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ABSTRACT — Coprolites, the fossilized feces of vertebrates, are usually identified in both the field and laboratory by their characteristic size, shape, and association with other fossil remains (Häntzscheletal, 1968 and Sawyer, 1981). However, it is not always possible to identify a suspected coprolite and frequently no conclusions can be made about the type of animal that is responsible for it.

The goal of this study is to determine if techniques of analytical chemistry can provide conclusive data that will verify that an unknown object is a coprolite and if any information about the animal can be obtained.

INTRODUCTION

Infrared spectroscopy was the technique selected for this study. Infrared spectroscopy has been a vital tool in analytical laboratories for many years because of its great power in qualitative identification and quantitative analysis. Infrared spectroscopy is suitable for the characterization of samples as small as a fraction of a milligram. This is important when the sample is small or when only a small amount can be removed from the specimen for analysis.

Infrared spectroscopy is useful for the study of both organic and inorganic materials (see Hill and Rendell, 1975; Bellamy, 1975 for general applications). Since coprolites may contain both organic and inorganic compounds, this capability was essential for the present study. Even if the sample is a multi-component mixture, an infrared spectrum provides an unambiguous fingerprint of the compounds present in the unknown sample.

EXPERIMENTAL TECHNIQUE

The samples used in this study were all obtained for analysis by removing 0.5 to 20 milligrams from the coprolite. The sample was ground to a fine powder to create a uniform mixture. After grinding the sample, 0.5 to 1.0 milligrams was mixed with about 500 milligrams of KBr. This uniform mixture was formed into a clear pellet using a die in a hydraulic press. The function of the KBr is to suspend the sample in the radiation beam and reduce light scattering. The KBr pellet containing the sample was placed into the sample holder of a Digilab FTS 14C spectrophotometer for the generation of an infrared spectrum.

All of the coprolites analyzed are in the collections of The Science Museum of Minnesota (SMM). When there were many coprolites from the same site, a random selection was made of large and small specimens with different physical configurations.

Whenever matrix was still attached or available, the infrared spectra was also obtained in order to determine if the coprolite's spectrum was influenced by the adjacent matrix. The samples were selected to obtain representation from different stratigraphic levels and localities.

An infrared spectrum is a graph of the transmission of infrared radiation through a sample as a function of the frequency of the incident radiation. It is beyond the scope of this paper to develop a detailed explanation of the physical and chemical processes involved in the absorption of the radiation and how the spectrum is generated by the spectrophotometer. The discussion will focus on what information an infrared spectrum provides about a sample.

An infrared spectrum occurs because each functional group in a molecule has a consistent frequency at which it absorbs radiation. The intensity of the absorption is directly related to concentration. That is, as the concentration increases the absorption increases and the transmission decreases. The relative intensity of the absorption bands provide information about the concentration of the components in an unknown sample.

The interpretation of a spectrum is based on knowledge of where specific functional groups absorb that are derived from the spectra of pure materials. These reference spectra provide the baseline data from which the interpretation of unknowns is made. If two samples have identical spectra, it is a certainty that they are made up of the same materials. If two samples have different spectra but have clearly identifiable absorption bands that can be assigned to a particular functional group then the samples are different but contain at least one common component.

DISCUSSION

An understanding of the organic and inorganic compounds likely to be found in fresh feces of various animals will help in the interpretation of the infrared spectra of coprolites. Most carnivorous animals ingest at least some, if not all, of the bones of the animals that they kill or scavenge. Carnivores frequently ingest the entire animal including all of the bones.

After the soft tissue and bone have entered the digestive system, a breakdown of the structure and absorption of the constituents occurs. Bone is about 85% water, fat, and other organic materials. The remaining 10-15% is inorganic calcium, phosphate or carbonate (Harrow and Mozur, 1955). This inorganic material has chemical and physical properties that are very similar to the mineral apatite.

Solid and semi-solid fecal material from vertebrates will contain the insoluble and unabsorbed organic and inorganic compounds including carbonates and the phosphates. Organic tissue that is not attacked by the digestive bacteria, enzymes and acids will also be found in the fecal material. These organic materials are certain to be ultimately biodegraded given sufficient time.

In the case of many animals the digested mass is dewatered, formed into semi-solid feces, and excreted. Assuming that the feces is not subjected to antiseptic burial, it will be attacked over time by bacteria and other organisms that will destroy all of the remaining organic matter. The only material left that may survive long periods of time in the earth are the carbonates and phosphates. That these materials can indeed survive is clearly shown by the fossil bones that are still intact but with greatly reduced strength due to the loss of the organic binding phase.

It is reasonable to assume therefore, that fecal material from bone-eating carnivores would contain microcrystals of apatite which will still be found in the coprolite. An infrared spectrum of the apatite will be generated regardless of the size of these crystallites since the infrared absorption phenomenon occurs on the molecular level.

The food ingested by herbivores is different from that ingested by carnivores. The plants eaten differ from one another in texture, shape, color and size and in all cases the amount of stable, inorganic material is very small. Plants contain many inorganic metals and non-metals in low concentrations and in many cases are quite soluble in water. As the ingested plant material passes through the digestive system it is attacked by bacteria, enzymes and stomach acids. Only the most resistant organic and insoluble/unabsorbed inorganic compounds will be found in the fecal matter. Waste products generated by the body are also passed by the body into the feces.

Fecal material from herbivores contains more biodegradable materials than that of carnivores and would contain traces of phosphates, and other stable metal oxides, but not apatite.

Based on these two scenarios the probability of a coprolite containing some of the original material is much greater for the carnivore than for the herbivore.

RESULTS

The infrared spectra of over 60 coprolites and matrix samples, fossil bone, and dried modern crocodile feces are studied and compared in this paper.

The spectra of calcium phosphate and the mineral apatite are shown in Figure 1 and calcium carbonate and magnesium carbonate are shown in Figure 2. Figure 3 is the spectra of two fossil bone samples. Each of the major absorption bands in the spectra of fossil bones can be assigned to a specific inorganic compound. The functional group assignments are based on the spectra of pure compounds, shown in Figures 1 and 2, that were obtained during this study and from published reference collections (Hummel and Scholl 1981, Miller and Wilkens 1952). The absorption at 1060 Cm^{-1} is due to calcium phosphate; absorption at 1480, 1420, 880 and 710 Cm^{-1} are calcium carbonate and [illegible] magnesium carbonate; the doublet at 580 and 600 Cm^{-1} is due to the unique phosphate absorption from the mineral apatite; water absorbed during sample preparation is at 1640 and 3450 Cm^{-1}, and organic material is at 2850 Cm^{-1}. These spectra show that it is possible to correlate each absorption band in the spectrum of bone with materials known to be present in bone during life. This data also shows that the spectrum of the mineral apatite has a unique absorption doublet at 580 and 600 Cm^{-1} that is not found in other types of phosphates.

A spectrum of modern crocodile feces, after being dried for 2 hours at 150°C, is shown in Figure 4. This spectrum shows that the composition of this modern material is a mixture of Ca/Mg carbonate and the mineral apatite, the same materials found in bone. This sample also contains several percent of organic material that was not absorbed by the digestive system but had not yet undergone destruction through biodegradation. The presence of organic compounds is detected in this spectrum by the strong absorption bands between 2800 - 2900 Cm^{-1}.

The spectra of 26 fossil coprolites and 6 matrix samples are shown in Figures 5-18. The spectra of all the coprolites shown in Figures 5-18 are very similar proving that the qualitative chemical composition is also the same. Based on the spectra of fossil bone and pure reference materials, the bulk composition of these coprolites is carbonate and the mineral apatite. These coprolite spectra are very similar to the spectra of fossil bone, indicating that the bulk composition of a coprolite has the same inorganic compounds that make up living bone.

The spectrum of the matrix of each sample was obtained whenever possible to determine if infiltration from the matrix to the coprolite had replaced part or all of the original fecal material. The spectra of five matrix-coprolite samples are shown in Figures 5-9. In every case, the coprolite and adjacent matrix spectra were different and, therefore, the chemical composition must also be different. The spectrum of the matrix varied from locality to locality while the coprolite spectra was the same for each sample regardless of its origin. This data clearly shows that the chemical composition of the coprolites was not significantly affected by the matrix in which they were found.

The spectra in Figure 10 are of two samples taken from the edge and center of the same coprolite. These two spectra show that the bulk compositon of this coprolite is uniform from center to edge. The appearance of a slightly higher concentration of organic material can be seen in the edge of this sample when compared to the center of this sample. This is probably due to organic contamination that occurred during storage and handling after removal from the field.

The two spectra in Figure 11 were also taken from two locations on the same coprolite. One area was the black bulk material and the other was from a gray inclusion. These two spectra are also very similar, showing that the bulk composition is also the same. The color difference did not have an effect on the inorganic composition of this coprolite.

The three spectra shown in Figures 12b, 13a, and 14a are believed to be crocodile and are from the Paleocene, Miocene and Eocene. The spectra are all very familiar and therefore the composition is also similar, in spite of a large difference in age and locality.

Figure 14b is a fish coprolite and it also shows the characteristic coprolite spectrum.

The eight spectra shown in Figures 15-18 are from two locations: the late Cretaceous, Hell Creek, Montana and the Paleocene, Berru, France. These eight spectra show the great similarity in chemical composition regardless of age and locality.

The coprolite spectra shown in Figures 5-18 are all very similar to each other, proving that the composition is also similar. These spectra are representative of all the coprolite spectra that were obtained during this study.

Exceptions to the ''bone-like'' coprolites are the spectra of coprolites from a titanothere (an herbivorous Tertiary mammal), a cretaceous coprolite and a Paleocene coprolite from Berru, France, shown in Figures 19-21. It is clear that there are major differences between the spectra of these coprolites and the spectra of the coprolites shown in Figures 5-18. These spectral differences result from major differences in the chemical composition of the coprolites.

The major components of the titanothere coprolite in Figure 19 are carbonates and silicates with no detectable evidence of apatite. The presence of inorganic phosphate cannot be detected in this spectrum because of the interference from the carbonate and silicate absorptions with the inorganic phosphate absorptions.

Figure 20 is [illegible] spectra of the Cretaceous coprolite. It also is composed of silicates and carbonates and, as in the previous sample, phosphate cannot be detected because of the interference from the silicates and carbonates. Figure 21 is a spectrum of a coprolite from Berru, France. It is a very light sample indicating that extensive leaching has occurred or that it was composed of organic material.

CONCLUSIONS

Based on the data presented, the following conclusions can be made about the chemical composition of coprolites, their origin and the usefulness of infrared spectroscopy for their characterization.

The chemical composition of the fossil bone sample was shown to be primarily carbonate and the mineral apatite. These minerals are known to be the major inorganic constituents of modern living bone. Only traces of organic material were found in the spectra of the fossil bone samples studied. The spectra therefore indicate that the fossil bone samples studied retained only the original inorganic materials carbonate and apatite and had lost all of the organic phases. There does not appear to be significant introduction of other inorganic materials into these bone samples.

With three exceptions, the coprolites studied were shown by infrared spectroscopy to contain carbonates and the mineral apatite. These are the same two materials that make up the inorganic phases of living bone.

Based on the assumption that carnivorous animals eat bones, or at least bone fragments, during their feeding process, coprolites, Figures 3-18, were excreted by carnivorous animals. Since we have shown earlier that bone retains its original carbonate and mineral apatite after undergoing fossilization, it is, therefore, reasonable to assume that the physically destroyed but chemically intact carbonates and apatite in the coprolite are preserved. The presence of the mineral apatite in a coprolite is convincing evidence that the original feces were excreted by a bone-eating animal.

Fecal material from hervibores, because of its much higher organic content, is less likely to become fossilized. Some plants contain significant amounts of silicates that would be insoluble in the normal biological digestive process; however, silicates are very common in all sediments and the presence of silicate in a coprolite may or may not be indicative of the original diet of the animal.

The spectra of the matrix in which the coprolite was found were also characterized by infrared spectroscopy. In all cases, the spectrum of the matrix was significantly different from the spectrum of the coprolite. Apatite was not found in any of the matrices. The matrix spectra varied greatly from location to location and even within the same site would vary. The spectra of the coprolites, on the other hand, varied only slightly from location to location. These spectra, therefore, prove that the matrix in which the coprolite was found did not significantly affect the chemical composition of the coprolite itself.

The absence of apatite in a coprolite may be due to: (1) the coprolite is from a plant-eating animal or (2) the apatite was leached away and is no longer present even though it was present in the original fecal material. The absence of apatite, therefore, cannot be used as conclusive evidence that the coprolite is from a non-bone eating herbivore.

A final conclusion that can be made based on this study is that modern techniques of analytical chemistry can provide new valuable insight into the interpretation of fossil material. It is the intention of the author to continue to explore analytical techniques that may provide similar evidence regarding coprolites that do not contain apatite.

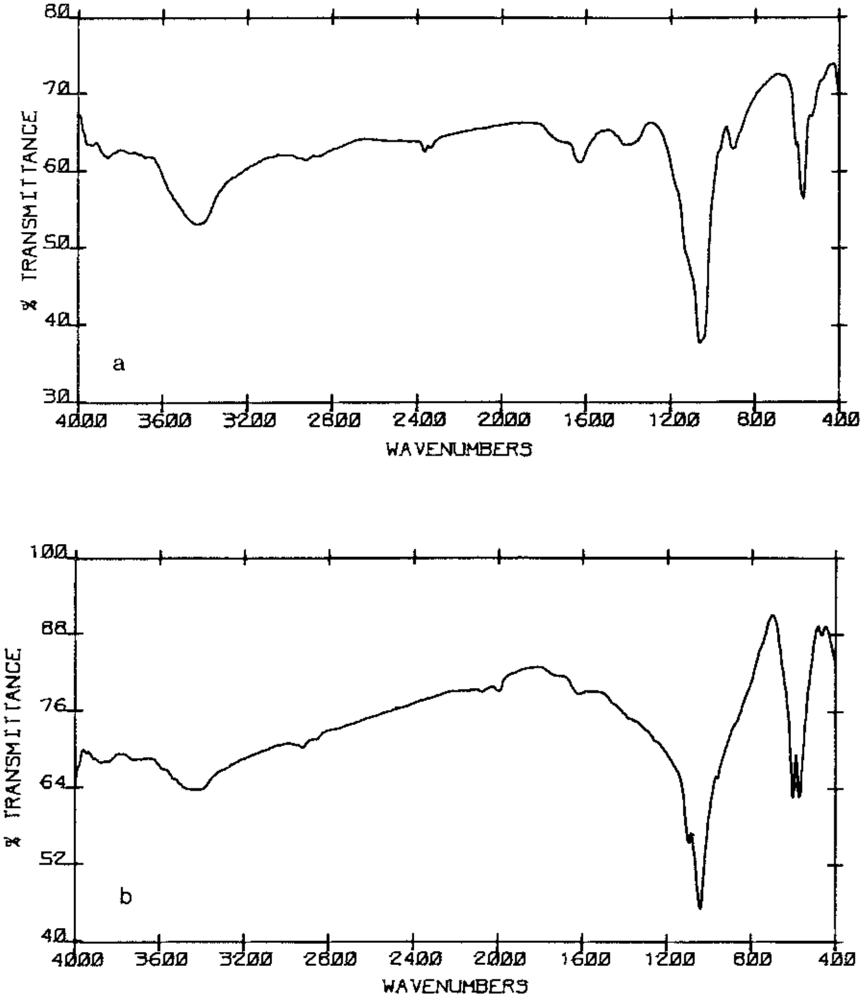

Figure 1. Infrared spectra of reference compounds (a) $Ca_3(PO_4)_2$, and (b) mineral apatite.

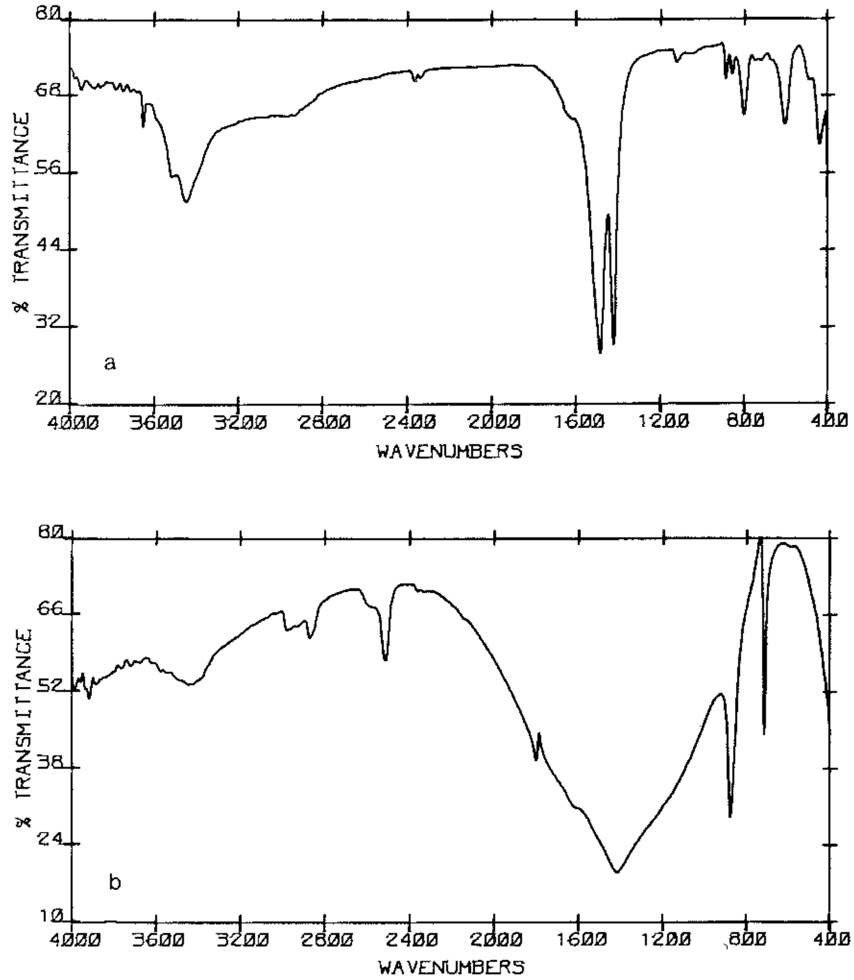

Figure 2. Infrared spectra of reference compounds (a) $MgCO_3$, and (b) $CaCO_3$.

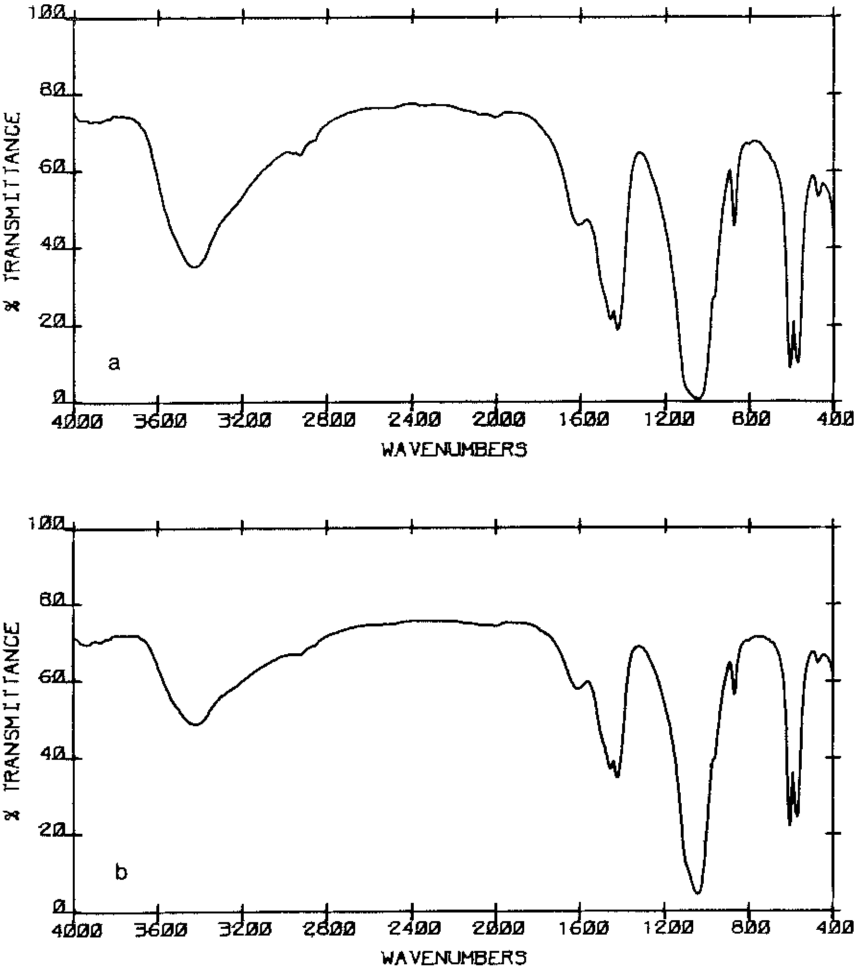

Figure 3. Infrared spectra of fossil bone (a) and (b).

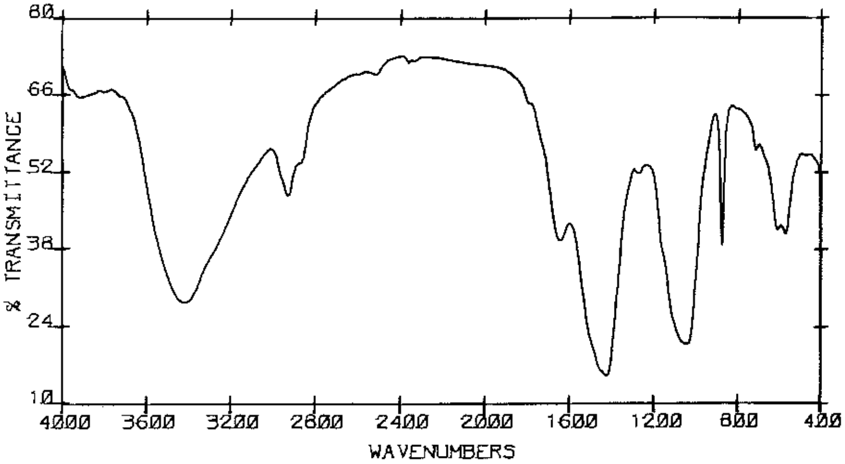

Figure 4. Infrared spectra of dried modern crocodile feces.

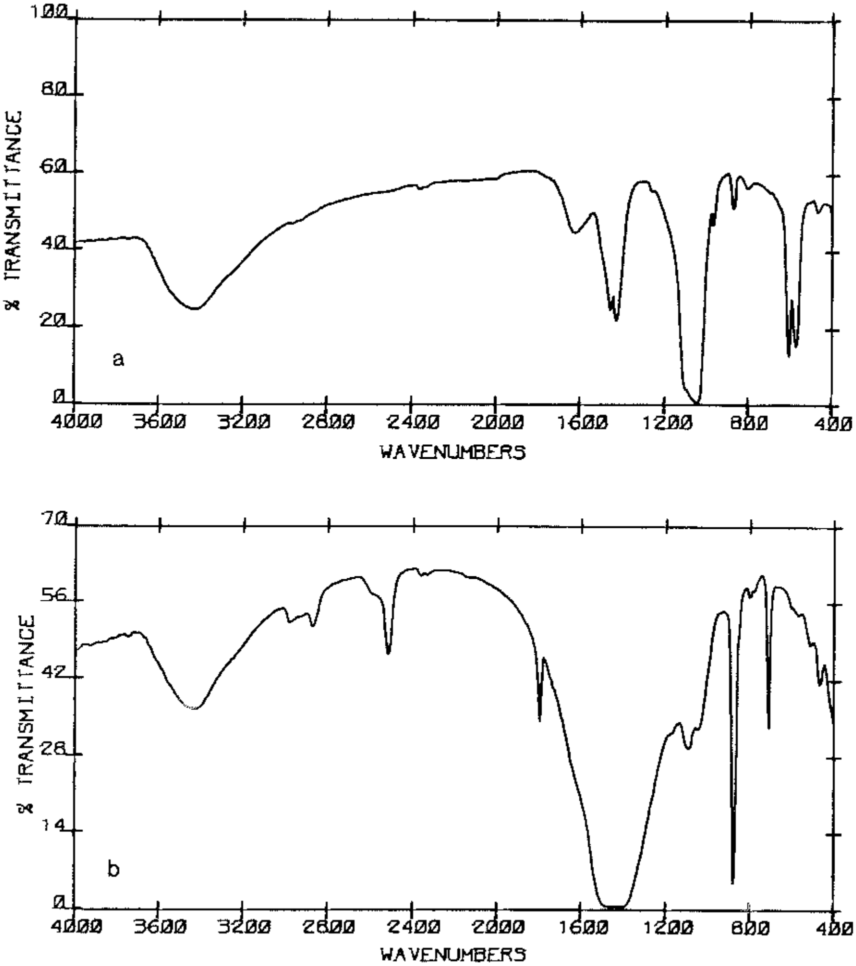

Figure 5. Infrared spectra of (a) coprolite, crocodile, SMM P80.8.1 and (b) matrix from Green River Formation, Eocene of Wyoming.

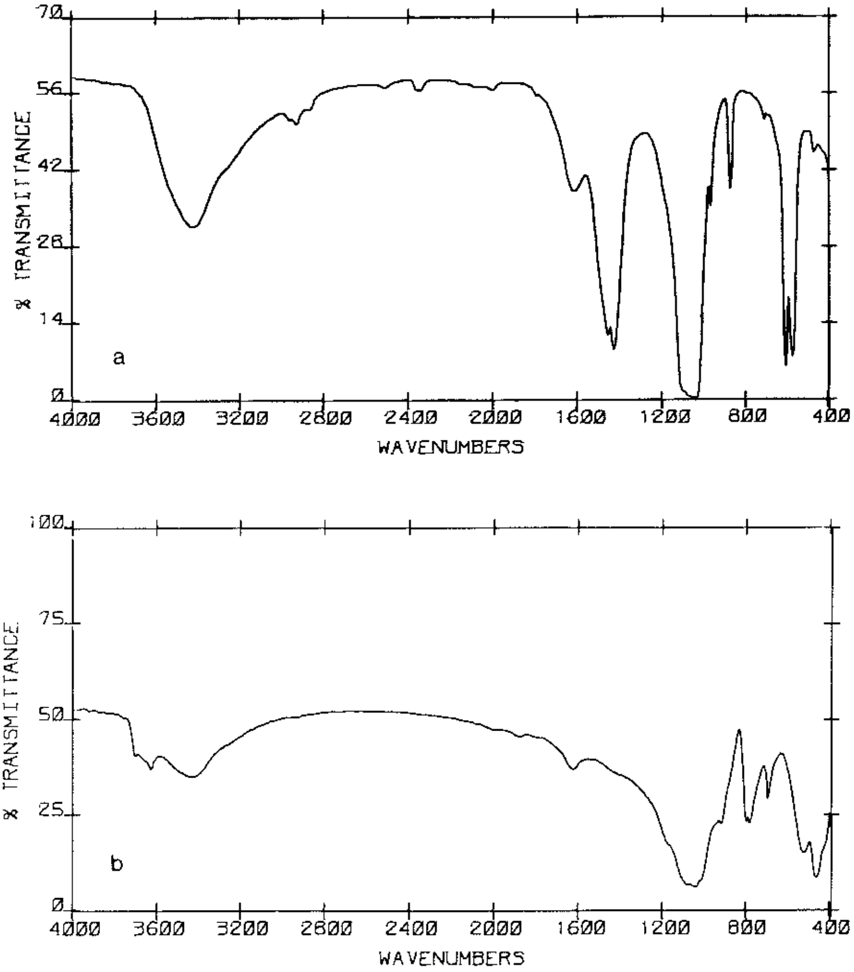

Figure 6. Infrared spectra of (a) coprolite SMM P64.2.1 and (b) matrix from mid Oligocene, White River, South Dakota.

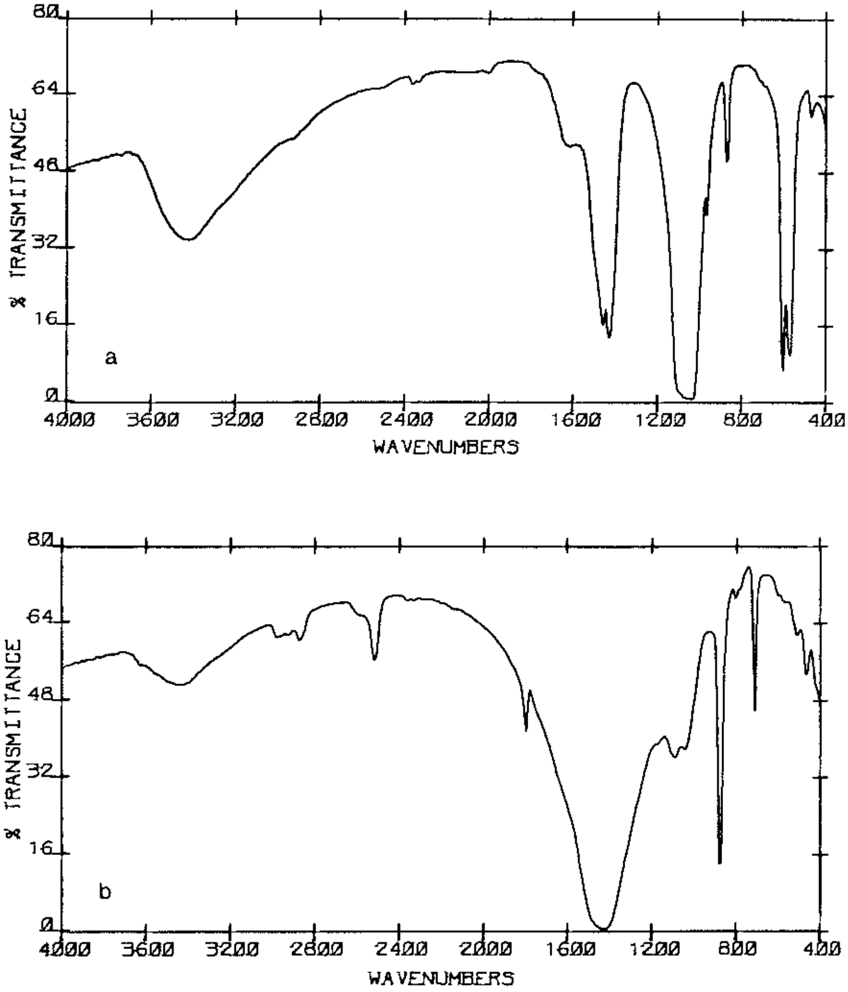

Figure 7. Infrared spectra of (a) coprolite SMM P80.8.2, crocodile, Green River Formation, Eocene of Wyoming and (b) matrix.

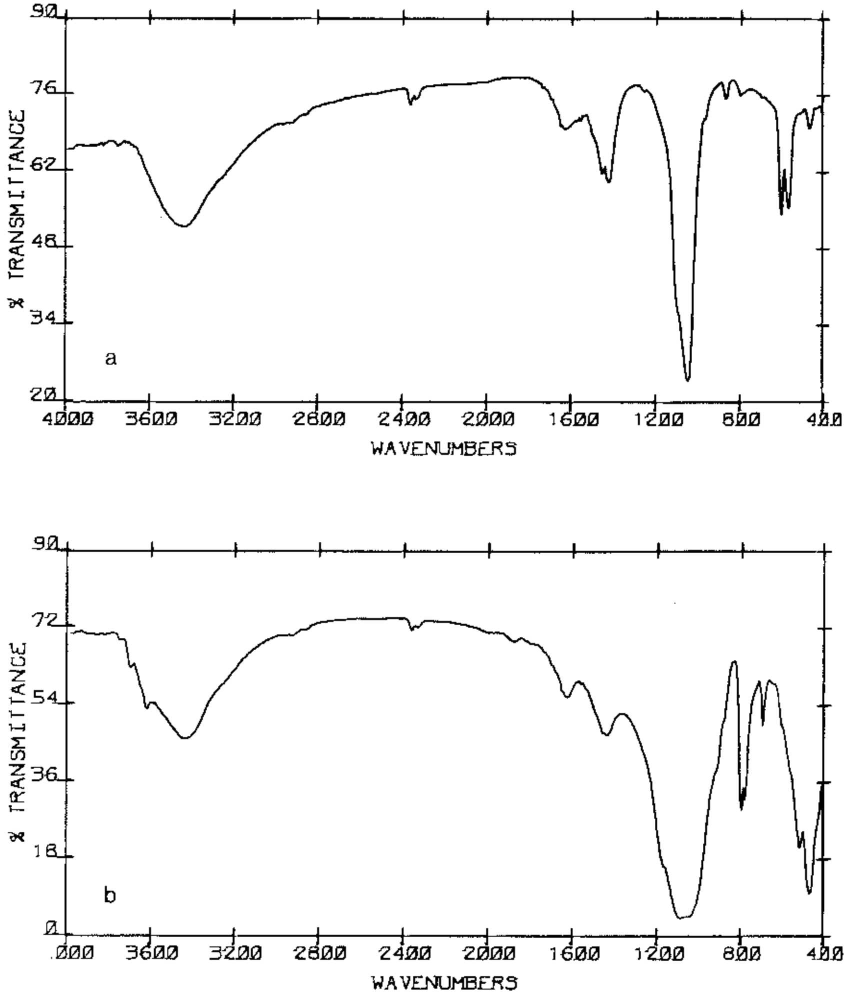

Figure 8. Infrared spectra of (a) coprolite, crocodile, SMM P79.6.205, Wannagan Creek, late Paleocene, South Dakota and (b) matrix.

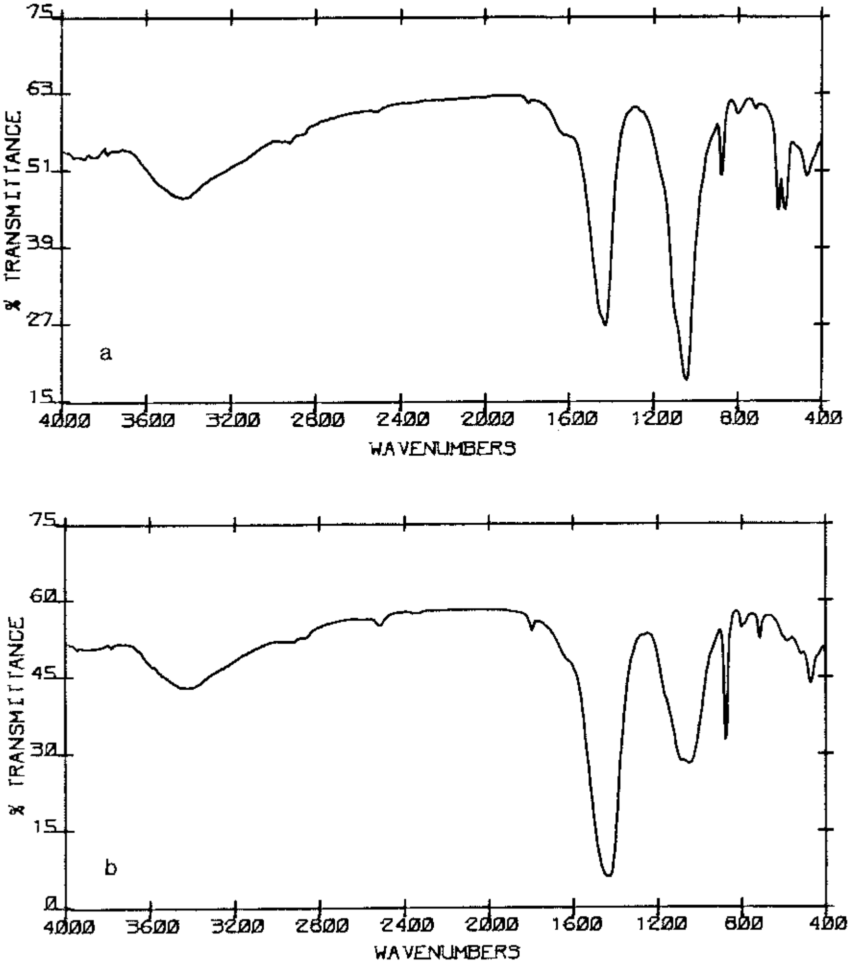

Figure 9. Infrared spectra of (a) coprolite, carnivore, SMM P69.30.1, White River, mid Oligocene of South Dakota and (b) matrix.

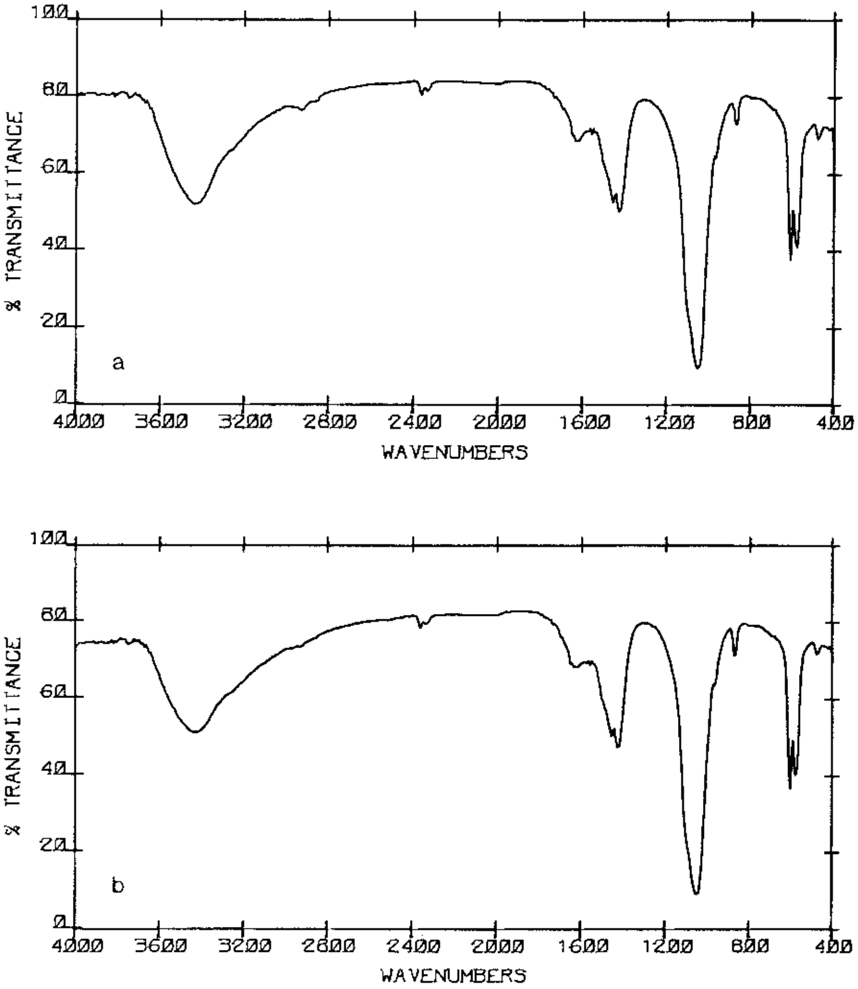

Figure 10. Infrared spectra of a coprolite, crocodile, SMM P80.8.1, Green River Formation, Eocene of Wyoming,(a) edge and (b) center.

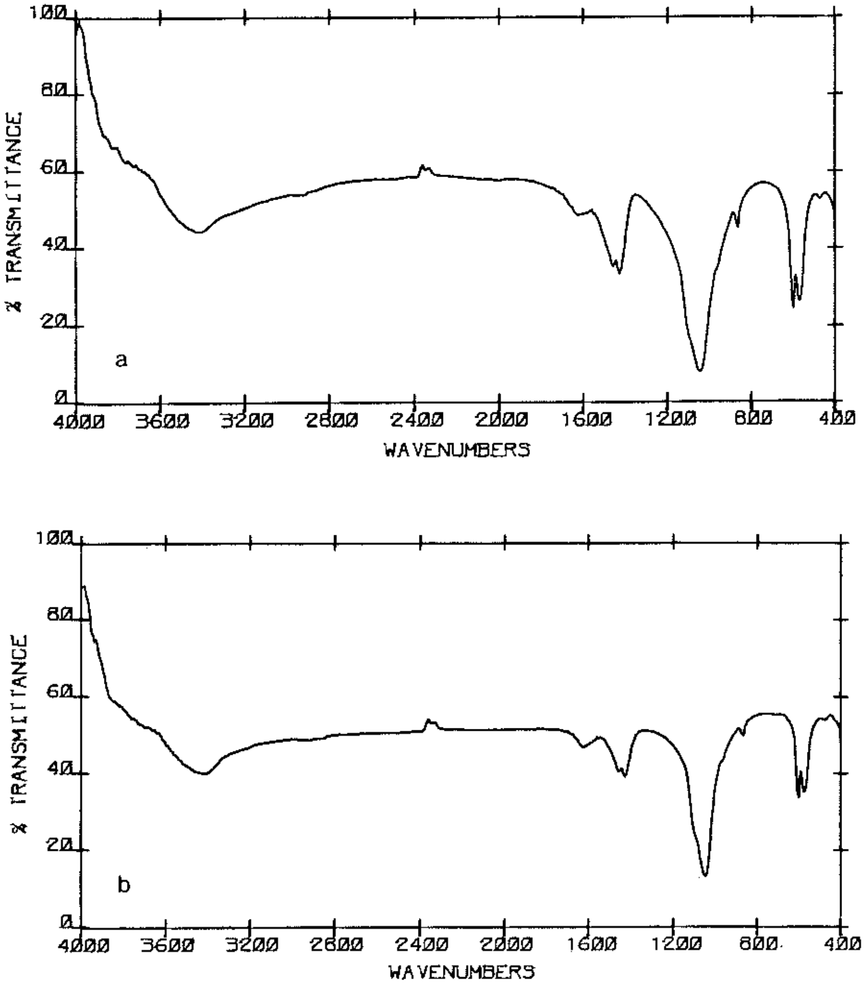

Figure 11. Infrared spectra of a coprolite, crocodile, SMM 84.12.5, late Paleocene, (a) black bulk and (b) gray inclusion.

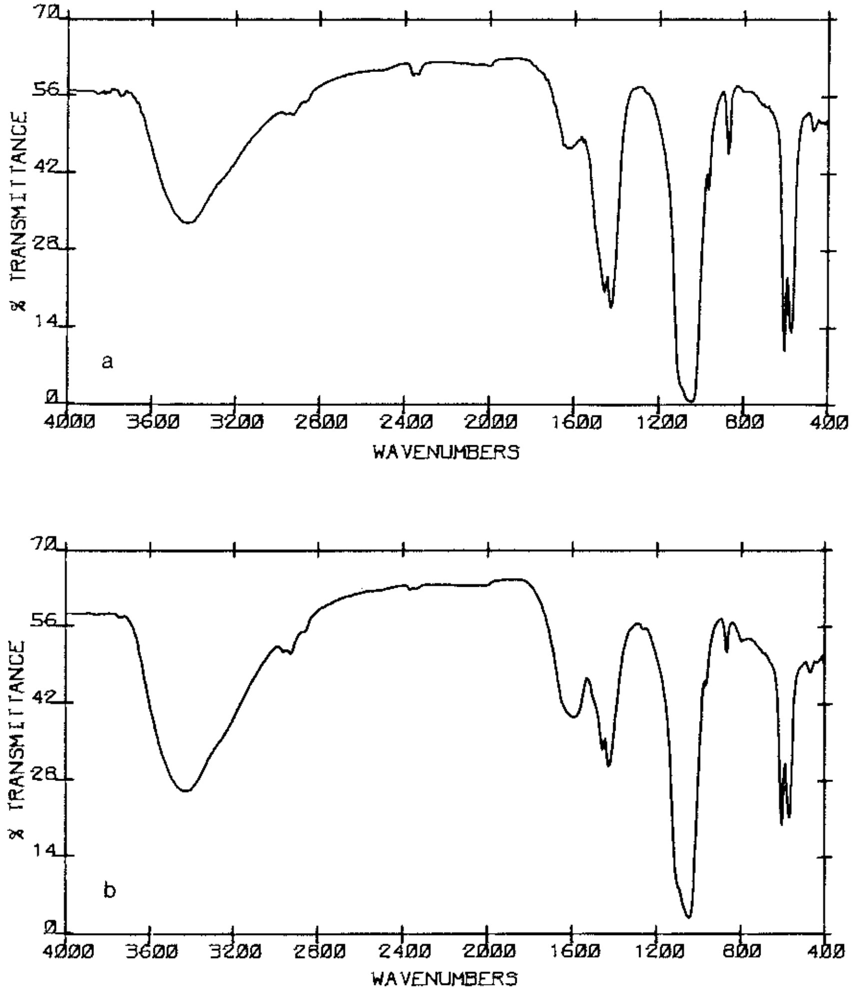

Figure 12. Infrared spectra of coprolites (a) SMM P79.17.1, crocodile, early Eocene of Wyoming and (b) SMM P79.6.104, crocodile, Wannagan Creek Quarry, late Paleocene of North Dakota.

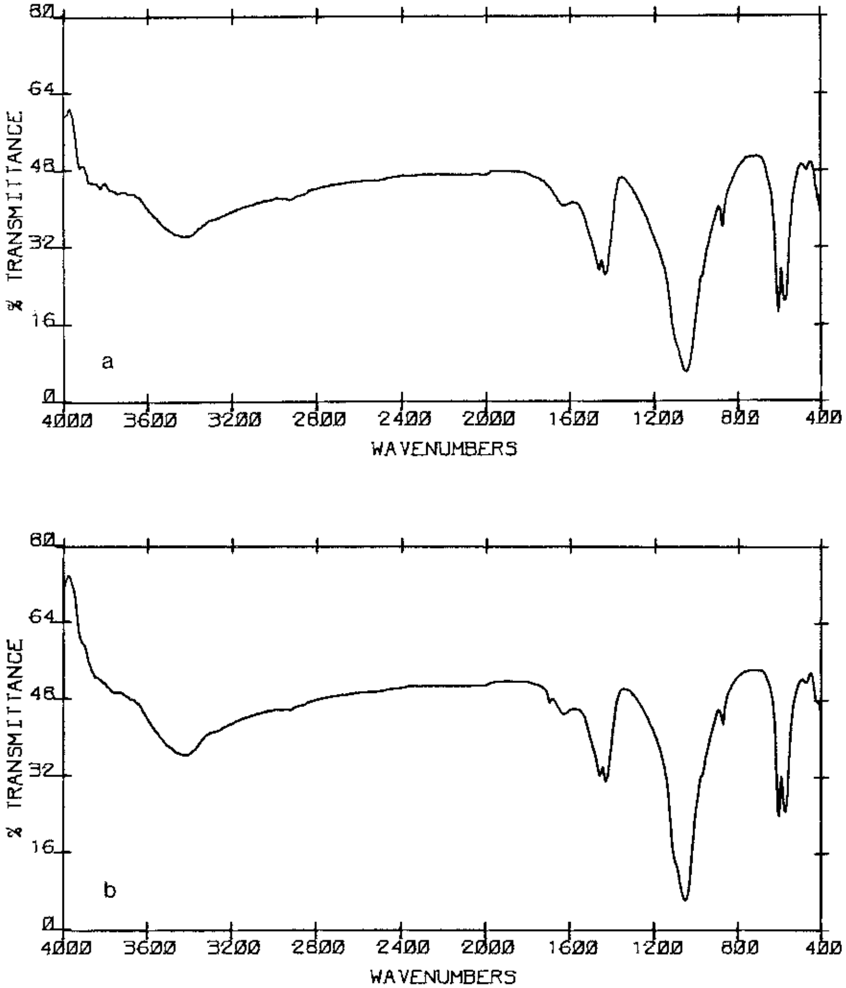

Figure 13. Infrared spectra of coprolites (a) SMM P80.2.134, crocodile, Black Mingo, Miocene, South Carolina and (b) SMM P84.12.5, crocodile, Clapp Creek, Paleocene of South Carolina.

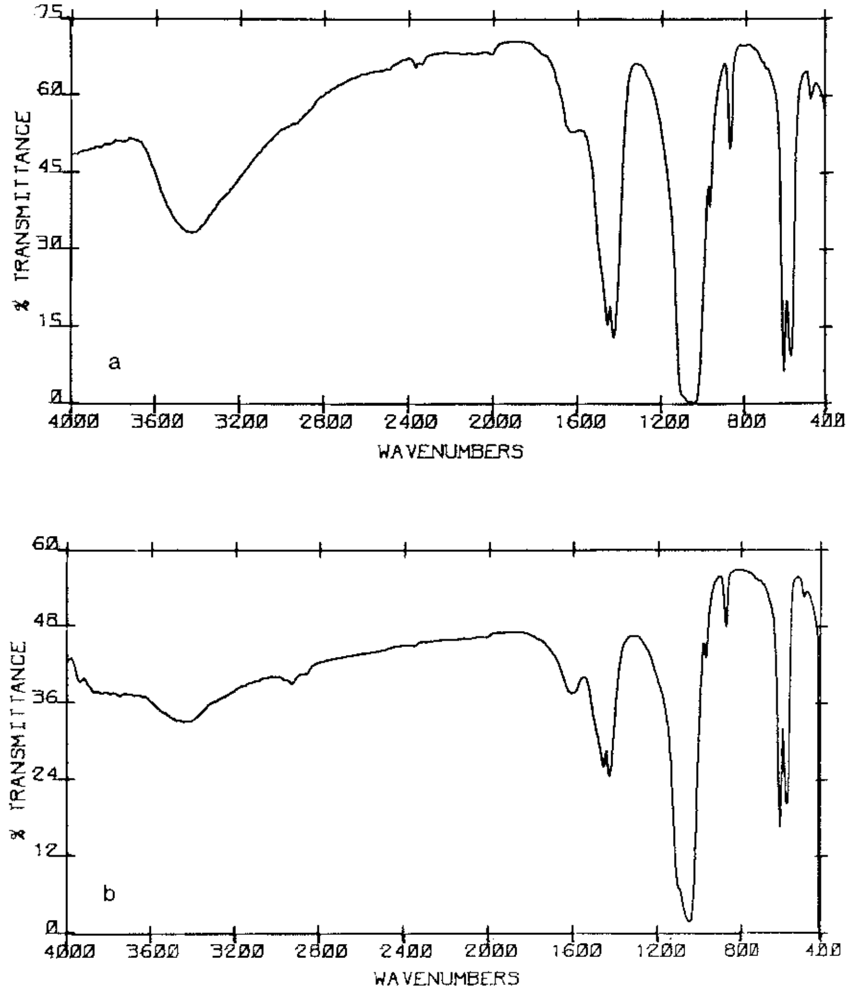

Figure 14. Infrared spectra of coprolites (a) SMM P80.8.2, crocodile, Green River Formation, Eocene of Wyoming and (b) P69.2.57, fish, Green River Formation, mid Eocene of Wyoming.

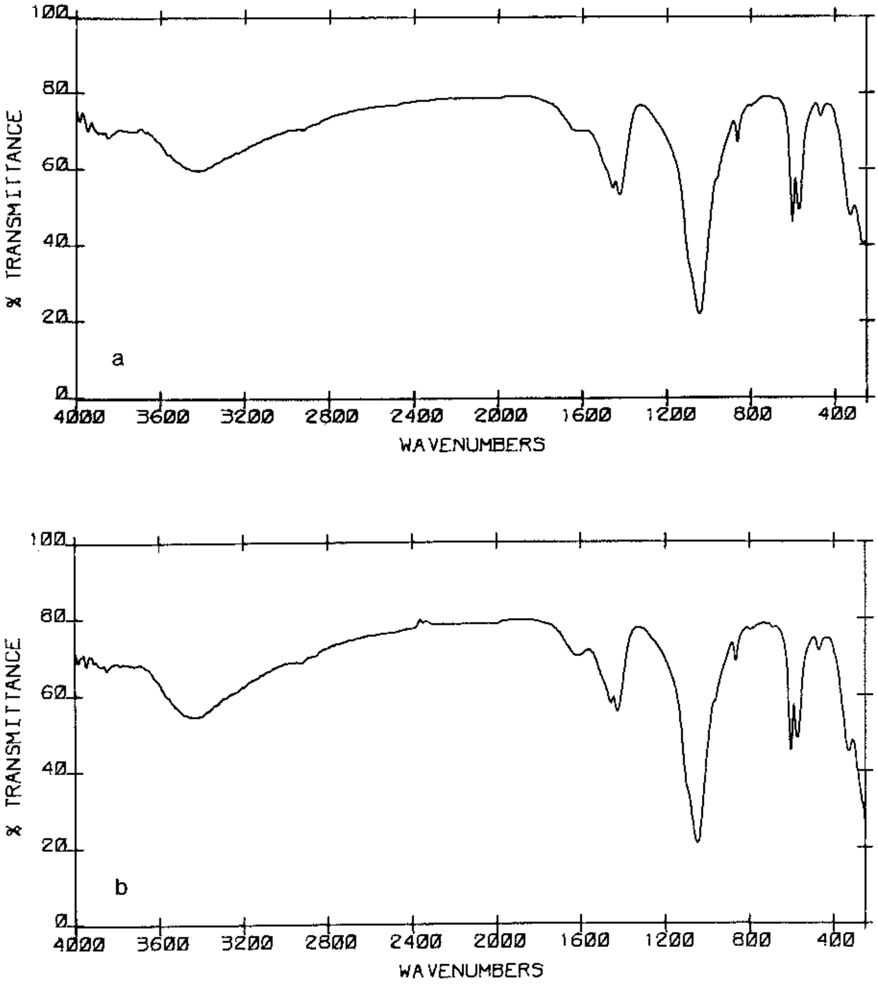

Figure 15. Infrared spectra of coprolites (a) and (b) SMM P69.38.1, reptile, late Cretaceous, Hell Creek, Montana.

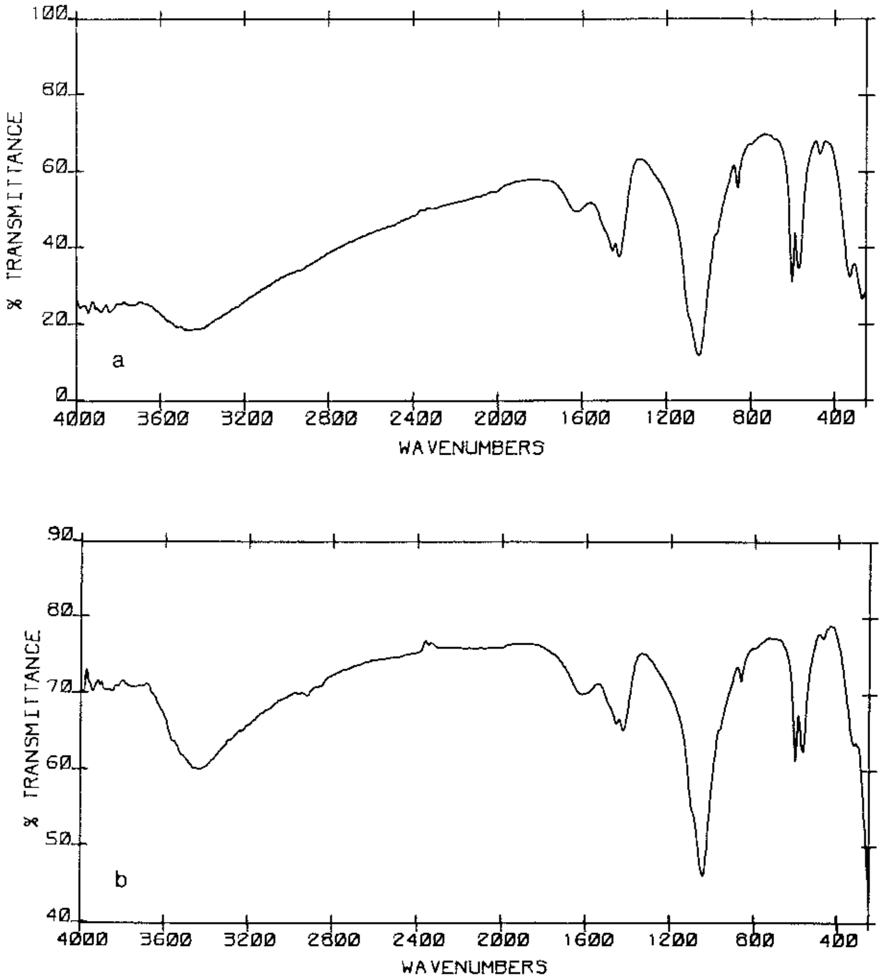

Figure 16. Infrared spectra of coprolites (a) and (b) SMM P69.38.1, reptile, late Cretaceous, Hell Creek, Montana.

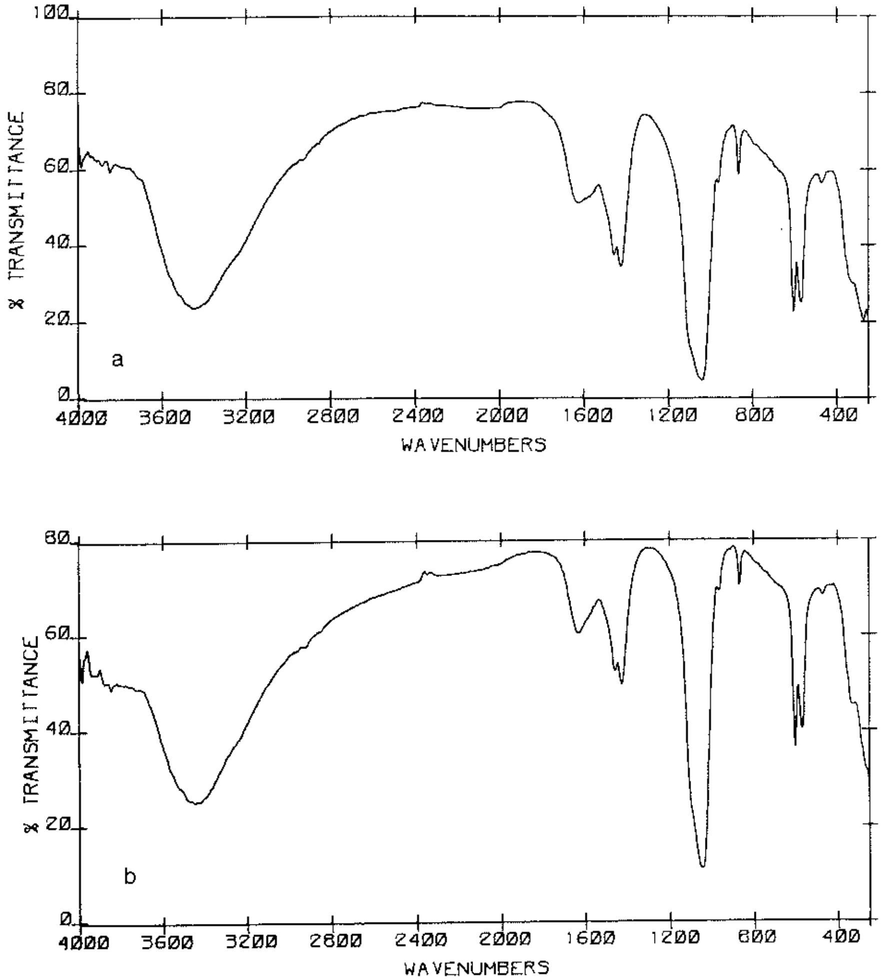

Figure 17. Infrared spectra of coprolites (a) SMM P80.17.5, Simoedosaurus, Paleocene, Berru, France and (b) SMM P80.17.23, Simoedosaurus, Paleocene, Berru, France.

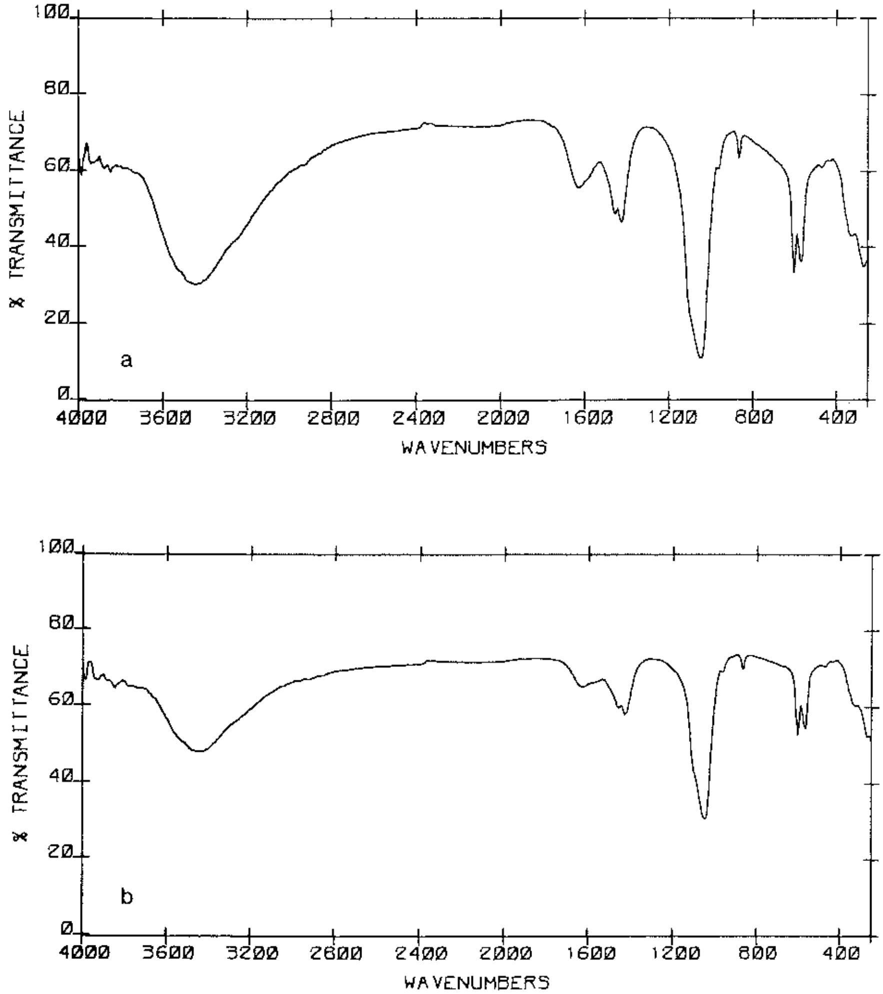

Figure 18. Infrared spectra of coprolites (a) SMM P80.17.22, Simoedosaurus, Paleocene, Berru, France and (b) SMM P80.17.6, Simoedosaurus, Paleocene, Berru, France.

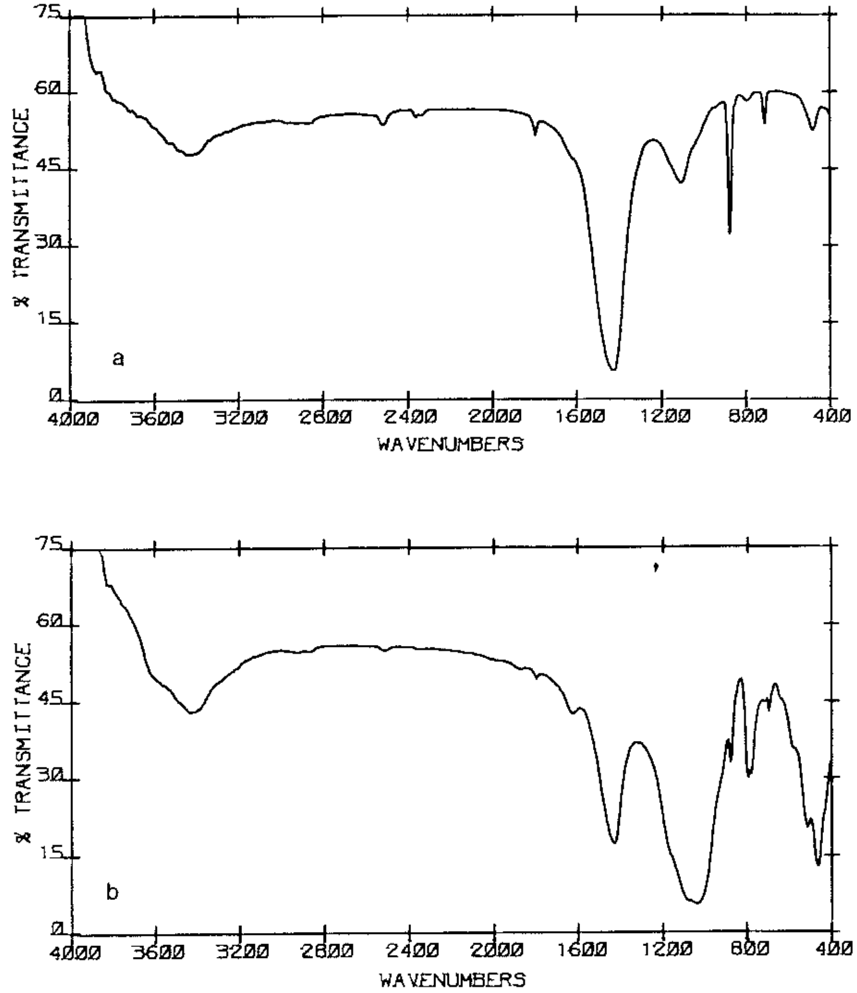

Figure 19. Infrared spectra of a coprolite (a) SMM Titanothere, Oligocene, White River, South Dakota and (b) matrix.

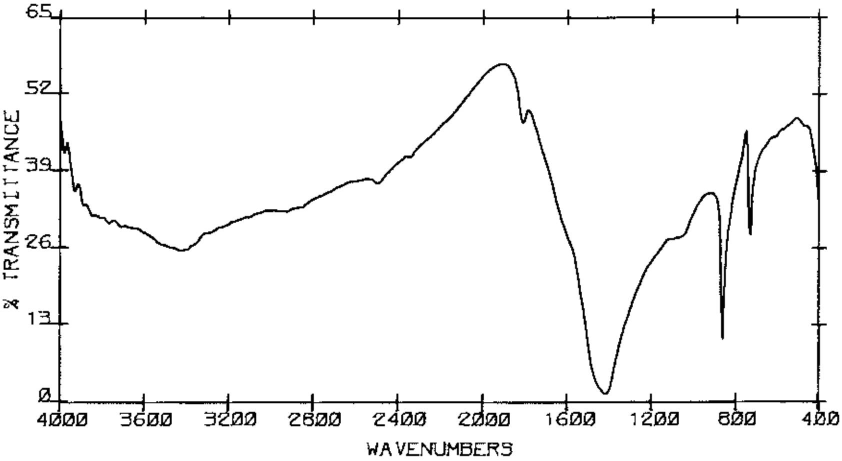

Figure 20. Infrared spectra of a coprolite, reptile, SMM P84.2.168, Cretaceous, Washington.

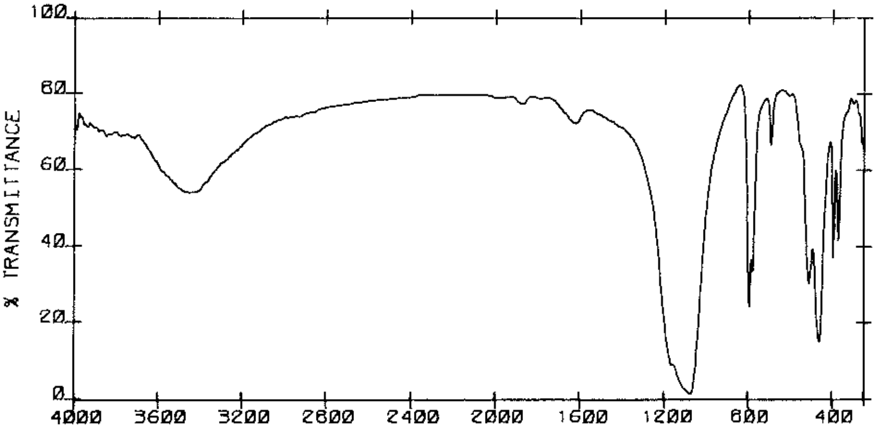

Figure 21. Infrared spectra of a coprolite SMM P80.17.16, Paleocene, Berru, France.

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