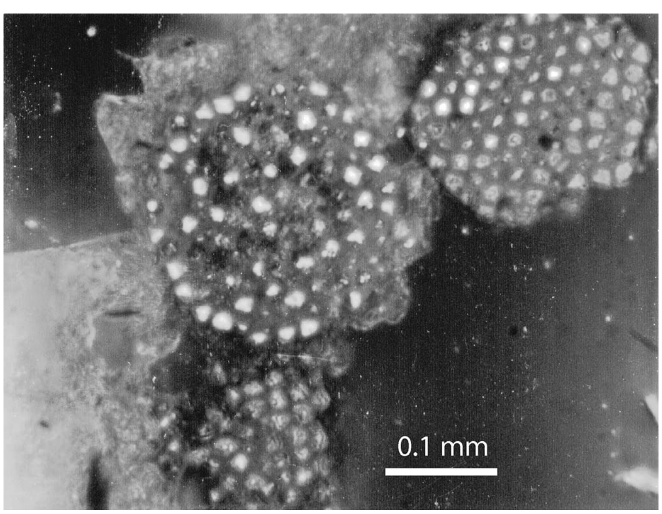

FIGURE 6—Reflected light photomicrograph of pyrite from the Hanna Formation. This appears to be pyrite replacement in a fossil diatom or pollen grain, though superficially appears nearly identical to pyrite framboids (see Machel, 2001). Scale bar is 0.1mm.

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