Organic Matter in Fossils

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Definition

Because all organisms on Earth consist of complex organic biomolecules, any fossil may contain organic matter. Indeed, organic matter represents one of the most common fossil materials, occurring within skeletal elements (shells and bones) and making up organically preserved microorganisms, plants, and exceptionally preserved eukaryotes (i.e., animals and algae with remains of non-biomineralized tissues).

Introduction

Remains of organisms in the geologic record occur in a variety of preservational styles, which vary with regard to fossil composition, scale, and dimensionality, in addition to anatomy and morphology. All fossils have the potential for preservation of organic matter, making such material an active area of paleontological and geobiological research. Overall, fossils vary widely in terms of organic matter quantity, composition, and form. The major types of fossils containing organic matter (Fig. 1) include organically preserved microfossils, skeletal fossils, carbonaceous compressions, fossils of secondarily mineralized soft tissues, and small carbonaceous fossils (thin carbon films freed from rock matrixes via hydrofluoric acid maceration). Skeletons (bones, shells, sclerites, spicules, tests, and teeth) produced by biomineralizing organisms make up the bulk of the fossil record, and observations of organic material within small shelly fossils (Martí Mus 2014), brachiopods (Forchielli et al. 2012), and vertebrate bones (Asara et al. 2007; Surmik et al. 2016) affirm that they sometimes retain organic matter. That said, the preservation of organics within skeletal fossils has historically received little attention. Instead, most research on fossils containing organic matter has focused on organically preserved microfossils, plants, animals, and macroalgae. These fossils occur less commonly than skeletal remains because microbial processes rapidly destroy non-biomineralized tissues in typical sedimentary environments (Muscente et al. 2017). Preservation of such fossils requires circumstances conducive to preservation of organics, specifically, conditions that limit scavenging and microbial decomposition of tissues and ensure organic matter survival over geologic time (Muscente et al. 2017). Regardless of the circumstances responsible for its preservation, the presence of organic matter ultimately allows for integrated studies of fossil morphology, ultrastructure, biochemistry, and physiology.

Sources and Post Burial Processes

Organisms contain various types of organic biomolecules. Proteins, carbohydrates, lipids, and nucleic acids represent the major groups, which in turn, make up an assortment of biopolymers (macromolecules with repeated subunits). Microbial and diagenetic (e.g., thermal maturation) processes result in the degradation and alteration of these biomolecules over time. Prior to burial and throughout diagenesis, microbes drive the chemical decay and decomposition of tissues, a process involving hydrolysis of large molecules into smaller ones. Although microbial decay always begins prior to thermal maturation, the two processes proceed concurrently late in diagenesis. Thermal alteration causes further degradation, leading to polymerization of biomolecules into long-chain aliphatic compounds (Stankiewicz et al. 2000). This process is sometimes called "kerogenization" (Cai et al. 2012) because it leads to formation of insoluble ("kerogen")

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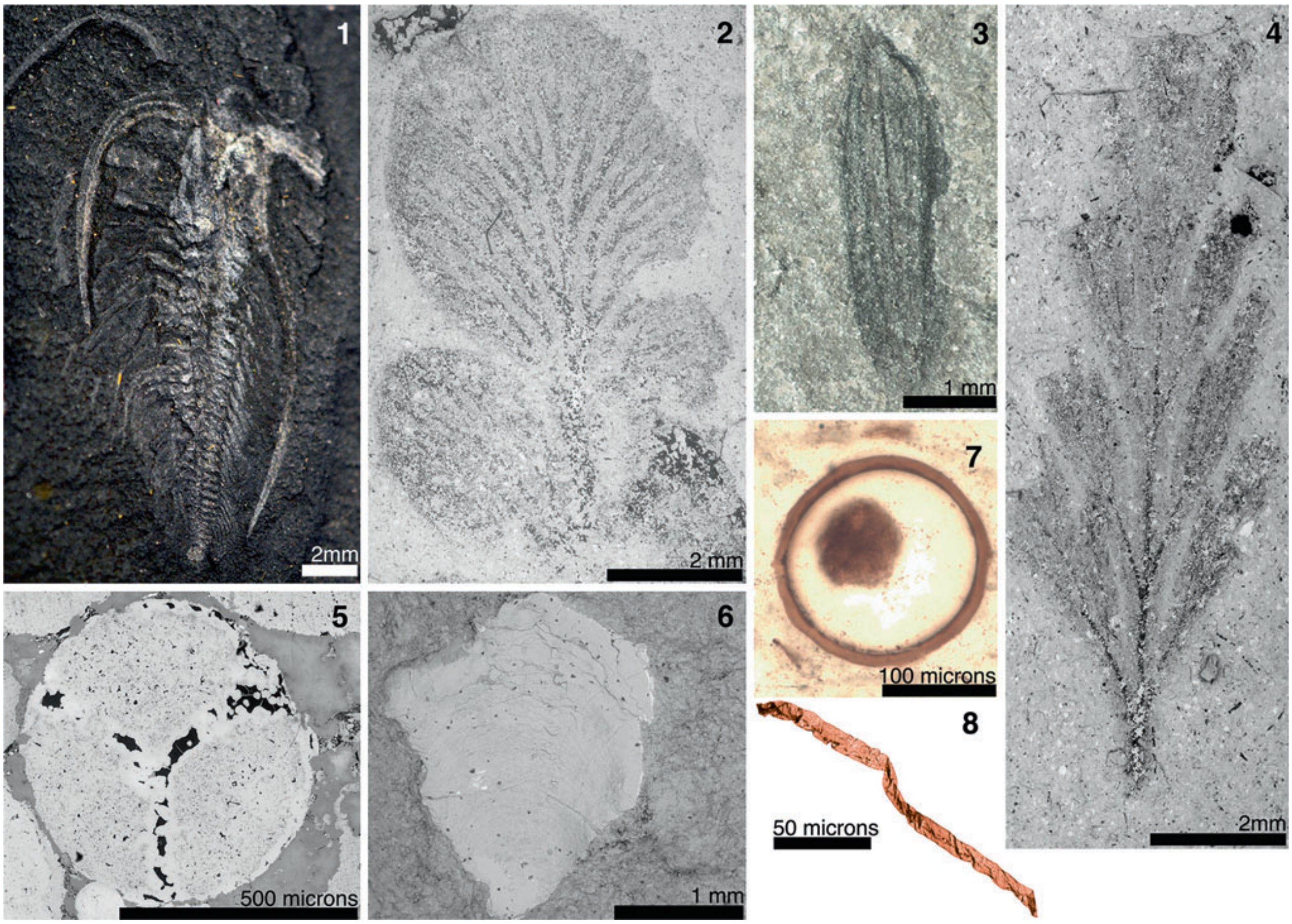

Organic Matter in Fossils, Fig. 1 Fossils containing organic matter. (*1*) Carbonaceous compression of *Marrella* from Burgess Shale, Canada (Muscente et al. 2017). (*2*, *4*) Carbonaceous compressions of plants, Solite Quarry, Triassic Cow Branch Formation, USA (Muscente and Xiao 2015b). (*3*) *Wiwaxia* sclerite, Cambrian Kaili Formation, Guizhou Province, China. (*5*) phosphatized embryo from the Weng'an phosphorite, Ediacaran Doushantuo Formation, Guizhou Province, China. Organic matter within embryo is *black* in the image. (*6*) Linguiform brachiopod shell containing organic matter, lower Cambrian Shuijingtuo Formation, Hubei Province, South China. (*7*) Organic-walled microfossil in thin section, Svanbergfjellet Formation, Svalbard. (*8*) Filamentous small carbonaceous fossil, Alinya Formation, Australia

components, which are characteristic of organic matter mixtures in the geologic record. Nonetheless, this term is misleading, as polymerization generates an array of compounds, and the mixtures themselves often retain soluble components, like remnants of proteins (Stankiewicz et al. 2000; Schweitzer et al. 2008). Other aspects of diagenesis also alter organic matter from its starting state. Microbial production of sulfide, for example, drives sulfurization and the formation of organosulfur compounds within fossil organic matter (Muscente et al. 2015; McNamara et al. 2016). In any case, the major groups of biomolecules vary considerably in their recalcitrance to microbial processes and thermal maturation, and therefore, in their potential for survival over geologic time. In terms of preservation potential and resistance to decay, biomolecules typically take the following order: nucleic acids < proteins < carbohydrates < lipids < biopolymers (Tegelaar et al. 1989; Briggs 2003).

Organic matter within a fossil may represent indigenous biomolecules of the organism, exogenous organics derived from hydrocarbon migration within a rock, or a mixture of sources. These possibilities can be explored through the application of advanced analytical methods (see below) along with taphonomic analysis. In carbonaceous compressions and small carbonaceous fossils, organic matter occurs as thin films on bedding surfaces. Such layers form through the collapse and coalescence of multiple tissues (Rex and Chaloner 1983) by way of diagenetic polymerization (Stankiewicz et al. 2000). The preservation of fine anatomical details suggests that each thin film derives from a single organism (Martí Mus 2014), and geochemical analyses of macroalgae compressions generally corroborate this interpretation, showing that within specific geologic deposits, different taxa contain organics with distinct isotopic signatures (Loduca and Pratt 2002). Similarly, geochemical analyses of carbonaceous microfossils, which are typically preserved as hollow, three-dimensional structures with walls and sheaths composed of organic matter, demonstrate that their organics derive from various pathways of carbon fixation (House et al. 2000) and do not record significant averaging of carbon isotope values due to hydrocarbon migration. Even so, diagenetic emplacement of carbonaceous material remains a concern for all types of organically preserved fossils, particularly secondarily mineralized fossils (Muscente et al. 2015).

In skeletal fossils, organics generally represent indigenous materials. These materials derive from the organic matrixes on which the biominerals originally formed and grew (Glover and Kidwell 1993). Fossils of organophosphatic brachiopods sometimes consist of alternating layers of organic-rich and organic-poor phosphatic material, and therefore, closely resemble recent specimens in terms of shell ultrastructure (Zabini et al. 2012). Taphonomically demineralized skeletal fossils also provide evidence of indigenous organic matter. Biomineral dissolution leaves behind carbonaceous residue. If weathering or lab preparation leads to demineralization, the carbonaceous fossil may retain its three-dimensionality, as exemplified in weathered organophosphatic brachiopods (Zabini et al. 2012) and tubular shelly fossils (Muscente and Xiao 2015a). Alternatively, if demineralization occurs early in diagenesis, concomitant with burial compaction, this residue coalesces into a compressed but cohesive fossil (Muscente and Xiao 2015a). This process provides a reasonable explanation for the preservation of skeletal elements as carbonaceous compressions (Martí Mus 2014) and small carbonaceous fossils (Butterfield and Harvey 2012).

Analytical Methods

Geochemical study of organic-walled microfossils has accelerated in recent years with the advent of a number of microanalytical techniques that allow for the analysis of individual fossils. A technique is chosen based on both the questions to be answered and the preservational conditions of the fossils. Some fossils can be extracted from their host matrixes via hydrofluoric or hydrochloric acid maceration, whereas others must be studied in situ in thin (~30 μm) and thick (~150 μm) sections. Applicable analytical techniques include energy dispersive spectroscopy (EDS), confocal laser scanning microscopy (CLSM), secondary ion mass spectrometry (SIMS, Nano-SIMS and time-of-flight SIMS), X-ray near edge absorption spectroscopy (XANES), Raman spectroscopy, and Fourier transform infrared spectroscopy (FTIR).

Scanning electron microscopy (SEM) is typically used to study fossil morphology and ultrastructure and, when combined with energy dispersive spectroscopy (EDS), allows for characterization of organic components and associated minerals (Muscente and Xiao 2015b). Confocal laser scanning microscopy (CLSM) is used to make two- and three-dimensional images of organic fossils based on their fluorescence (Schopf et al. 2006). Kerogen fluoresces weakly with laser excitation, and the strength of the emission is inversely related to the degree of thermal alteration so that more thermally mature fossils are more difficult to image (Czaja et al. 2016).

Mass spectrometry is a common technique to study the carbon isotope compositions of fossil organic matter, which can help constrain the physiology of ancient organisms. Secondary ion mass spectrometry (SIMS) provides the capability of collecting in situ measurements of carbon isotopic values from individual microfossils (House et al. 2000, 2013; Williford et al. 2013). This method and its relatives (Nano-SIMS and time-of-flight SIMS) can be used to produce 2-D elemental or molecular maps of small areas (up to 100 × 100 μm). These can be used to show the relationship of various elements within fossil structures. Such work can illuminate elemental relationships within fossil material and provide data for assessing the biogenicity of objects of uncertain origin (Oehler et al. 2009).

Several techniques are used to determine the composition of organic matter in fossils and to provide evidence of biological origin. XANES is used to characterize molecular components of organic matter (Boyce et al. 2001; De Gregorio and Sharp 2006). This technique typically has a high spatial resolution and can be used to study individual fossil microorganisms and produce 2-D maps (Muscente et al. 2015). Raman spectroscopy and FTIR spectroscopy are in situ techniques that measure the molecular structure of organic and inorganic materials based on vibrations of molecular bonds and larger molecular structures using lasers for excitation. These techniques are typically used to determine the carbonaceous nature and molecular structure of possible fossil organic material (Arouri et al. 2000; Kudryavtsev et al. 2001; Olcott Marshall and Marshall 2014; Schopf and Kudryavtsev 2005). Raman spectroscopy is also used to measure the degree of thermal alteration of fossil organic matter and reconstruct the metamorphic histories of geologic units containing organically preserved fossils (Beyssac et al. 2002; Schopf et al. 2005; Kouketsu et al. 2014).

Complex Organic Biomolecules

As mentioned above, complex biomolecules vary in their rates of degradation. Nucleic acids, for example, contain the most biological information but are also the quickest to degrade. The oldest sequenced genome is from a ~700,000 year old horse preserved in permafrost (Orlando et al. 2013) and extremely degraded DNA has been reported on the scale of millions of years. It is possible that with advancements in analytical techniques, this ancient DNA can become a rich source of information.

Proteins can provide details of an organism's physiology and evolutionary relationships and can preserve on significantly longer time scales than DNA. In vertebrates, proteins like collagen, which break down into bonded amino acids called peptides, have been reported from a ~68 million-year-old *Tyrannosaurus rex* bone (Asara et al. 2007) and amino acids fragments have been reported from ~235 Ma reptiles (Surmik et al. 2016). Such bold claims, however, require strong support and just as mentioned above, exogenous organic matter and contaminants from the field and lab are a major concern. Indeed, follow-up studies have called into question the provenance of the *T. rex* biomolecules (Buckley et al. 2008) and this story continues to develop. The oldest complete protein so far detected comes from an ostrich eggshell (~3 Ma; Demarchi et al. 2016); the structure of the shell and the protein's affinity for calcite are hypothesized to have enabled this long-term preservation.

Chitin is a long-chain polymer and major constituent in the exoskeletons of arthropods. A modified chitin-protein complex containing up to 59% of the chitin concentrations seen in modern animals has been found in fossil arthropods (310 and 417 million years old; Cody et al. 2010). The decay of this complex is prevented by condensation of fatty acids onto a structurally modified chitin-protein molecular scaffold.

Melanin is a common pigment, which occurs within organelles (melanosomes) in numerous clades of animals. Different types of melanin produce different colors, and the melanosomes that contain them vary in shape and size. Notably, the discovery of fossilized melanosomes ushered in a novel field of paleobiology: the study of color patterns in ancient animals. By studying melanosomes in feathers, for example, paleontologists determined that the well-known feathered dinosaur *Sinosauropteryx* possessed a red and white striped tail (Zhang et al. 2015). Even so, fossilized melanosomes have been a subject of debate (Vinther 2016), as some authors have proposed that the structures are actually fossils of microbes. Recently, various studies have presented evidence that fossilized melanosomes of various ages contain chemical traces of melanin (Lindgren et al. 2012; Colleary et al. 2015; Clements et al. 2016). Such traces represent maturation products of melanin rather than the original biomolecules (Colleary et al. 2015). Nonetheless, such data support the use of fossilized melanosomes for analyses of coloration in ancient life and affirm that work on biomolecule preservation in fossils should remain a top priority.

Summary

Regardless of preservational style, any fossil may contain organic matter, as evidenced by observations of carbonaceous material within skeletal elements, small carbonaceous fossils, carbonaceous compressions, and secondarily mineralized tissues. The organic matter within a specific fossil may represent biomolecules indigenous to the organism, organics introduced via hydrocarbon migration, or compounds derived from both sources. In all cases, organically preserved fossils constitute important windows to the evolutionary history of life on Earth, particularly the rise of microbial life and the radiation of animals. Fossils with indigenous organic matter merit particular attention. Such fossils may contain biomolecules (e.g., chitin and melanin) of paleobiologic and geobiologic significance in diagenetically altered but recognizable forms. Thus, analyses of the organic matter in such fossils may illuminate the original biochemical makeups and affinities of those ancient organisms.

Cross-References

- ▶ Biopolymers and Macromolecules
- ▶ Carbon
- ▶ Carbon Isotopes
- ▶ Diagenesis
- ▶ Geochemistry
- ▶ Kerogen
- ▶ Organic Geochemistry
- ▶ Organic Matter Degradation and Preservation
- ▶ Organics: Sources and Depositional Environments
- ▶ Precambrian Geochemistry
- ▶ Precambrian Organic Matter
- ▶ Raman Microspectroscopy

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