The potential for U-Pb Dating of Coprolites, Hartford Basin, Connecticut

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Introduction

There is a great need for more precise absolute ages for sedimentary rocks. We have been actively involved in developing techniques to directly date sedimentary rocks, rather than using associated igneous rocks, or using relative dating techniques. Sedimentary phosphate nodules (i.e. coprolites) are ideal candidates for absolute dating of sedimentary rocks. Phosphates occur commonly within the rock record, they are composed of francolite which precipitates authigenically early in the diagenetic sequence, and they are enriched in radiogenic Pb. We can vastly improve the resolution of the rock record by dating the time of sedimentation and placing absolute date constraints on the existing relative age boundaries.

Formation of Sedimentary Phosphates

Sedimentary phosphate deposits commonly form in marine settings characterized by increased biological activity due to water upwelling (Froelich, et. Al., 1988; Verzilin and Kalmykova, 1993). The processes of apatite formation in phosphate nodules is believed to happen in one of three ways: (1) biogenesis, (2) carbonate epigenesis, and (3) precipitation (possibly with microbial mediation) (Slansky, 1986). Biogenesis is often intimately associated with precipitation. Often organic matter is intimately associated with phosphate nodules suggesting that organic matter was the likely source of the phosphate in the nodules (Ece, 1990). The increasing number of examples of recent and fossil phosphatized microbial materials have convinced many researchers of the importance of precipitation with microbial mediation (Lewy, 1990).

Carbonate fluorapatite (francolite), the stable form of apatite in sea water (Balson, 1990), is the phosphorous bearing mineral of nearly all sedimentary phosphates. Francolite may form authigenically in organic rich muds or as a diagenetic replacement of precursor carbonate (Benmore, 1983). Authigenic francolite may precipitate within the sediment at depths ranging from 6 to 18 cm below the sediment surface (O'Brien, et al., 1990; and Heggie, et al., 1990). The limiting factor in controlling francolite precipitation is most likely the supply of phosphorous to the pore waters, while the limiting factor in francolite growth is likely the inability of the mineral to accommodate increasing carbonate substitutions, leading to increasing carbonate concentrations below the usual depth interval where francolite is observed (Riemer, et al., 1996). Although extensively studied, the processes of phosphatization remain enigmatic. Physical and (bio-)chemical pathways along which phosphates concentrate, precipitate and accumulate are still poorly understood (Follmi, 1990).

Characteristics of Coprolites

Coprolites (fossilized excrement) have been shown to play an important role in the formation of phosphatized nodules (Lamboy, 1994, Lamboy, et.al., 1994; Verzilin and Kalmykova, 1993, Ece, 1990). Fecal pellets may provide nucleation sites for the precipitation of apatite cement (Ece, 1990). The dissolution of fish debris composed of hydroxyapatite at the sediment - water interface produces a biogenic source of dissolved phosphate into the pore waters promoting carbonate fluorapatite precipitation. The precipitation of francolite is most likely occurring in restricted microenvironments (Froelich, et.al., 1987; Krajewski, 1984). Petrographic and SEM studies show direct precipitation in micropores (1-4 μm in size) (Ece, 1990). Phosphatic coprolites exhibit several characteristics: (1) predominately homogeneous porous apatite structure with a few fish remains, poor in non-apatite particles, (2) nannostructures are composed of inframicron-sized and botryoid-type apatite microparticles, and (3) precipitation of phosphate occurs around microbial organisms. The phosphatization apparently took place first on the external surface of the bacteria, before the complete decay of organic matter associated with the microbial structures. It appears that the bacteria which colonized the initial feces transformed them into hard coprolites by microbial processes. Within coprolites, phosphatization occurs only within the soft copronodule itself and the particular apatite nannostructures can be explained by the presence of abundant organic matter (Lamboy, 1994; Lamboy, et.al., 1994).

A variety of apatite nannostructures in phosphorites link several macroscopic aspects (color, brightness, hardness and density) of phosphorites with the porosity of the apatite structures. In porous types, the apatite appears as ovoid, dumbbell-like, botryoid, micron-sized and inframicron particles and flakes, associated with light-colored, dull and friable phosphates. The structures are most likely formed as a result of microbially mediated apatite precipitation. The compact phosphorites are composed of tightly packed microparticles of apatite, associated with hard, dense, frequently dark colored and shiny phosphorites. The porosity is reduced in compacted during early diagenesis, obscuring the original porous phosphorite nannostructures (Lamboy, 1994).

Nannostructures of coprolites consist of inframicron-sized botryoid-type apatite particles, overall exhibiting a homogeneous porous apatite structure with a few fish remains. Spherical cavities and cavity-infilled inframicron sized apatite globules are typical in the coprolites, most likely formed by extracellular precipitation of phosphate around microbial organisms. The coprolites are presumed to have belonged to carnivorous fishes, due to the inclusion of fish remains and the high abundance of organic matter and phosphate. The phosphatization appears to be a process controlled by the microenvironment within the coprolite. The most predominant nannostructures are those consisting of spherical cavities and cavity filled inframicron-sized globules. These structures are similar to those reported in other laminated phosphorites and mineralized stromatolitic microlayers, interpreted as extracellular remnants of mat-forming microorganisms, suggesting that the mineralization processes are similar to those in coprolitic bodies. Nannostructures observed in the coprolites differ from those observed in other phosphatic grains, from the same sample, which are mainly heterogeneous and consist of ovoid-type apatite particles (Lamboy, et al., 1994).

Sedimentary Apatite as an Early Diagenetic Mineral

Francolite may be precipitated authigenically during early diagenesis in the SO_4 reducing environment (Benmore, 1983). In studies of the mineralization of soft bodied fossils, $CaCO_3$ crystal bundles are very early diagenetic features. They often begin to precipitate in shrimp carcasses within three days after death. Some $CaCO_3$ bundles enclose phosphatized muscle fibers, showing that these bundles began precipitating *after* the tissue had been phosphatized (Briggs and Wilby, 1996). Because phosphate is often mobilized by bacteria that initiate decay, apatite may be precipitated very early as cryptocrystalline aggregates (Wilby, et.al., 1996). A general diagenetic sequence of apatite - calcite +/- gypsum - pyrite +/- chalcopyrite - galena is observed in soft tissue mineralization. Laboratory experiments show that mineralization of soft tissues by apatite can occur within two to four weeks after death, other decay experiments show apatite preserving morphological details within hours after the onset of decay (Wilby, et. al., 1996).

Lack of signs of biological activity (eg., borings and traces of biological abrasion), and the good preservation of organisms suggest that the organisms were buried rapidly. Prolonged exposure at the sea floor would have destroyed such organisms, either through disintegration by scavenging organisms, chemical dissolution, or physical disarticulation. Therefore the observations suggest that phosphogenesis was an early diagenetic process which took place after the rapid burial of the to be phosphatized organisms, but prior to total decay of the buried organic matter (Follmi, 1990). Soft copronodules which are buried during periods of high sedimentation rates, may be compressed into a lenticular lense in argillaceous sediments (Lamboy, et.al., 1994). Phosphate cements have been recognized as indicators of early diagenesis. Porous and compact apatitic structures that form during early diagenesis are usually not modified during later diagenesis (Lamboy, 1994).

Stratigraphy of the Triassic-Jurassic Newark Supergroup and Occurrences of Coprolites

The Triassic-Jurassic Newark Supergroup basins of the eastern North America margin are interpreted as half-grabens formed by extension related to the opening of the Atlantic Ocean. Rocks within the basins consist primarily of basal and border fanglomerates, arkosic and lithic arenites, gray to black siltstones and shales, and red-brown mudstones. Several depositional environments have been recognized as representing zones in and around deep lakes developed in a half-grabens. The environments are; (1) fault-scarp breccias and synsedimentary grabens, (2) alluvial fans and river systems, (3) swamps and marginal lake environments, (4) deltas and shorelines, (5) open water shallow lakes and, (6) deep water lakes (lacustrine environment). Within the open water shallow lake environments fish fossils and phosphoric coprolites are common. The deep water lake environment contains remarkably well preserved fishes and coprolites. Laterally extensive gray-black siltstones deposited in a lacustrine setting volumetrically comprise the majority of these beds. Within the Newark Supergroup the cyclic lacustrine shales and mudstones are interpreted to have formed in fluvial and deltaic environments under lacustrine conditions reflecting the cyclic rise and fall of lake level. These cycles, termed 'Van Houten Cycles' consist of gradational sequences of (1) thin bedded silty mudstone exhibiting polygonal cracks or sandstone having oscillatory ripples, reflecting shallow lake deposition, (2) a middle section ranging from very finely laminated, organic-rich, black shale to thin-bedded gray mudstone, reflecting deeper water deposition, and (3) an upper massive mudstone or interbedded sandstone and mudstone commonly containing root casts, reflecting shallow water deposition to subaerial deposits . Black shales (Midland fish bed) of the Culpeper Basin, Virginia contain calcium-phosphate nodules (coprolites) (Gore, 1899; Gore, personal comm.). Much of the black shale in the Culpeper Basin was most likely deposited in anoxic waters of relatively deep, stratified lakes. The black shales also contain pyrite which indicates anoxic conditions associated with the decomposition of organic matter (Gore, 1988). Other examples of these cyclic lacustrine beds are found in the Deerfield-Northfield, Hartford, Newark, Gettysburg, Culpeper, Dan-River-Danville Basin, and the Deep River Basin. Many of these basins contain beds which have excellent preservation of fish fossils and coprolites (Manspeizer, 1988; Olsen, 1988; Smoot and Olsen, 1988; and Smoot, et. al. 1988).

Van Houten Cycles have been used to show stratigraphic relationships between the Newark Basin and the Hartford Basin. While this does not imply that the two basins ever experienced lateral continuity it does suggest a period of regional cyclicity such as periodic climatic changes. The Newark Supergroup is correlated biostratigraphically on the basis of fossil pollen and spore assemblages recovered from major sedimentary units. Locally, the occurrence of megafossil plant remains are abundant and well preserved for stratigraphic correlation. In lacustrine sediments, fossil fish (ex: *Semionotus, Redfieldius,* and *Diplurus*) are well preserved with superb morphological details, providing fine internal correlation of the strata. Also with excellent preservation are reptile footprints. The regional correlation has been based on the distribution of palynomorph taxa and Tetrapod data (as both skeletal remains and footprints) (Olsen, 1990; Oslen, 1988). Constraints can also be places on the ages of some formations by the dating of Mesozoic basalts (ex: Deerfield basalt and Holyoke Basalt) within the basins. The formations of the Newark Supergroup are regionally correlated with other early Mesozoic sequences, including the Chinle formation of the Southwestern United States.

With the biostratigraphy developed for the Triassic - Jurassic Basins on a local and regional scale, we can place absolute age constraints on the time of sedimentation improving the resolution of the rock record in the Lower Mesozoic.

Results

Coprolites from the East Berlin formation (North Branford location) of the Hartford Basin, Connecticut have been analyzed. The Lower Jurassic East Berlin formation consists predominantly of mudstones, siltstones and shales, minor units are green-gray mudrocks and shales, black shales, and sheet sandstones. The formation is considered to represent an alluvial and lacustrine succession deposited in a semi-arid climate. The coprolites occur within the black shale unit of the formation (Gierlowski-Kordesch and Rust, 1994). The East Berlin formation is stratigraphically younger than the New Haven Arkose, which our lab has successfully dated, which will give us a check on our coprolite ages.

The coprolites range in length from 3 to 7 cm, and are approximately 2 cm wide. The coprolites are commonly flattened into lenses, but some exhibit thickness up to 2 cm. The coprolites are dense and compact, dark gray to black in color and shiny. The coprolites are very similar to those described by Lamboy (1994), in which the coprolite was compacted during early diagenesis reducing the porosity and obscuring original porous phosphorite nannostructures. The coprolites are composed of francolite (John Hubert, personal comm.).

Several analyses of one coprolite from the East Berlin formation (North Branford location) were collected to evaluate the possibility of dating coprolites by the U-Pb method. The coprolites are strongly enriched in uranogenic Pb, and slightly so in thorogenic Pb. (Table 1)

	Common Pb isotopic ratios	Range of measured Coprolite Pb isotopic ratios
$^{206}Pb/^{204}Pb$	18.5	424 - 3914
$^{207}Pb/^{204}Pb$	15.3	24 - 220
$^{208}Pb/^{204}Pb$	37.5	67 - 268

Table 1. A comparison of common Pb isotopic values and Pb isotopic values obtained for coprolites from the Hartford Basin, Connecticut.

The Pb concentration of the coprolites ranges from 40 to 70 ppm. The Pb data allow construction of a $^{207}Pb/^{204}Pb$ - $^{206}Pb/^{204}Pb$ isochron, which yields an age of about 300. These results are encouraging because this age, based only on Pb isotopic ratios is relatively close to the expected age of about 200 m.y.. U-Pb abundance analyses on the same sample should allow us to evaluate whether coprolites can be used to date the time of sedimentation.

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