1959

A review of fossilization processes in different sedimentary environments (With special reference to the time factor of deposition of ore minerals associated with fossil material, in particular the coprolitic phosphate deposits)

Giovanna Reggiori Ligasacchi

Recommended Citation

Ligasacchi, Giovanna Reggiori, "A review of fossilization processes in different sedimentary environments (With special reference to the time factor of deposition of ore minerals associated with fossil material, in particular the coprolitic phosphate deposits)" (1959). *Masters Theses*. 5548.
https://scholarsmine.mst.edu/masters_theses/5548

A REVIEW OF FOSSILIZATION PROCESSES IN DIFFERENT SEDIMENTARY ENVIRONMENTS

(With special reference to the time factor of deposition of
ore minerals associated with fossil material, in
particular the coprolitic phosphate deposits)

BY

GIOVANNA REGGIORI LIGASACCHI

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE, GEOLOGY MAJOR

Rolla, Missouri

1959

Approved by

(advisor) a. c. Spreng

Don L. Frizzell

TABLE OF CONTENTS

LIST OF TABLES

TABLE PAGE

LIST OF FIGURES

FIGURE PAGE

ABSTRACT

This thesis offers a crossection through some principal fossilization processes involving organic matter (animals and plants) during and after sedimentation. The influence of different environments during fossilization is considered. The chemical composition of some classes of living invertebrates and plants is compared with the chemical composition of same organisms as found in consolidated sediments as fossils.

Some literature on carbonates,oxides,silicates,phosphates,and sulphides in fossils is reviewed with particular attention to those instances where the fossils are associated with ore minerals. Special consideration is given to the occurrence and composition of fecal matter in recent and consolidated sediments.

Emphasis was placed throughout on the time value of depositional criteria such as fillings and replacements. It was found that workers in the field of fossilization and sedimentation consider filling and replacement processes to be pre- or syndiagenetic and thus syngenetic. The samples studied for this thesis appear to corroborate the conclusions offered in this literature.

INTRODUCTION

The importance of organic matter in the geological history of the sediments is easily underestimated.Many sediments are composed almost exclusively of complete or partial skeletal remnants of animals and vegetals.Many other sediments owe their origin to bacteria which influenced the precipitation of salts from solutions,or may have resulted from precipitation in an environment created by the decomposition products of certain animals and plants.In many sediments, regardless of their origin,the fossils allow ~~to~~ establishment of the stratigraphic sequence.

The stratigraphic and ecologic values of a fossil are far more appreciated than any other character.Too often it is forgotten that a fossil may reflect the nature of formation of the enclosing sediment not only at the time of deposition, but also during all the processes which a sediment may undergo, such as diagenesis,replacement,folding,metamorphism,etc.

The study of the type of fossilization a fossil has undergone,the consideration of the minerals contained in it compared with those of the original organism and those of the sediment,should help in gaining a correct understanding of the origin of many rocks and mineral deposits.

The main purpose of this thesis was thus to collect a great number of data from the literature,together with some observations in nature,in order to find some criteria useful to the determination of mode and time of formation of the fossils and whatever mineral deposits may be related to them.

ACKNOWLEDGEMENTS

The writer wishes to thank Dr. Ing. G. C. Amstutz, Associate Professor of Geology at the Missouri School of Mines And Metallurgy, for his helpful information~~s~~ and suggestions, and for his continued interest during the preparation and writing of this thesis.

Thanks are also due to various Staff Members of the Geology Department whose courses the writer has attended, particularly to Dr. D. L. Frizzell.

To Dr. A. C. Spreng of this School and to Dr. Mehl of the University of Missouri, many thanks for their information~~s~~ with regard to the coprolite chapter.

CHAPTER I

THE INORGANIC CONSTITUENTS OF LIVING ORGANISMS

The influence of animals and plants in the formation of sedimentary rocks has been recognized long ago.It could be divided into two parts:an indirect and a direct one.

The indirect action of organisms on sediments is well explained in the following sentences by SUJKOWSKI (1958)[1]:"The oxidation of organic matter,proceeding as far as conditions permit,will not only cause reduction of sulphates and iron compounds,but will also promote diagenesis.This takes place as a result of pressure increase due to gases evolved (CO_2, CH_4,etc.)and also by solution of other organic compounds resulting from bituminization."The precipitation of many salts and metals from solutions,the reduction or oxidation of many metal compounds by bacteria and decaying organic matter (see uranium deposits of Colorado Plateau,cinnabar ores of Monte Amiata,Italy,and the excellent summary by KRAUSKOPF,1955) are other examples of this influence of organic matter.

The direct contribution of the hard parts of animals or plants to the forming sediments is well known.Corals and shells contribute mostly calcium carbonate,diatoms and radiolaria furnish silica,while the bones of the vertebrates and some brachiopods are a source of phosphates.

The knowledge of the mineralogical composition of many animals and plants is thus very important in order to ascertain

---

[1] All references are in bibliography

which substances each class of organisms contributes to the sediments.This knowledge is also important in order to determine if the minerals a fossil contains are of primary origin or have been introduced after the death of the animal or plant through filling and/or replacement processes.

1. ANIMALS

CLARKE and WHEELER (1922)published a study on the inorganic constituents of marine invertebrates with analyses of several specimens of different classes of organisms.They tabulated two groups of analyses for each class.In the first one the loss on ignition,comprising carbon dioxide,organic matter,and water,is reported.The other group representing reduced analyses was calculated in the following way:"The carbon dioxide was calculated to satisfy the bases,and the amount thus determined,subtracted from the total loss on ignition gave a fair but rough estimate of organic matter plus water.From the crude analyses thus obtained the reduced or rational analyses,recalculated to 100 per cent,were computed"(p.2).

A table giving the average composition for each class has been compiled for this thesis from the analyses published by CLARKE and WHEELER and is reproduced from page 8.

The analyses given in Table I can not be considered representative of every single specimen,they have only a general value,because of the many difficulties met during their preparation either by the analysts or by the writer.

The possibility of contamination by extraneous material, specially in the case of porous organisms such as sponges, was always present.The organic matter was in such excess in some analyses as to make impossible the reduction to a standard form.The apparent difference between the analysis and the reduced analysis of some groups of organisms,i.e.sponges and holoturians,is due to this fact.Some invertebrates,such as sponges,brachiopods,and crustaceans,have very different amounts of calcium carbonate and silica,or of calcium carbonate and calcium phosphate.With the exception of the sponges two different sets of analyses were given by CLARKE and WHEELER (1922)for the two different types.

Only complete analyses were considered in the preparation of table I,and only the analyses by CLARKE and WHEELER were included.Older analyses or those reported by other authors were omitted.

Calcium oxide appears to be the most common constituent of marine invertebrates,and only a few siliceous organisms are free from it.

Silica is very abundant only in radiolarians,diatoms[x](not studied by CLARKE and WHEELER),and siliceous spicules of sponges. According to CLARKE and WHEELER the silica reported in the other groups might be an impurity due to sand grains not removable from the specimens.

Magnesia is contained in notable proportion specially in alcyonarians,echinoderms,and crustaceans.Magnesia is associated mainly with the calcitic organisms,not with the aragonitic ones.

CLARKE and WHEELER (1922)point out that:"in certain groups of organisms the proportion of magnesium carbonate is dependent upon or determined by the temperature. . . .As a rule the organisms from warm waters are much richer in magnesia than those from cold waters"(p.61).The comparison between fossil and Recent crinoids shows an interesting decrease in the proportion of magnesium carbonate during fossilization.No reasons, besides a possible infiltration of calcium carbonate and a consequent lowering of the proportion of magnesium carbonate, ~~is~~ are given by CLARKE and WHEELER.

Phosphorus is abundant only in the series of phosphatic brachiopods and crustaceans.It appears also in other analyses,but,as with sulphur,it might be contained in the organic matter.Sulphur might also be derived from the sea salts.

From the study of the reported analyses it appears that the calcium carbonate found in invertebrate fossils could be considered,with few exceptions,as the primary chemical constituent of the living organisms.Mineralogically it could,however,have changed from aragonite to calcite,or have undergone ~~to~~ solution and recrystallization processes.

A foreign origin has to be sought in the case where other minerals are main constituents of fossils;this is the case of silica (with the exception of animals with siliceous skeletons,such as radiolarians,and some sponges),calcium and magnesium carbonate,magnesium carbonate,carbonates of iron, zinc,lead,copper,manganese,etc,sulfides and oxides.

A more detailed discussion on the various "mineral=

ized"fossils is offered in the second chapter.

TABLE I

THE INORGANIC CONSTITUENTS OF MARINE INVERTEBRATES

	FORAMINIFERA	SPONGES
	Analysis(5)*	Analysis(15)
SiO_2	4.684	51.162
$(Al,Fe)_2O_3$	1.794	2.026
MgO	3.420	0.608
CaO	46.380	2.986
P_2O_5	trace	0.374
SO_3	--	0.182
Ignition	42.892	41.188
CO_2 needed	40.222	--
Organic matter	3.338	--
	Reduced analysis(5)	Reduced analysis(2)'
SiO_2	4.934	4.585
$(Al,Fe)_2O_3$	1.866	5.585
$MgCO_3$	7.426	6.685
$CaCO_3$	85.774	76.390
$Ca_3P_2O_8$	trace	--
$CaSO_4$	--	(?)

*The number in parenthesis indicates the number of analyses used in the calculations.

'Only calcareous sponges.

TABLE I (continued)

	MADREPORIAN CORALS	ALCYONARIAN CORALS
	Analysis(28)	Analysis(20)
SiO_2	0.126	0.270
$(Al,Fe)_2O_3$	0.133	0.173
MgO	0.225	3.895
CaO	53.063	37.398
SO_3	(?)	0.825
P_2O_5	trace	0.727
Ignition	45.122	56.794
CO_2 needed	41.973	32.485
Organic matter	2.415	23.570
	Reduced analysis(30)	Reduced analysis(20)
SiO_2	0.173	0.437
$(Al,Fe)_2O_3$	0.149	0.233
$MgCO_3$	0.498	10.952
$CaCO_3$	99.199	79.943
$CaSO_4$	(?)	0.990
$Ca_3P_2O_8$	trace	0.224

TABLE I (continued)

	HYDROIDS Analysis(6)	STARFISHES Analysis(27)
SiO_2	0.100	0.435
$(Al,Fe)_2O_3$	0.091	1.163
MgO	0.245	3.437
CaO	53.233	32.399
SO_3	0.548	0.354
P_2O_5	trace	0.054
Ignition	45.018	60.984
CO_2 needed	41.796	29.196
Organic matter	3.288	31.564

	Reduced analysis(6)	Reduced analysis(27)
SiO_2	0.103	0.632
$(Al,Fe)_2O_3$	0.095	1.891
$MgCO_3$	0.535	10.760
$CaCO_3$	97.805	85.661
$CaSO_4$	0.961	0.896
$Ca_3P_2O_8$	trace	0.156

TABLE I (continued)

	CRINOIDS	FOSSIL CRINOIDS
	Analysis(24)	Analysis(10)
SiO_2	0.372	6.174
$(Al,Fe)_2O_3$	0.365	1.362
FeO	—	0.502
MgO	4.267	1.609
MnO	—	0.052
CaO	40.562	48.967
P_2O_5	0.103	trace
Ignition	52.735	41.149
CO_2 needed	36.572	—
Organic matter	16.287	

	Reduced analysis(24)	Reduced analysis(10)
SiO_2	0.542	6.214
$(Al,Fe)_2O_3$	0.522	1.377
$FeCO_3$	—	0.826
$MnCO_3$	—	0.083
$MgCO_3$	10.862	3.430
$CaCO_3$	83.902	88.060
$CaSO_4$	—	—
$Ca_3P_2O_8$	0.290	trace

TABLE I (continued)

	BRYOZOA	SEA URCHINS
	Analysis(10)	Analysis(12)
SiO_2	2.694	1.586
$(Al,Fe)_2O_3$	0.446	1.130
MgO	1.781	3.670
CaO	42.246	44.135
P_2O_5	0.135	0.105
SO_3	1.046	0.533
Ignition	49.835	47.620
CO_2 needed	34.493	38.150
Organic matter	15.272	9.470

	Reduced analysis(11)	Reduced analysis(12)
SiO_2	3.902	1.788
$(Al,Fe)_2O_3$	1.087	1.245
$MgCO_3$	5.520	8.506
$CaCO_3$	87.174	87.130
$Ca_3P_2O_8$	0.472	0.292
$CaSO_4$	2.319	1.037

TABLE I (continued)

	OPHIURANS	HOLOTHURIANS
	Analysis(15)	Analysis(4)
SiO_2	0.357	3.205
$(Al,Fe)_2O_3$	0.894	3.785
MgO	3.942	1.765
CaO	38.698	9.160
P_2O_5	0.060	1.465
SO_3	0.258	0.507
Ignition	54.933	81.140
CO_2 needed	34.352	—
Organic matter	20.380	—

	Reduced analysis(15)	Reduced analysis(1)
SiO_2	0.487	0.150
$(Al,Fe)_2O_3$	1.208	0.340
$MgCO_3$	10.586	13.840
$CaCO_3$	86.753	83.290
$Ca_3P_2O_8$	0.180	trace
$CaSO_4$	0.662	2.380

TABLE I (continued)

	CALCAREOUS BRACHIOPODS	PHOSPHATIC BRACHIOPODS
	Analysis(5)	Analysis(4)
SiO_2	0.218	
$(Al,Fe)_2O_3$	0.228	
MgO	1.102	
CaO	52.732	
SO_3	0.472	
P_2O_5	0.084	
Ignition	44.856	
CO_2 needed	41.984	
Organic matter	2.676	
	Reduced analysis(5)	Reduced analysis(4)
SiO_2	0.226	0.687
$(Al,Fe)_2O_3$	0.234	0.642
$MgCO_3$	2.420	2.970
$CaCO_3$	96.096	3.445
$CaSO_4$	0.834	3.870
$Ca_3P_2O_8$	0.190	82.907

TABLE I (continued)

	PELECYPODS Analysis(11)	SCAPHOPODS-AMPHINEURANS Analysis(2)
SiO_2	0.172	0.890
$(Al,Fe)_2O_3$	0.133	0.235
MgO	0.101	0.170
CaO	52.691	53.655
P_2O_5	trace	trace
SO_3	---	0.100
Ignition	44.879	44.610
CO_2 needed	42.107	42.285
Organic matter	2.771	2.325

	Reduced analysis(11)	Reduced analysis(2)
SiO_2	0.181	0.505
$(Al,Fe)_2O_3$	0.140	0.245
$MgCO_3$	0.220	0.325
$CaCO_3$	99.414	98.750
$CaSO_4$	---	0.175
$Ca_3P_2O_8$	trace	trace

TABLE I (continued)

	GASTROPODS Analysis(20)	CEPHALOPODS Analysis(3)
SiO_2	0.496	0.046
$(Al,Fe)_2O_3$	0.322	0.106
MgO	0.129	1.103
CaO	53.052	48.880
SO_3	(?)	---
P_2O_5	trace	trace
Ignition	44.750	49.146
CO_2 needed	41.761	44.076
Organic matter	2.989	5.070
SiO_2	0.519	0.093
$(Al,Fe)_2O_3$	0.339	0.113
$MgCO_3$	0.290	2.600
$CaCO_3$	98.735	97.193
$CaSO_4$	(?)	---
$Ca_3P_2O_8$	trace	trace

TABLE I (continued)

	CALCAREOUS CRUSTACEANS	PHOSPHATIC CRUSTACEANS
	Analysis(6)	Analysis(13)
SiO_2	0.428	0.374
$(Al,Fe)_2O_3$	0.348	0.936
MgO	0.796	1.960
CaO	52.096	26.113
P_2O_5	trace	3.590
SO_3	—	0.441
Ignition	44.681	65.664
CO_2 needed	41.743	19.086
Organic matter	2.938	46.712
	Reduced analysis(6)	Reduced analysis(13)
SiO_2	0.453	0.767
$(Al,Fe)_2O_3$	0.366	1.641
$MgCO_3$	1.750	8.204
$CaCO_3$	97.301	70.385
$Ca_3P_2O_8$	trace	17.216
$CaSO_4$	—	1.711

2. PLANTS

It is well known that plants have a very high content of organic matter and that even their hard parts are mainly composed of carbon, hydrogen, oxygen, nitrogen, and some sulphur. There are, however, exceptions like the calcareous algae with as much as 80 per cent of $CaCO_3$.

CLARKE and WHEELER (1922) analyzed marine algae in the same way they did for the marine invertebrates and their results are reported in table II. No other papers have been found with quantitative analyses of other living specimens of the vegetable kingdom.

DEAN (1957, ref. DEUL, 1958) lists, besides the five fundamental ones, eleven other elements necessary for the life of the green plants. They are: P, K, Ca, Mg, Fe, Cu, Cl, Mn, Zn, B, and Mo.

DEUL (1958) reports semiquantitative spectrographic analyses of 21 samples of coal flora. 32 elements were detected in the ashes, and their distribution in the specimens is represented in table III (after DEUL).

The relatively high number of elements present in the fossil plants is, however, only a very small part, quantitatively speaking, of them. It is reasonable thus to assume that the mineral matter found in petrified plants is, in the great majority of the cases, of later introduction after the death of the organisms.

TABLE II

THE INORGANIC CONSTITUENTS OF CALCAREOUS ALGAE

	MAGNESIAN ALGAE	HALIMEDA
	Analysis(15)	Analysis(4)
SiO_2	0.456	0.897
$(Al,Fe)_2O_3$	0.259	0.515
MgO	7.244	0.272
CaO	41.325	48.762
P_2O_5	trace	trace
SO_3	0.468	0.202
Ignition	49.104	49.020
CO_2 needed	40.248	38.045
Organic matter	8.566	10.725

	Reduced analysis(15)	Reduced analysis(4)
SiO_2	0.528	1.010
$(Al,Fe)_2O_3$	0.298	0.580
$MgCO_3$	16.861	0.647
$CaCO_3$	81.340	97.362
$Ca_3P_2O_8$	trace	trace
$CaSO_4$	0.965	0.400

The illustration of table III is given through sentences by DEUL (1958), after whom the table is reproduced. "The data . . . are tabulated . . . as a frequency distribution of the elements within the concentration ranges detected. . . . The ranges are separated by broken lines, indicating that elements may be present in higher or lower concentrations. Furthermore, elements not detected in certain samples are not assumed to be present in the next lower range, nor are they presumed to be totally absent, hence, the tapered boundary pointing downward."

TABLE III

FREQUENCY DISTRIBUTION OF ELEMENTS IN ASH OF 21 COAL FLORA

%	K	Ca	Mg	P	Fe	Mn	B	Cu	Mo	Zn	Si	Al	Na	Ti	Ba	Sr	Pb	Li
10.	17	9	3								11	4						
5.	2	6	6								5	3	2					
1.	2	6	10	8	2	2					4	5	16	1	1			
.5			2	8	3	3	7				1	1	3	3	8	2	2	
.1				5	15	4	7	2						3	8	17	3	
.05					1	4	7	15				2		9	4	2	8	17
.01						8		4						2			1	4
.005									2					2			7	
.001									8					1				
.0005									2	21								
.0001									9									

TABLE III (continued)

%	As	Cr	Zr	V	Ni	Co	Sn	La	Nd	Ga	Y	Yb	Sc	Ag	Be
10.															
5.															
1.															
.5															
.1															
.05	1														
.01	20	3	1	3	4		1	2	1						
.005		6	3		16			4	1	1	2				
.001		12	7		1	12	7	15	19	7	7		3		
.0005			8	9		9	13			13	12	1	2	8	
.0001			2	9								7	16	13	1
.00005												13			20

CHAPTER II

REVIEW OF THE GEOCHEMICALLY DIFFERENT TYPES OF FOSSILIZATION

Fossils are in many different ways of interest for the science of mineral deposits. As guide fossils they may serve as stratigraphic markers. By their composition, which often differs from that of the surrounding rock,they may serve as indicators of the conditions which existed in the environment where they lived or in which they were deposited and incorporated into the sedimentary rock.

The difference between fossils and their host rock, for example sulphidic fossils in carbonate sediments or coal, phosphatic fossils in shales, dolomitic or siliceous fossils in carbonates, fossils consisting of iron oxide in limestones and shales, etc., are the same differences that often exist between mineral deposits and their host rock. As a matter of fact these "mineralized " fossils are actually small mineral deposits. It appears therefore logical to suspect that the origin of at least a part of the sulphidic, phosphatic, oxidic, siliceous, etc. mineral deposits may be related to the same processes as take place during fossilization. The small scale mineral deposits inside and around the fossils may reveal features which are interesting for the formation of sedimentary mineral deposits.

In this connection it is interesting to note an observation made by AMSTUTZ (1959). Small sulphide and oxide deposits of no commercial value are often called syngenetic sedimentary. TARR (1928) for example described "syngenetic pyritization in local reducing areas of Pennsylvanian shales in Missouri". As soon as such mineral deposits become of economic size and interest, an epigenetic theory involving epigenetic hydrothermal fluids from "unknown sources and unknown depth" is assumed, although the difference is merely of size and economic value but not of geochemistry and geometry.

Not only the origin of certain mineral deposits, but also the meaning and scope of certain terms which will be used is often a controversial matter. Therefore the following subchapter is entirely devoted to the definition of terms as used in this thesis.

1. DEFINITION OF TERMS USED

A <u>fossil</u>, according to the definition of WEBSTER's dictionary, is: "any impression, or trace of an animal or plant of past geological ages, which has been preserved in the earth's crust." Many authors tried to give a complete illustration of the complex characters of a fossil and to restrict it to a definition, but without unanimous consensus of opinions. An account of the characteristics common to most of the definitions is given by TWENHOFEL and SHROCK (1939, p. 14-15) who wrote:

> . . . a fossil must be some evidence of an animal or plant that once lived. . . . it must also furnish some idea of the character (size, shape, form, structure, ornamentation, etc.) of part or all of the organism. . . . must have age, . . . must have been preserved in the materials of the earth's crust by natural agencies and processes.

<u>Mineralization, mineralized</u>, are used in the body of this thesis without any genetic connotation. They only indicate a change in the mineral composition of a fossil in relation to the original organism and/or structure. When refering to fossilization processes, mineralization is used in accord with ~~to~~ MORET's classification of such processes (see beginning of subchapter on fossilization processes).

<u>Diagenesis</u>, according to a definition given by SUJKOWSKI (1958, p. 2692), includes "all those processes which turn a fresh sediment into a stable rock of some hardness, under conditions of pressure and temperature not widely removed from those existing on the earth's surface."

According to standard definitions syngenetic ~~is~~ refers to any rock, mineral, or mineral deposit formed contemporaneously with the enclosing rock; epigenetic any of the above formed later than the enclosing rock. In spite of the apparent simplicity of their definitions syngenetic and epigenetic are highly controversial terms. Many authors assume that the chemical and physical characteristics of a rock during diagenesis are very close to those of a freshly deposited sediment and consider all the diagenetic changes and alterations as syngenetic. Others include these processes in the epigenetic side.

In many papers of recent years sedimentary petrologists, have started to divide the time of formation of calcareous concretions, cherts, septaria, etc.; of dolomitization, silicification, etc.; into syngenetic, diagenetic, and epigenetic (PANTIN, 1958, p. 369). In the present thesis, however, all the changes occurring during diagenesis have been considered as syngenetic.

Replacement is "a process of essentially simultaneous capillary solution and deposition by which new minerals are substituted for earlier minerals or rocks" (BATEMAN, 1950). Replacement in economic geology is usually considered an epigenetic phenomenon, even if no mention of time is made in the definition. Economic paleontologists, petroleum geologists, however, speak more and more of syngenetic replacement, that is of replacement occurring during diagenesis.
The changes in the fossil matter could be considered in

relation either to the living organism and/or organic structure, or to the sediment which encloses the fossil. If the organism was the comparison point every change in the organic or mineral structure should be regarded as epigenetic and the term replacement would obtain, in this thesis, the time connotation of the economic geologists. If, however, only the change subsequent to diagenesis and not every process involving a change in the fossil itself is defined as epigenetic, it is possible to speak of syngenetic or epigenetic replacement.

2. SUMMARY ON THE FOSSILIZATION PROCESSES

Fossilization is the process through which hard and soft parts of animals and plants are preserved regardless of their composition and age. All the changes an organism has undergone before its finding in recent times as fossil are usually comprised in the term fossilization.

The possible fossilization processes can be subdivided into those occurring to the hard, organic or inorganic parts of animals and plants and those regarding the organic compounds contained in such hard parts.

Animals

Immediately after death the soft tissues of an animal body start to dissolve and may be carried away. Also the hard parts undergo some changes becoming more porous because of the frequent destruction of the associated organic matter. The formation of a fossil is strictly related to that of the enclosing rock. It varies according to the changes occurring in a sediment during diagenesis.
The most frequent cases of formation of a fossil are, according to MORET (1948):

Mineralization. The chemical composition of a shell, or even the original color of a shell,can be preserved.
SUJKOWSKI (1958) reports, among the examples of sediments in which diagenesis has worked very little or not at all, molluscan shells in the Tortonian sand near Poczajow in Poland, where the primary shell color is exceptionally well preserved. CLOUD (1941) mentions a specimen of Crananea thomasi Stainbrook

ornamented with radial, maroon-colored bands. The absence in the sediment of agents capable of producing that color in the homogeneous shell substance allows CLOUD to state that the color is the original preserved one.

Recrystallization occurs often in calcareous environments and also those changes tending toward a stable chemical and physical equilibrium. Aragonite always converts into calcite and opal into chalcedony.

A complete replacement of the original mineral, either during diagenesis or later on, is also a relatively frequent case.

Incrustation, according to MORET (1948), is frequently caused by calcareous or siliceous waters, rarely by other types of mineralized waters, which cover the organisms with a protective deposit of $CaCO_3$ or SiO_2, thus assuring a perfect conservation of the shape and hard parts of the specimen.

Casts and molds of an organic structure are found when the original body, embedded in soft sediments, is dissolved by circulating or connate waters. An external mold is an impression of the exterior, of the original surface of a shell. The internal mold is a filling upon which is impressed the internal surface of it. In the case of permeable sediments the space left empty between the internal and external molds can be filled up with minerals deposited by circulating waters. We have thus a specimen with the exact form and shape of the original animal and this is called a natural cast. As compared with the products of the so-called mineralization process we do not have in this case the minute, microscopic interior structure of the living organism.

The different ways in which a hollow shell can leave a fossil record of its former presence are illustrated by TWENHOFEL and SHROCK (1939, p. 17, Figure 6) and are reported in Figure 1.

Plants

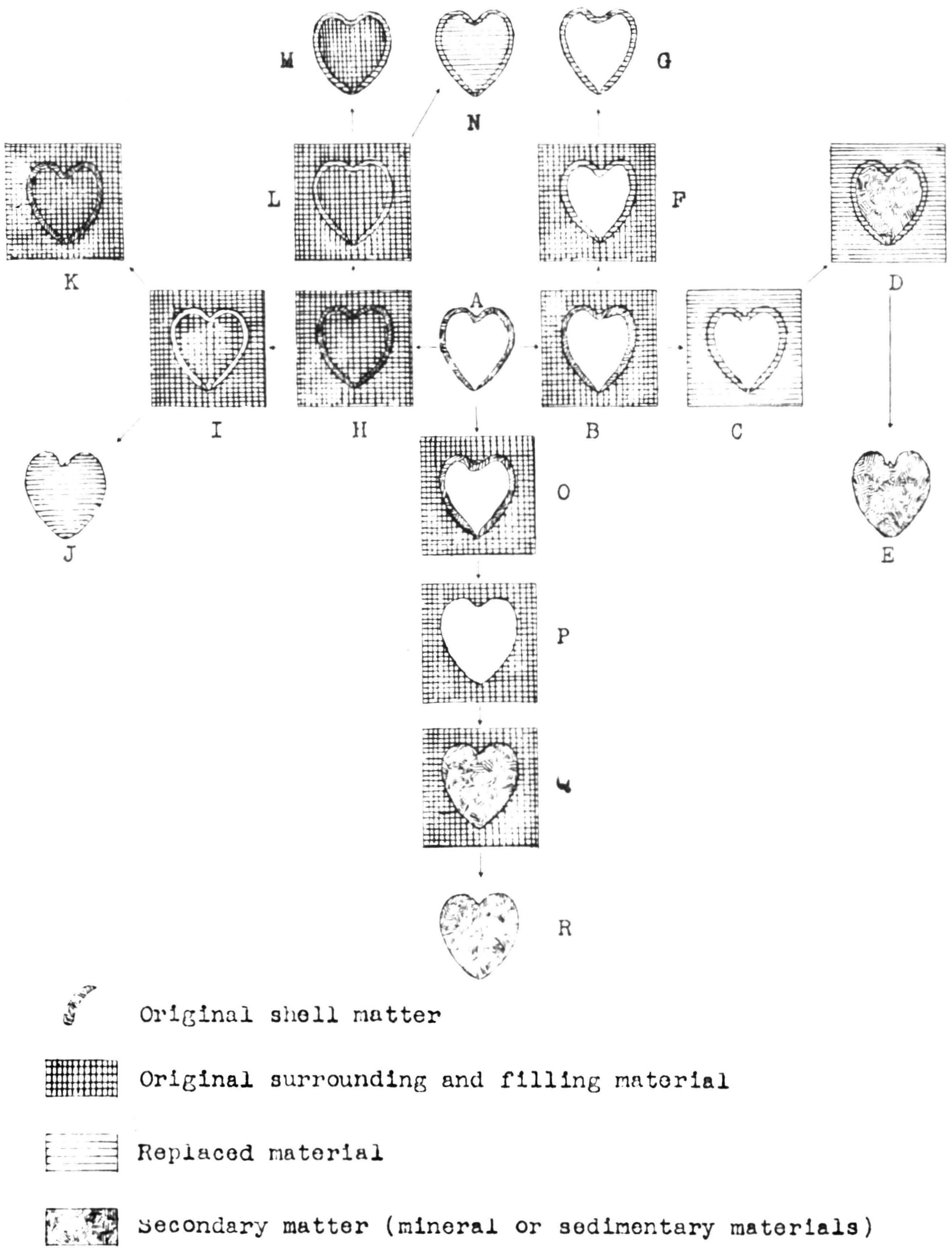
Plants, according to DARRAH (1939), are most often preserved by carbonization or coalification. This type of fossilization is greatly influenced in its first stage by biochemical processes that break down and change the organic compounds of the original material. The bacterial action may cease well before the total decomposition of the vegetable matter because of the changes in the environmental conditions, such as exhaustion of oxygen or development of toxins in the sedimentary basin. It is thus very likely to find well preserved masses of plant fragments or complete plants in the coal.

If the burial conditions retarded or completely preserved bacterial decomposition the structural details of the fossil plants will be greater. According to DARRAH such conditions frequently occur for burial in stagnant water, complete burial under fine-grained sediments or rapid infiltration by mineral substances. The infiltration of mineral substances, possible only if the surrounding sediments are still unconsolidated or are extremely porous, produces a petrif~~ic~~action. Petrif~~ic~~action is the term used by DARRAH in his textbook of Paleobotany, but other terms as infiltration or replacement are also widely used.

Figure 1 - Diagram showing the different ways in which a hollow shell can leave a fossil record of its former presence.

A. Original shell. B. Shell buried without interior filled. C. Shell and surrounding material replaced. D. Original cavity filled with secondary material. E. Filling of internal cavity freed from containing rock. This filling is an internal mold. It has impressed on its surface the counterpart of the internal surface of the original shell. F. Only shell matter replaced, with cavity remaining. Crystals sometimes grow into the cavity. G. Replaced shell released from containing rock. H. Shell filled and then buried. I. Shell matter removed by solution, with the remaining cavity representing the position of the original shell. J. Original filling released from rock. This is an internal mold exactly like E except in the manner of formation. K. Cavity left after solution of original shell filled with secondary material to form a natural cast. L. Shell alone replaced; filling and surrounding material unaffected. M. Replaced shell, with unaltered filling, freed from surrounding rock. N. Shell and filling replaced and then released from surrounding rock. O. Shell buried without interior filled. P. Shell matter dissolved leaving an external mold. The surface of the cavity bears an impression which is the counterpart of the exterior surface of the original shell. Q. Cavity left after solution of shell filled with secondary matter. R. Filling of cavity released from surrounding rock. This filling is a replica of the original surface of the shell.

(After TWENHOFEL and SHROCK,1935,p.17,figure 6)



Circulating mineral solutions do not, however, have to have been introduced into the sediment in some stage of its consolidation; they can be connate. SUJKOWSKI (1958) shows that during diagenesis calcium carbonate and silica are easily dissolved and redeposited in other places of the forming rock, often around organic structures, such as skeletons of sponges, shells, plant debris, etc.

The petrifying agents are many and different. St. JOHN (1927) reports the following ones, on the basis of a study of the literature: silica, by no means the most frequent, in the form of opal, chalcedony, cornelian, onyx, amethyst, jasper, or agate; hematite; limonite; calcite, aragonite, dolomite, malachite, siderite; pyrite, marcasite, chalcopyrite, cinnabar, galena, bornite, covellite; fluorite; barite, gypsum; sulphur; phosphorite; halloysite, chlorite, pyrophyllite, melacolite, talc.

Petrification, always according to St. JOHN, could take place in three different ways: 1, True replacement, with complete obliteration of the vegetable structure; 2, infiltration, leaving the entire cell walls marking the outlines of the cell; 3, infiltration, followed by replacement of the cell walls. Only a detailed, microscopic study of every single sample could allow a statement on the genesis of petrified wood.

Organic compounds

Organic constituents of the shell of marine invertebrates, such as proteins and amino-acids, can be found fossil, and their presence can constitute a guide to the thermal

history of the host rock. KEILIN (1953) considers the conditions in which such fossilization is possible. He writes: ". . . stability of biological substances can be expressed in terms of the time during which these substances will retain their specific biological properties and therefore the integrity of their structure . . ." He refers to some examples of haematin found unchanged in the frozen body of the mammouth, or to the porphyrins extracted from crude mineral oils, bituminous shales, asphalt, coal, as old as Silurian, and to the succinic acid which may constitute from 3% to 8% of amber.
The following factors were found by the same author to favor the preservation of haemoglobin and of the enzymes in these samples: 1, Protection from bacterial infection; 2, absence of oxygen; 3, protection from light; and 4, high concentration of proteins.

The mentioned paper by KEILIN was one of the references used by ABELSON (1957) in the study of the organic matter in the fossils. He states that the amino-acids, which are the constituents of today's proteins have been found in fossils as old as 360 millions years. ABELSON worked out a method of dissolution of the shells in order to obtain the eventual organic compounds contained in them. The conclusion of his study was that the occurrence of proteins in the shell of recent invertabrates is a general phenomenon and that, for this reason, it is easy to suppose that many, if not all, fossils originally contained proteins.

The conditions found by this author necessary for the preservation of these substances are almost the same as those found by KEILIN: 1, Freedom from bacterial distruction (this requirement is satisfied by the matter preserved within a dense inorganic shell); 2, inorganic parts of the fossils should not be dissolved or replaced; 3, the organic matter should not be diffused or transported away from the inorganic matrix; 4, the organic compounds must possess sufficient chemical stability to exist unchanged for long periods of time. ABELSON thus established the conditions necessary for the preservation of the organic matter during fossilization concluding (p. 92):

> The thermal studies on alanine suggest the possibility of a geological thermometer for sediments. Although the amount of degradation of a substance depends on both time and temperature, rates of reaction are more strikingly influenced by temperature than time. Ordinarily, time can be estimated from the fossil record. Thus, if amino-acids are found in a fossil, an upper limit can be set on the maximum temperature to which the fossil has been exposed. This in turn can be related via geothermal gradients to an estimate of burial history.

Experimental fossilization

At conclusion of this summary on the fossilization in nature an example of experimental fossilization in the laboratory will be referred to. SABBATONI (1920) treated animal and vegetal tissues with potassium permanganate and obtained a colloidal specimen, with the original form, but consisting of inorganic manganese oxide. Two molecules of potassium permanganate are reduced to two molecules of manganese oxide, loosing three oxygen atoms. SABBATONI derived from that equation, that in a cellule MnO_2 will form in quantity variable with the quantity of oxygen necessary to oxidize the cellular tissues, that is with the chemical nature and also with the apparent bone structure. Because of the scarce solubility of MnO_2 SABBATONI could obtain and maintain for a long time those pseudo-fossil structures at the beginning in a colloidal state and then as gels.

3. CARBONATE DEPOSITS

Carbonate fossils are the most common fossils in any type of sedimentary rock. The carbonate in the majority of the cases represents the original, unchanged mineral which formed the shell or the skeleton of the living organisms. Calcite is by far the most abundant carbonate followed next by dolomite. Not frequent but also found in fossils are siderite (AMSTUTZ, 1958c), smithsonite (ROGER, 1952), azurite and malachite (ROGER, 1952), and cerussite (ROGER, 1952).

Calcium carbonate in its two forms, calcite and aragonite, is the main constituent of the shells of the marine invertebrates, as has been pointed out in ~~the~~ I chapter, but only calcite, the stable form, is usually found in the fossils. Naturally the crystallographic change from aragonite into calcite is followed by a change of the structure of the shells, as MORET (1948) mentions in regard of the shells of the Gasteropods. EARDLEY (1938) attributes to such change the radiate structure of the fecal pellets when they serve as oolite nuclei, explaining that:

> . . . the writer believes that the submicroscopic, outwardly oriented, aragonite crystals revert to the more stable form calcite and in so doing unite, forming much larger crystals, such that they are easily visible under the microscope. The larger crystals are in bundles radiating from the nucleus . . . .
>
> . . . .
>
> In the inversion of aragonite to calcite there is an increase in volume of 8.26 ± .05 percent. The only direction that the expansion can take is outward, thus directing the enlarging calcite crystals to radial orientation. In the faecal pellets the direction of expansion upon inversion is radial although the original submicroscopic aragonite crystals are not known to have any definite orientation (p. 1380-1383).

The importance of the organisms as carbonate rock-mentioned here, even though it is not possible to go into more details and to mention all the sediments of certain organic origin. P. and E. NIGGLI (1952, p. 399-404) discuss the role of fossils in the formation of calcareous sediments. The subdivision of the various types of formation of inorganic rock portions by organic matter, in particular by fossils, and the processes of fossilization in carbonaceous environments are discussed in detail. With regard to the classification of organisms which are contributing to the formation of rocks, these authors refer to WALTHER (1893/95). WALTHER used and/or created the following classification: I. Halobios for living matter in the oceans (with benthos, plankton, pseudoplankton, and nekton as subdivisions); II. Limnobios for living matter in fresh water; and III. Geobios for plants and animals on the land.

It is also impossible to list the occurrences of carbonate fossils because of the innumerable descriptions in literature and frequence in most of the sedimentary strata of the earth.

The possibility of using carbonate fossils in which the carbonate is the original shell forming mineral, in the interpretation of the time of origin of the enclosing sediments, will be the subject of the following brief discussion.

R. C. MOORE (1957) resuming the different theories on the origin of the cherts of Missouri writes:

> Some geologists. . . have interpreted the chert as entirely secondary in origin, its occurrence in the Mississippian rocks being interpreted as due to circulation of silica-bearing ground waters at a time long subsequent to original sedimentation. Other geologists have considered the chert

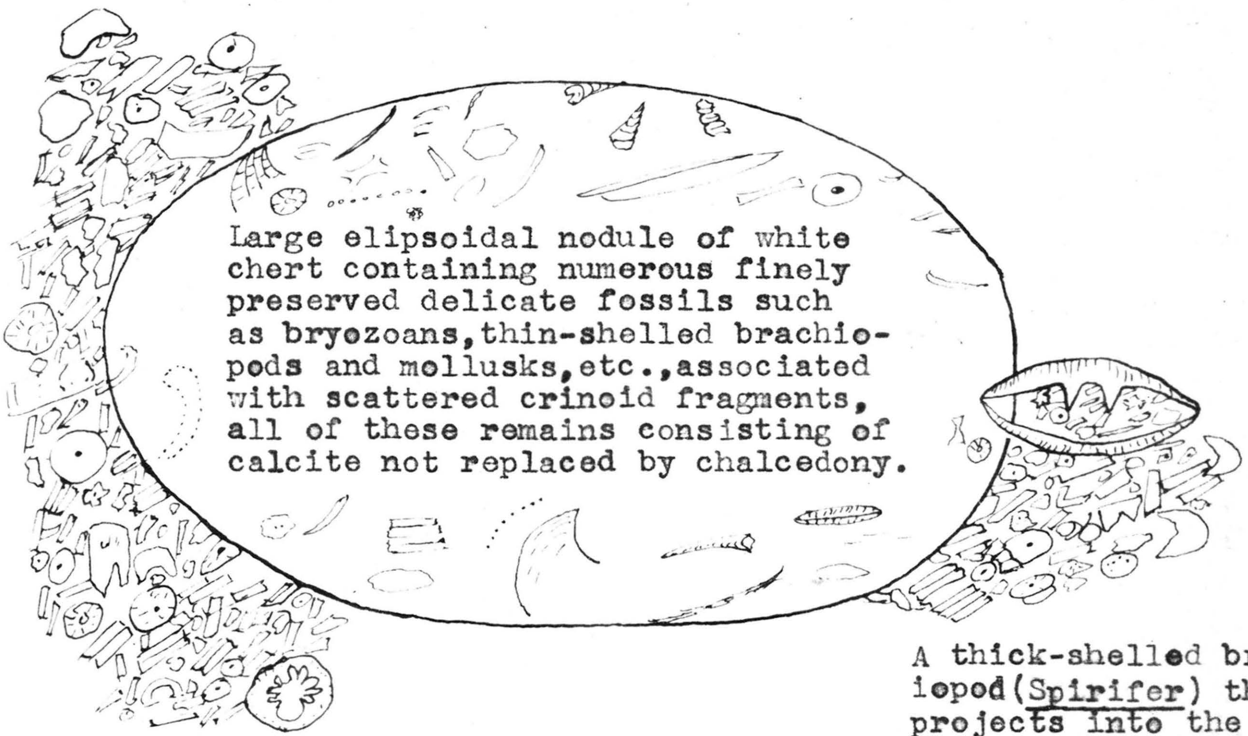
> to be of primary origin, produced either as a colloidal gel on the sea floor in beds alternating with carbonate deposits, or locally segregated in the form of nodules; and if not thus originally concentrated, precipitated silica disseminated in the calcareous deposits is presumed to have been very soon, perhaps syngenetically, concentrated in places where it is now observed. In either instance it is a primary constituent of the chert-bearing formation.(p.120).

One of the criteria MOORE advances for a syngenetic origin of such cherts is based on the presence and position of carbonate fossils. His statement no. 3 and the drawing related to it is reported here in full length, and in Figure 2, being a short summary, but fully explanatory: "(3) The occurrence of many well-preserved, delicate fossils in some Burlington chert nodules, whereas immediately surrounding crinoidal limestone lacks such fossil remains (Figure 2), furnishes irrefutable evidence of the primary nature of this chert"(p. 121).

A sample collected by Dr. G. C. AMSTUTZ a few miles south of Joplin, Missouri, in a roadcut of the turnpike, shows the faunistic association illustrated by the peel of Figure 3.

Some foraminifera use materials available on the sea bottom to build their tests. A. G. FISCHER (1949) recognized that such foraminifera (*Eodictyoconus*, *Coskinolina*, *Dictyoconus*, *Discorinopsis* and others) had been preserved only as molds in the dolomite rocks of Citrus County, Florida. From that fact he infers that they built their tests of calcite rather than dolomite, and that the bottom sediments, at the life time of those organisms, were chiefly composed by calcite.

The source of the $CaCO_3$ forming carbonate concretions in coal, shales, and clays is naturally found in the sea water.



Coarse-grained crinoidal limestone with space between the crinoid fragments filled by clear crystalline calcite; other observed fossil remains consist only of scattered thick-shelled forms.

Large elipsoidal nodule of white chert containing numerous finely preserved delicate fossils such as bryozoans, thin-shelled brachiopods and mollusks, etc., associated with scattered crinoid fragments, all of these remains consisting of calcite not replaced by chalcedony.

A thick-shelled brachiopod (<u>Spirifer</u>) that projects into the chert; entire shell consists of fibrous calcite, including part inclosed by chert.

Thick-walled zaphrentid coral embedded in coarse crinoidal limestone identical with rock which surrounds the chert on all sides.

Figure 2. Fossiliferous chert nodule in coarsely crinoidal limestone, diagrammatically showing evidence that is inferred to demonstrate primary nature of the chert. (After R.C.Moore, p.120, figure 2)

Figure 3 - Peel of a specimen of dolomite and chert from Eastern Oklahoma.Calcareous fossils are present both in the dolomite and in the chert.Silica does not replace the fossils.
The peel displays the same criteria used by R.C.MOORE (1957) for syngenetic origin of chert in Missouri.In this figure,however,the fossils are abundant only in the first centimeters of the chert layer,close to the contact chert-dolomite.

The deposition of carbonate concretions, commonly containing fossils such as ammonites and fishes, is related by WEEKS (1957) to a change of pH of the local environment otherwise unfavorable to the carbonate precipitation. According to this author and also to CONDIT and MILLER (1951) release of ammonia from the decaying organic matter would increase the pH sufficiently to permit the precipitation of the bicarbonate in solution as carbonate. In regard to the time of deposition of the concretions WEEKS writes: "That most of the fossil fish are full-bodied indicates that calcification and concretion growth were early enough to withstand compression from overburden. . . . These facts and the excellent state of preservation of the fossils, both plant and animal, all indicate a syngenetic origin" (p. 100).

4. OXIDE DEPOSITS (exclusive of SiO_2)

Excluding silica which will be considered in another subchapter, oxides are not abundant in fossils. Limonite is relatively frequent in traces or completely replacing the shells of pelecypods, ammonites, gastropods, foraminifera, and in general in all the fossils in which pyrite can be found. In most of the cases limonite is a secondary mineral, and it is the product of the oxidation of the ferric sulphide. A discussion on the formation of pyrite in sediments will follow in another subchapter.

An example where limonite is considered to be primary is the ammonites filled with limonite in the iron deposits of the Dogger in the Fricktal in Switzerland.

Two other oxides are listed by ROGER (1952) as sometimes occurring in fossils, but no mention is made of their possible origin. According to him, shells of pelecypods are replaced by hematite in the Liassic strata of the Gold Coast, and psylomelane gives origin to some rare incrustations and nodules, but never to complete replacements. GROSS (1956) pictures in his figures 7a and 7b; 18, 19 coffinite filling the cells and uraninite replacing the cell walls. He writes (p. 639): "Nearly all the uraninite occurs as replacement of wood, but it also occurs as cementing mineral in sandstone, generally adjacent to carbonaceous material." Also at page 644: "Replacement of carbonaceous debris by calcite and uraninite is fairly common. Calcite occupies the cell and uraninite replaces the walls."

5. SILICEOUS DEPOSITS

Silica, after calcite, is the second most frequent mineral found in fossils. It is the "primary" mineral in some cases, as for example in the fossil Radiolaria, diatoms, and in some sponges, but most often it is present as incrustations, fillings, and replacements.

A biological origin has been proposed for many siliceous sediments but this is very difficult to prove because of the frequent obliteration of the organic structure. According to MASON (1952) the opal of some sea organisms is changed into soluble silica during diagenesis. The same hypothesis has been often suggested by many authors, for example CORRENS (1926), CRESSMAN (1955), BRAMLETTE (1946), KRAUSKOPF (1959).

Radiolaria, diatoms, and sponges would protect their siliceous skeletons from dissolving with a film of organic matter and/or magnesium or aluminum silicates. After the death of the organisms these materials would stop their protective action allowing the silica to dissolve slowly. Solution and deposition of silica would take place contemporaneously, the solution at the points and thin edges of the skeletons, deposition on the flat surfaces.
This origin has been indicated for many formations in which organic remains are abundant, but it has not to be discarded for older sediments in which the diagenesis and metamorphic processes can have produced a total dissolution of any structure previously present.

The occurrences of silicified fossils, either animals or plants are very numerous, according to the literature; and it is impossible to mention even a part of them. Some of the references used for the present discussion are listed in the bibliography, without any assumption of completeness. The main part of the chapter will thus be dedicated to the origin of the silica as mineralizing agent and to the environments more favorable to its deposition.

According to KRAUSKOPF (1959) the principal sources of silica in natural aqueous solutions are: "volcanic emanations, direct solution of silica [quartz, opal and chalcedony] and decomposition of silicate minerals"(p. 15).

The hot waters of volcanic areas are often saturated with silica and their cooling produces a temporarily supersaturation with consequent silica precipitation. ALLEN and DAY (1935) noted that small wooden blocks, exposed for a period of 8 to 10 months to the action of hot springs in the Yellowstone National Park, were abundantly covered with silica and that opal had started to precipitate in the cells. Opal lined the walls of the cells and filled them in many cases, preserving all the microscopic characters of the wood structure. This precipitation of opal should represent the first stage in the petrification of wood. According to the authors, the fact that many specimens presented part of the wood removed without substitution of any material seems to point to a filling process in the formation of petrified wood.

Volcanic activity, besides the direct deposition of silica from thermal waters, is an indirect source for large amounts of the same material. Volcanic ashes and tuffs are widely believed to have originated, through weathering, many siliceous deposits, such as those of the Cordilleran area, those of the Ouachita facies in eastern Oklahoma and western Kansas, (BISSELL 1959, GOLDSTEIN 1959), only to mention a few papers of more recent publication.

A comprehensive study of volcanic ashes as a source of silica for the silicification of wood has been carried out by MURATA (1940) who refers an extensive bibliography on the occurrence of petrified wood in the United States. In order to demonstrate the percentage of silica obtainable from volcanic materials the author reports the following analyses:

Analyses by ROSS, MISER, and STEPHENSON	Trachyte	Bentonitic mineral concentrated from bentonite derived from trachytic pumice
SiO_2	62.97	45.12
Al_2O_3	19.00	28.24
$SiO_2:Al_2O_3$	5.6:1	2:7:1

Analyses by BRAMLETTE	Volcanic Ash	Bentonite derived from the decomposition of the same volcanic ash
SiO_2	65.66	50.03
Al_2O_3	12.71	16.75
$SiO_2:Al_2O_3$	8.8:1	5.1:1

Assuming no changes in the amount of alumina, the loss of silica, in the above analyses, was respectively 52% and 22% of the original amounts. MURATA also states that:

> A similar liberation of silica takes place during the katamorphism of igneous rocks . . . however, the porous and finely divided condition and the highly unstable nature of glassy volcanic ash allow a far more rapid alteration of ash than of a massive, crystalline rock (p. 588).

According to the same author the association of large deposits of diatomite and volcanic ash in fresh and marine waters would indicate that the liberation of silica from the altered ash was very rapid relatively to the deposition of other sediments.

Volcanic ash and other volcanic materials are more widespread than it was believed, and their decomposition products are contained in many sedimentary formations. It is thus logical to assume that silica which originated from volcanic material is one of the most important in the silicification of wood and other fossils.

Direct solution of silica, according to KRAUSKOPF (1959), gives different concentrations, depending on the form of silicon oxide dissolving. Quartz, a highly stable mineral against chemical and mechanical actions, and chalcedony would contribute very little, while gelatinous silica should dissolve readily up to its equilibrium solubility. It is, however, impossible to know how much silica should be expected from that source, because the amount of opal on the earth's surface is very little known.

The direct weathering of silicate minerals contributes large amounts of silica to solutions but the slowness of the process has to be taken into account when considering the low concentration of this oxide in natural waters.

According to KRAUSKOPF "direct precipitation of gelatinous silica by sea water can take place only locally, where volcanic activity under the sea or near shore supplies solutions with abnormally high concentrations of silica" (p. 16). Biological action, as illustrated at the beginning of this chapter, is considered another means of silica accumulation together with adsorption processes in shallow waters.

As it has been previously noted fossils can be one of the criteria for the determination of the syngenetic or epigenetic origin of the mineral deposit with which they are associated.

R. C. MOORE (1957) found in carbonate fossils a support for his syngenetic interpretation of the origin of Missouri cherts. VAN TUYL (1918), describing silicified fossils, also reached the conclusion that the chert is syngenetic, but calls those cherts secondary. He wrote:

> The presence of an abundance of silicified fossils in the limestone layers associated with cherts would sppear to furnish strong evidence of the replacement origin of such chert . . . (p. 453)
>
> . . . .
>
> Many of the cherts which have come to the writer's attention contain silicified fossils, . . . (p. 454)
>
> . . . .
>
> it is believed that in the case of most secondary cherts the silicification has proceeded on the bed of the sea, possibly contemporaneously with the deposition of the limestone (p. 456).

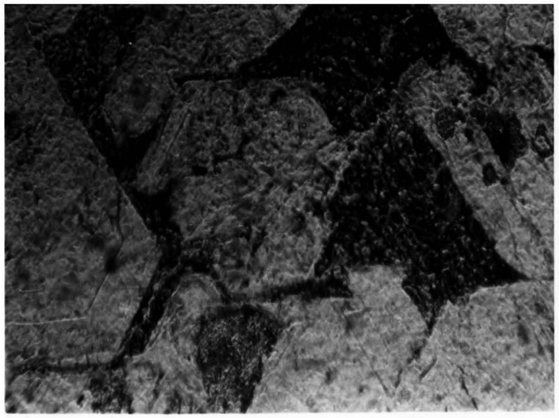
WETZEL (1957) describes some examples of selective silicification.

Because of the ubiquitous nature of silica, silicified fossils can be found practically in any type of sediment. The first occurrence of silicified wood in dolomite was described by BARKSDALE (1939); corals completely replaced by silica are mentioned by CADY (1950) in a sericitic phyllite of Vermont; shales and limestone yield innumerous specimens as well as the sandstones. BUCHER (1953) published an extensive review on fossils in metamorphic sediments, listing numerous interesting examples of compositional differences between host rock and fossil filling matter, also discussing possible processes and origins.

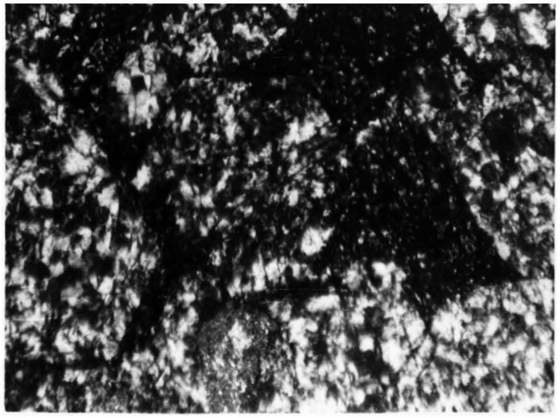
A specimen of petrified wood examined for this thesis contains elongated hexagonal crystals, some of them as big as 1 cm. in diameter and 3-5 cm. long. Some of the crystals show only partially idiomorphic contours due to the intergrowth of two or more of them into a uniform mass. All the insides of the crystals show a medium grained mosaic of quartz and are not homogeneous crystals. The shape and the present composition seem to indicate, however, that originally these crystals were homogeneous prismatic crystals of quartz. The crystals are very much elongated in the direction of the c-axis, their long dimension is at least twice or three times the basis diameter. All the crystals have the same orientation, with the c-axis perpendicular to the tree axis. The crystals may have grown before the petrif~~ic~~action of the wood. This assumption is supported by the observation of the "pushed away" pattern of the wood cells in between many of the crystals (Figures 4, 5, 6 and 7).

Figure 4 - Microphotograph of thin section vertical to the hexagonal crystals grown inside a tree trunk from Eureka, California. The crystals show crystallographic zoning. The matrix consists of petrified wood matter (carbon, calcite, etc.). Plane light; enlargement about 50 X.

Figure 5 - Same as Figure 4, but with crossed nicols. Chalcedonic spheriods fill the idiomorphic quartz (?) crystals and contain occasional carbonates. These occur usually in the center but sometimes are scattered all through. The latter ones appear to be more idiomorphic than the ones clustered in the center. Enlargement 50 X.



· MAY · 59



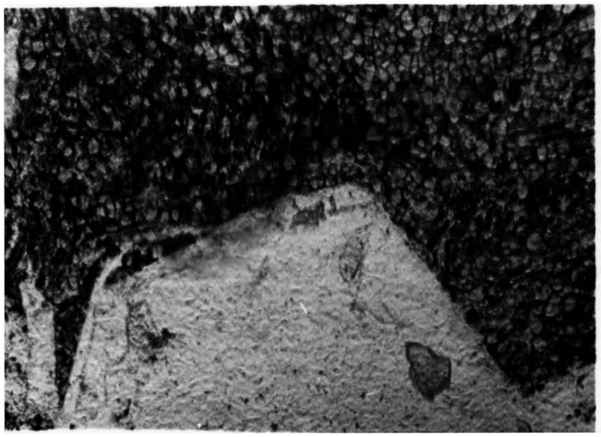
· MAY · 59

Figure 6 - Microphotograph showing the hexagonal crystals pictured in Figures 4 and 5. The strings of cells bend partly around the hexagonal crystals which may indicate an early growth of the crystals or even a growth of the wood around the crystals. Plane light; enlargement 50 X.

· MAY · 59

Figure 7 - Hexagonal (quartz ?) crystal in petrified wood. Same locality as for Figures 4, 5, and 6. The few high relief crystals inside the quartz are carbonates. Plane light; enlargement 50 X.

· MAY · 59



6. PHOSPHATE DEPOSITS

As it has been shown in the first chapter of this thesis some groups of organisms, especially brachiopods and crustaceans, have a very high content of calcium phosphate in their shells. The skeleton of the vertebrates may, however, be a more important source of phosphorus than invertebrate remains (CLARKE and WHEELER, 1922). Extensive deposits of phosphates are today formed through the accumulation of remains and excrements of animals, chiefly sea birds, in arid climates. Guano deposits, older than the recent ones, have not been found in the geological column (RANKAMA and SAHAMA, 1950, p.592), but an organic origin for many calcium phosphate deposits has been postulated long ago (NICHOLSON, 1889; HAYES and ULRICH, 1903, ref. EMIGH, 1958; BLACKWELDER, 1916).

Partly or completely phosphatized fossils are reported in the Tennessee phosphorites by SMITH and WHITLATCH (1940, ref. EMIGH, 1958). Biochemical and physiochemical agents precipitated the phosphorus from the sea water and the replacement of the shells occurred while the sediments were still unconsolidated.

CAYEUX (1940) believes that some contrast exists between the deposits of phosphates in the older seas and in more recent times. In the former case the phosphate concretions are abundantly preserved, whereas in similar sediments, in more recent times, they show extensive evidence of decomposition by the plankton.

DIETZ, et al. (1942) describe foraminiferal pellets and partially replaced calcareous fossils in the groundmass of phosphate rock. According to these authors, the phosphate has been accumulated in situ on the ocean floor.

EMIGH (1958, p. 47) writes about the genesis of the phosphate pellets in the Phosphoria formation:

> . . . there is concrete evidence that many of the pellets result from phosphate having replaced existing objects. This evidence is in the form of recognizable, partly or completely phosphatized fossils. . . . phosphatization of a fossil can proceed to a stage where all evidence of skeletal structure is obliterated and the resulting pellet is structureless. Most of the phosphate pellets in Tennessee and Arkansas are recognizable fossil pellets or encased fossil pellets.

NEUMANN (1958) gives a summary of the genesis of phosphate deposits in connection with a description of occurrences in Vietnam.

The suggestion that coprolites were the main factor leading to many phosphate deposits has been advanced in many instances (BRANNER and NEWSON, 1902, ref. EMIGH, 1958; CAYEUX, 1939, ref. EMIGH, 1958; MOORE, 1939; DIETZ et al., 1942). Sedimentary phosphate deposits are discussed briefly by P. and E. NIGGLI (1952, p. 454-457). Pseudo-oolithic textures were observed according to these authors in numerous lower Eocene phosphates of the Sahara desert; they were rich in coprolites and bone remnants, and frequently contained iron and clay. A more detailed description of fecal pellets and coprolites in recent and fossil sediments is given in the third chapter.

7. SULPHIDE DEPOSITS

The nature of the coal balls and sulphidized fossils will be briefly discussed in this subchapter together with the environmental conditions more likely to produce deposition of sulphides.

Coal balls are concretionary accumulation of sulphides or carbonates found in coal seams. According to ANDREWS (1951, p. 432) "The petrifying process . . . was by no means selective as to the place or quality of the plants which it preserved . . . the contained plants may be badly decayed or exquisitely preserved." The most frequent minerals occurring in them are calcite, magnesite, pyrite, marcasite. STOPES and WATSON (1908, ref. ANDREWS, 1951) give the following analyses for carbonate coal balls from England:

	I (p.193)	VI (p.193)	VI (p.194)
Calcium carbonate	51.2	91.1	64.4
Magnesium carbonate	42.8	...	1.8
Ferrous carbonate	2.3	4.0	6.0
Calcium phosphate	0.5	...	...
Iron pyrites	0.3	...	21.9
Silicate of alumina	0.1	1.1	1.2
Carbonaceous matter	1.9	3.6	...

DARRAH (1941) reports the following mineral content in an American sulphide coal ball:

Sulphur	32.3
Iron	27.1
Iron oxide	0.8
Calcium oxide	19.6
Calcium dioxide	14.9
Water	1.5
Silica	0.7
Organic matter	3.1

As ANDREWS points out these analyses by no means give the extremes in carbonate or sulphide composition of the coal balls. Botanically the carbonate coal balls are more interesting because usually they yield better preserved plants than those that contain appreciable amounts of iron sulphide either as pyrite or marcasite.

In regards to the particular mineralization of the plants ANDREWS writes:

> In some instances we find the most fragile parenchymatous tissues well preserved, and in many cases this probably indicates that petrification [sic] followed soon after the deposition of the plants. At the other extreme petrification [sic!] may have taken place after the accumulated plant debris had been altered and closely approximated the relatively amorphous structure of the coal (p. 437).

In this and in any other case a source of sulphides or carbonate minerals should be readily available. In this subchapter only sulphides will be considered.

The presence of small pyrite concretions in recent not consolidated sediments has been mentioned by HOUBOLT (1957), STRØM (1939), KUENEN (1950), SVERDRUP, JOHNSON, FLEMING (1942) and others. According to KUENEN (1950) the absence of oxygen causes anaerobic conditions and iron sulphide may form. In a previous paper (1939) the same author wrote:

> When the water in a basin is not renewed sufficiently the oxygen is used up and H_2S forms. This process is well known from colder climates. The Kaoe Bay is the first example from the tropics and is of importance in showing that the peculiar black, pyritic, or marcasitic shales generally attributed to similar conditions, may very well have been formed in a hot tropical climate (p. 354).

There is no doubt that the author considers the formation of the pyrite concretions contemporaneous to that of the shales in which they are contained.

If the formation of H_2S is the first step necessary for the production of iron sulphide, it is useful to review the conditions in which H_2S forms. STRØM (1939) gives an excellent summary of such conditions and of the consequent formation of "blackish (pyritic) muds" (p. 357) and writes:

> When the bottom waters of a basin become stagnant for a long time, the results of oxidation processes entirely preponderate over the feeble photosyntesis by plants which is possible in the deep. The waters thus become depleted of oxygen, and hydrogen sulphide, which commences to form in the mud even when the waters themselves still contain oxygen, will gradually dissolve into the waters. The deep waters eventually contain great quantities of hydrogen sulphide, which gradually diminish towards the surface, until a limit is reached where there is an equilibrium between hydrogen sulphide and oxygen, the quantities of both gases being nought.

A section through a typical land-locked basin and the formation of H_2S is reported in Figure 8.

According to STRØM the bottom waters of a basin become stagnant for lack of ventilation and/or for differences in density of the upper and lower waters. Lack of ventilation might be expected where marginal basins have shallow thresholds, as, for example, tectonical basins, craters filled by the sea, estuaries, lagunas especially in tropical climates, fjords. Salt lakes in arid regions get surface waters with less salt content than those of the deep, which thus must stagnate. The great amounts of organic substance deposited may produce muds high in hydrogen sulphide even at depth along coasts or in fresh water lakes. The great regularity of the climate, with very little variations between day and night, or between seasons, typical of tropical regions is also very likely to produce stagnation of the deep waters, because of the changing density of the water at different temperature.

The formation of iron sulphide in a reducing environment is very common. RANKAMAand SAHAMA (1950) state: "Iron sulphide may be precipitated from solutions containing humic

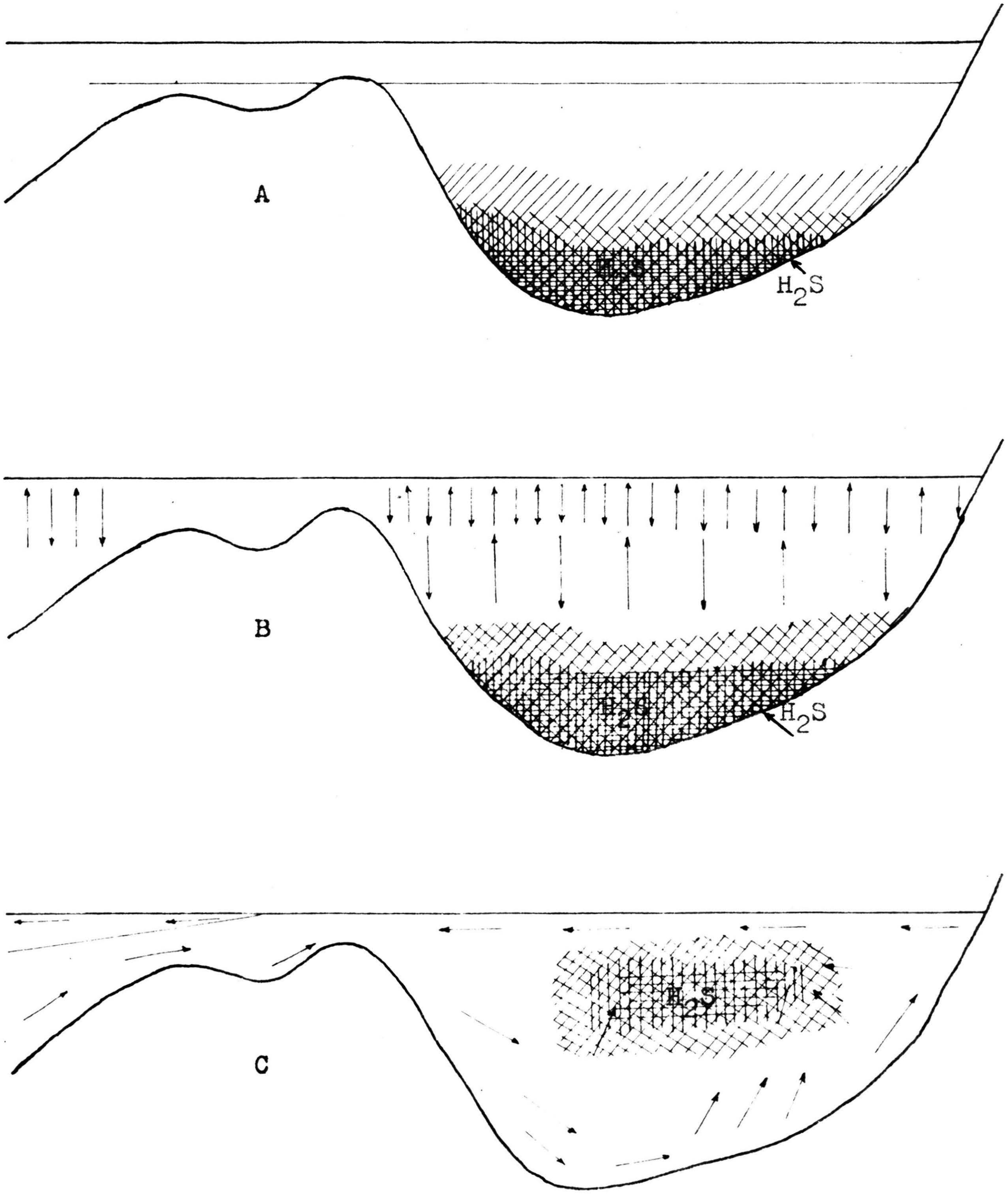


Figure 8. Section through a typical land-locked basin.
(After STRØM, 1939, p.358)

complexes of iron in the absence of oxygen" (p. 674). A more detailed explanation of such processes is given by DOSS (1912, ref. HARDER, 1919). According to him the iron carried in solution as soluble ferrous carbonate is precipitated, in presence of abundant decaying matter, in euxinic conditions, either directly as black colloidal hydrated ferrous sulphide or as ferric hydroxide. The ferric hydroxide under the prevalent reducing conditions created by the presence of H_2S is also changed into hydrated ferrous sulphide. This compound, by loss of water and addition of sulphur, which occurs as free sulphur in the mud is changed to melnikovite, FeS_2 and then, gradually into pyrite.

VAN HISE (1904) refers to the transformation of ferrous sulphate in FeS_2. The basic ferric sulphate produced by the oxidation of the ferrous sulphate may be deposited, together with ferric hydroxide, in the bottom of lagoons, where it is reduced by the decaying organic matter.

It is well known that the coal formed in " . . . small depressions with poor drainage . . . along the marine shore . . . common salt-marsh . . . into lagoons . . . " (DARRAH, 1939, p.50), all places most favorable to the formation and accumulation of H_2S. It is thus not necessary to call for "streams of water heavily charged with minerals that seeped through the swamps" as ANDREWS (1946, p. 1) mentions, but it is probably enough to refer to the conditions of sedimentation and to consider the geochemical behavior of iron in such sedimentary environments.

An interesting and in any respect new mode of sulphide concentration in which organic matter plays a certain role, was proposed by SOSMAN in 1950. SOSMAN set up what he called a "centripetal genesis of magmatic ore deposits". This consists of the following steps of "centripetal" ore mineral concentration. "In the first stage . . ., organisms accumulate certain metals. In the second stage, the skeleton of the organism becomes part of a sedimentary rock. In the third stage, the metal is dissolved in a dilute water solution, which then travels toward the intrusion because the water is soluble therein. This leaves the concentrated ore deposit on the border of the intrusion where it has arrived from the outside rather than from the inside, as has usually been assumed" (personal communication).

This mode of accumulation is actually nothing but a variation of the lateral secretion theory developed and defended strongly by SANDBERGER (1885). It has found a recent defendant in KNIGHT (1957). These theories can be reduced best to the basic problem of syngenesis and epigenesis as shown by AMSTUTZ (1959) and are in this light better understood. Sulphidic saprophylic sediments and the role of organic matter in their precipitation was also discussed by P. and E. NIGGLI (1952, p. 344-349).

The geochemistry of sedimentary sulphide deposits was discussed in detail at a "Kolloquium" on "sedimentary ore deposits of the sulphur cycle" at the School of Mines of Freiberg, Germany, in 1957. The following papers presented at this meeting are of special interest to the role organic matter plays in the deposition of suphide ore minerals: SCHWARTZ, The bacteria of the sulphur cycle and their living conditions; KAUTZSCH, The sedimentary ore deposits of the lower Zechstein; LOMBARD-MOUSSU, Sedimentary copper deposits of the Kupferschiefer type in Marokko; BORCHERT, The initial magmatism and ore deposits associated with it.

Pyrite and marcasite are the most frequent sul~~f~~phides found in fossils, but not the only ones.

WESTOLL (1955) in a discussion on a mineralization in the English Marl Slate, similar to that of the Kupferschiefer, uses mineralized fossils as a means for determinating the time of the mineralization. He states:

> There is some interesting evidence from fossil fishes that this mineralization is, at least in part, syngenetic. The original largely cartilagineous endocrania of these fishes were usually destroyed before diagenesis, but sometimes one found partial replacement of the crania by sulphide ores, including galena, blende [sphalerite] , chalcopyrite, etc. This could only have happened before diagenesis was far advanced . . . .
>
> . . . .
>
> It seems clear that the concentration can happen during diagenesis. For example, ammonites from the Yorkshire Lias shales often have their gas chambers filled to some extent with blende sphalerite , galena, etc. and the consolidated rocks we know it today must be a serious barrier to mineralizing solutions. Therefore these infillings were probably formed during the process of consolidation and lithification.

AMSTUTZ (1956a) mentions a tree stem from Santa Ena, Peru, in which copper minerals, chalcocite, bornite, and covellite have selectively filled the interior of the cells. According to this author the copper bearing horizon, in which the trees are contained, can be classified as a submarine exhalative ore deposit because of "the association of the copper minerals with volcanic microbreccia minerals, the absence of igneous rocks and apparent fissures, and the horizontal consistency . . ."(p. 11).

WIESE (1957) reports wood replaced by pyrite, chalcopyrite, tetrahedrite-tennantite, sphalerite, galena, chalcocite, and covellite; with pyrite first, followed by the copper sulphides, essentially all contemporaneous, and by sphalerite and galena. The origin of the sulphides is discussed in the following way:

> It is evident that the sulphides have been introduced into a shaly and limy sandstone containing abundant organic matter, which served as the chief control causing precipitation of the sulfides. . . . .
>
> . . . .
>
> Organic debris occurring in more sandy members is not replaced, suggesting that the degradation and coalification of the plant remains in the less permeable shaly horizon was retarded relative to that of organic matter elsewhere.
>
> . . . .
>
> Solutions carrying the metal ions may have traversed the entire section with deposition of the sulfides taking place only where organic matter in a receptive stage of decay was abundant (p. 80-81).

The non-mineralization of the organic material in sandy members is explained by WIESE as due to a difference in permeability of the horizon and in plant decay. Could it not be due possibly also to a change in the sedimentary basin? To an environment more favorable to the development of H_2S? In this case the mineralization could be accounted for as syngenetic, not anymore epigenetic. This suggestion could be supported also by a statement by WIESE: "It is thought that the decaying organic matter is receptive to ore solutions for only a limited time, probably early in the degradation sequence(R. M. GARRELS, personal communication)"(p. 81). It would be very interesting to determine whether the early degradation occurs before, during or after diagenesis.

LOVE (1958) describes two new genera of microfossils found exclusively in pyrite grains. He writes:

> It is suggested that during their [of the microfossils] lifetime they generated hydrogen sulphide . . . the gas continually passing outwards into the adjacent mud or water. Reaction with iron in this immediately surrounding medium would precipitate iron sulphide on the organism, . . . later to become crystallized as pyrite (EMERY & RITTENBERG 1952) (p. 434).

According to LOVE the pyrite framboidal grains found containing microfossils are very similar to those described by SCHNEIDERHOHN (1923) in the Kupferschiefer, by EAGAR (1952) in various rocks, and also by BARRINGER in the pyrite ores of Spain and Portugal, but the same origin can not be stated at the present stage of knowledge.

GREENSMITH (1958) in a contribution to LOVE's paper postulated a diagenetic origin of the pyrite, after the burial of the pyrite-generating organisms, because of the occurrence of the pyrite spheres in shells of molluscs and brachiopods. The syngenetic replacement of calcite by pyrite, in some instances, was as much as 75%.

Many more examples of fossils containing sulphides can be found in the literature. CAYEUX (1916) refers to pyrite included in the ~~loges~~ chambers of foraminifers and to echinoderms replaced by pyrite with their unaltered cellular structure. TARR (1928) and MATHIAS (1928) studied pyrite concretions and pyritized fossils in Missouri concluding that the pyritization occurred soon after death because of the well preserved details of the organic structures. BUTLER (1938) refers to mineralized plants with bornite, chalcopyrite, and chalcocite. EMMONS (1940) reproduces sections of chalcocite said to replace coal in one case and wood in the other. In the second case the chalcocite is said to retain cellular structure of the wood, in the first one it is shown to replace random portions. KELLER (1947) describes a fossil fern fruit replaced by galena and, in very little extent, by sphalerite and pyrite. BATEMAN (1950) records replacement of wood cells structure by chalcocite in the Red Bed type of copper deposits. The woody material was first replaced by bornite and only later on by chalcocite, which inherited the wood structure from the bornite. MAMAY and YOCHELSON (1953) refer to pyritized, or silicified, or calcareous ostracods, brachiopods, and pelecypods contained in the Kansas collection of coal balls. HOWE (1956) mentions a pyritized Marginifera muricatina in shales. GROSS (1956) writes: "Sulfides occur in close association with uranium-vanadium ores and are especially common in wood replacement. . . . Galena is observed with greenockite in desiccation cracks of replaced wood" (p. 641). FINNEL (1957) reproduces a photomicrograph of fossil plant cell structure preserved by uranium minerals and pyrite. Pyrite and uraninite fill the pore spaces, uranophane and becquerelite form the cell walls.

A specimen of sulphides in wood from Mitterberg, Austria, has been photographed for this thesis. Besides pyrite, the most abundant mineral, chalcopyrite, sphalerite, and arsenopyrite are also present, but in different positions with respect to the wood cells, as shown in the paragenetic chart (see table IV) and on the colored microphotographs (see Figures 9 and 10).

TABLE IV

PARAGENETIC SEQUENCE OF THE SULPHIDES IN A WOOD SPECIMEN MITTERBERG, AUSTRIA

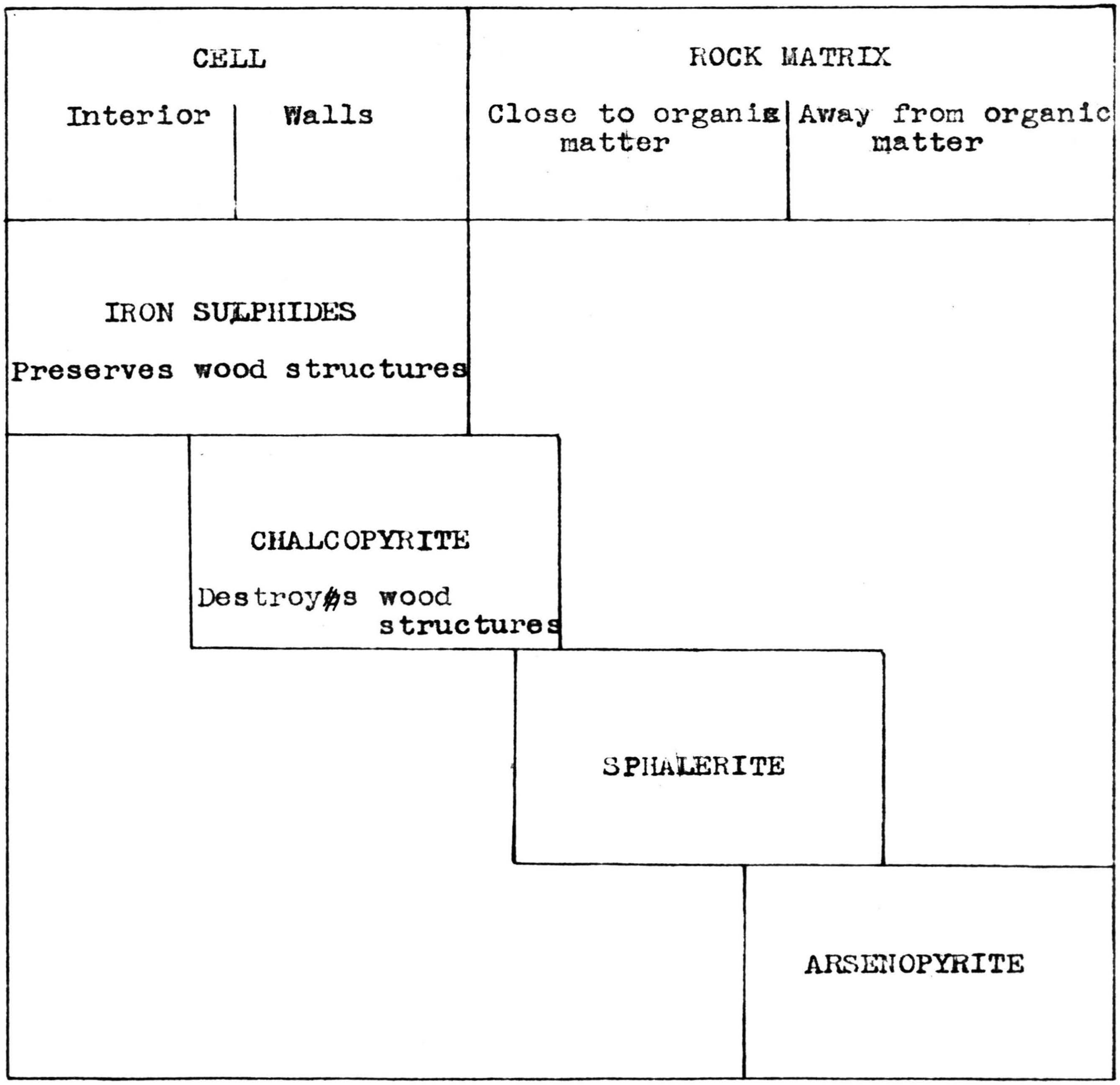
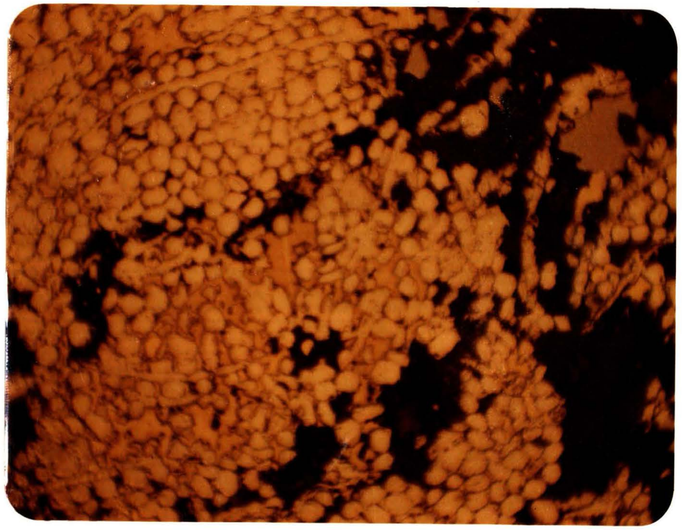
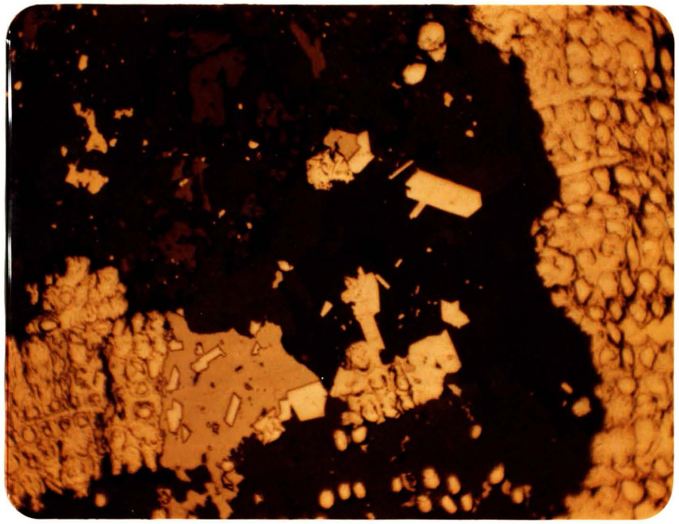


Figure 9. Microphotograph of polished section of sulphides in fossil wood, from Mitterberg, Austria. Pyrite fills cells and replaces walls preserving their structure. Chalcopyrite occurs between cells and destroyed the wood structure.
Plane reflected light; enlargement 60x.

Figure 10. Same as figure 9. Sphalerite occurs in the matrix in proximity of wood. Arsenopyrite occurs at a certain distance from the organic matter. The paragenetic sequence seen in figure 9 and 10 is pictured in Table IV.
Plane reflected light; enlargement 60x.





CHAPTER III

AN ILLUSTRATION OF FOSSILIZATION WITH THE EXAMPLE OF THE COMPOSITION OF THE COPROLITES AND FECAL PELLETS

Bodies of excremental nature seem to be widely spread at every depth and latitude in most of the recent and actual sediments.There is no reason to believe that consolidated sedimentaty rocks are devoid of them.According to H.B.MOORE (1939,p.522)"various structures have been described as being fossil faeces of some animals . . .for some there is considerable presumptive evidence of the corpolitic origin."

1.BRIEF DEFINITION OF COPROLITIC FOSSILS

AMSTUTZ (1958) showed that the terms fecal pellet,coprolite,are used in different ways.Fecal pellets,according to TWENHOFEL (1950,p.194) are:"aggregates of various organic and inorganic substances held together by some sort of cement provided by the animal.This cement is often so poor that the pellets crumble on ejection."PETTIJOHN (1957,p.220)defines fecal pellets as"organic excreta (mainly of invertebrates)" thus essentially agreeing with TWENHOFEL,and defines coprolites as"analogous to . . .faecal pellets, . . . but larger structures (1/2 to 6 inches in length)and . . .characterized by light to dark-brown or black color."

ROGER (1952,p.17)uses the term"coprolithes"either for the excrement~~s~~ of mamm~~ifers,~~als reptiles and birds,or for those of invertebrates.

Not every author agrees on these definitions,but in general the excreta of marine invertebrates,and always those in not diagenized marine sediments,are mentioned as fecal pellets, whereas the term coprolite is limited to dung in diagenized sediments.This restriction of the meaning of the term is also in agreement with WEBSTER's definition of coprolite as "fossil dung"and of fossil as"any impression,or trace of an animal or plant of past geological ages,which has been preserved in the earth's crust."

According to AMSTUTZ (1958)a deep discrepancy of opinion on the quantity of fossil feces in sediments,exists between TWENHOFEL (1932) and PETTIJOHN (1957).This is true only if the comparison is made,as AMSTUTZ did,between the frequency of the fecal matter in general,on one side,and the coprolites on the other.In reality PETTIJOHN states that some sediments consist of 30-50% of fecal pellets and that"coprolites are a relatively uncommon constituent of sediments" (p,220).TWENHOFEL does not make any distinction and writes: "nearly all marine deposits pass through the intestinal tracts of organisms and . . .the major portions of marine deposits are excretions, . . ."(p.152).

In order to avoid as much as possible any misunderstanding due to discordance in the use of the two terms in the following pages the terms fecal pellet and coprolite are going to be quoted as used by the respective authors.

The identity of some small ovoid masses in sediments, sometimes glauconitized or even pyritized,with animal feces has been recognized not long ago.The true nature of these structures had to be determined by biological studies before the phenome=

na in older sediments could be interpreted.
"The idea that the objects [collophane bodies in the Miocene brown shales of California] might be excrements was not con= sidered plausible" stated GALLIHER (1932,p.46) referring to one of his papers published only one year before(1931).
Probably the best help for the understanding of the true nature of the fecal pellets was provided by H.B.MOORE.Beginning in 1931 he began a study of size,shape,composition of the excreta of many living marine invertebrates.Certain animals,he found out,produce feces of characteristic form,but unfortunately, this fact of big paleontological importance,is hampered by the fact that "a large number of animals produce unsculptured pellets of the simple ovoid type"(p.518)thus making the con= nection between feces and animal very difficult and impossible in many cases,and providing a geometric transition to common concretions.

2. FECAL PELLETS IN RECENT SEDIMENTS

One of the first mentions of fecal pellets in Recent sediments was made by BUCHANAM (1890,ref.DAPPLES 1942,p.123) who described many pellets in the bottom sediments off the island of Arran,Scotland,and also near the mouth of the Congo.

VAUGHAN (1924,p.327)described ellipsoidal aggregates in fine-grained muds of Florida and the Bahamas.Those grains did not exhibit the concentric structure of the true oolites and the author compared them for size,shape,and structure to glauconite and greenalite grains.According to TAKAHASHI and YAGI (1929) and ILLING (1954) the grains described by VAUGHAN are fecal pellets.

TAKAHASHI and YAGI (1929) found peculiar mud-grains contaminating the Recent marine deposits along the coasts of Japan.A study of the grains showed that they ranged in color from light gray to dark green,being mostly ellipsoidal and also varying in density and purity,from 1.6 in the gray grains to 2.2 or more in the green ones.A detailed description of the grains is here reported as follows:

> Under high magnification,the gray varieties reveal rather heterogeneous constituents;extremely fine fragments of quartz and feldspar with a 'clayey' matrix that is dark yellow or brownish in color. . . .Tests of diatoms and fragments of kelp are not infrequently observed in the gray grains,as well as very small globules of iron sulphide. . .
>
> The 'clayey'materials of the gray grains are found to be gradually replaced by a green gelatinous mineral,as the green color increases.In advanced stages,the gelatinous mineral becomes glauconite. . . .It is noticeable,in the course of the glauconization,that the constituents of the grains are little by little replaced by the green gel which at the same time becomes gradually degelified to glauconite. The glauconization may thus be interpreted as the gradual

> replacement or excluding of other constituents out of the mud-grains, and at the same time degelification of the green gel to form glauconite. . . . In the final stage, the grains are largely free from either detrital mineral or fossils. (p.844-846).

The grains above described were considered by the authors as "excretions of the mud-eaters that live in estuarine and littoral regions" and were tentatively termed "coprolite" if not yet completely glauconitized. TAKAHASHI and YAGI report also of "coprolites" found in certain oil-measure rocks of late Tertiary age, in calcareous sandstones, and in glauconitic sandstones of various age.

According to H.B.MOORE (1931, ref. DAPPLES, 1942, p.123) fecal pellets form the entire sedimentary material of the Clyde sea and contain as much as 30% of P_2O_5.

THORP (1931, ref. DAPPLES, 1942, p.123) reports the presence of coprolitic material in one-half of the samples collected from the floor of the Atlantic ocean off Panama. The pellets in deep water become glauconitized according to THORP and also to BUCHANAN (1890), MOORE (1931), TAKAHASHI (1939) etc.

DAMAS (1935, ref. DAPPLES, 1942, p.124) states that along the Belgian coast a population of Cardium of 1000 per square meter will result in a yearly deposit of fecal pellets 45 cm. thick. DAPPLES, referring to DAMAS, comments the statement as impossible or extremely improbable because the pellets do not constitute a definitive deposit but constantly pass through a cycle of being digested and deposited again.

THORP (1936, ref. ILLING, 1954, p.24) describes the fecal pellets found in calcareous sands and muds of ~~the~~ Andros Island as somewhat loose and of friable nature.

EARDLEY (1938) describes and illustrates the small rod-shaped fecal pellets of the brine shrimp Artemia gracilis in the Great Salt Lake, Utah. The chemical analyses he reports are: (p. 1404)

SAMPLE	% ORGANIC MATTER			CaO MgO	% CLAY	MINERAL FRAGMENTS
Map Loca= tion	N_1	N_2	$\frac{N_1 N_2}{2} \times 14$	Soluble in weak hot HCl	Occluded in bamds and nuclei	Held partly in rod-shaped nuclei
F_1				40.6 3.2	17.3	5.3
F_2	.065	.060	.87	38.1 2.9		
Average	.065	.060	.87	34.4 3.05	17.3	5.3

The pellets in EARDLEY's description are symmetrical, cylindrical, white or faintly stained in reflected light, but cloudy and cryptocrystalline in transmitted light. They are often surrounded by lamellar layers, being in that case the nuclei of oolites. Only when the fecal pellets serve as nuclei of the oolites they are strongly radiating. This fact accounts for a later, secondary origin of the radiating structure and the interpretations are in agreement with the observation of TAKAHASHI and YAGI that the fecal pellets are "neither concentric nor radial in their internal structure" (p. 844).

Fecal pellets are described by MOORE (1939) who states he found some of them in deposits at least 100 years old (p. 521) not to mention those in intertidal waters or in abysmal depth, where the glauconization processes are more likely to preserve them.

THORP (1939, p. 289) refers to "ellipsoidal bodies . . . composed of finely divided and loosely consolidated calcareous material . . . thought to be fecal excrement of unidentified organisms, possibly maldanid worms". The calcareous material composing the pellets is held together by a mucoid cement in which some reduced iron is present. THORP compares the color of the fecal pellets he saw with those brown or green ones of other regions suggesting that the white or whitish gray of the Florida and Bahamian pellets could be due to the almost complete absence of iron compounds in those sediments (p. 289).

HANTZSCHEL (1939) studying the tidal flat deposits states:

> The excrement of other animals likewise contributes to the formation of mud. In fact, some muds may be designated as coprolitic muds. In such muds, the abundant admixture of small ellipsoidal bodies about a millimeter in diameter, which represent the excrement of the Polychaete worms *Nereis*, *Heteromastus*, the pelecypod *Cardium*, and the gastropods *Littorina* and *Hydrobia*, can be recognized even with the naked eye.

STARK and DAPPLES (1941, ref. DAPPLES 1942, p. 124) noted ellipsoidal ~~shaped~~ fecal pellets in the coarse size sand of the Raiatea, Society Island, lagoon sediments. Those pellets formed at a maximum 1% of the samples and consisted of very fine sand and silt rather poorly cemented by a gelatinous substance secreted in the alimentary canal of the organism.

DAPPLES (1942) dedicates a part of his paper ~~on~~ to the effects of macroorganisms upon sediments to the fecal pellets of such organisms, mentioning that they are widely distributed especially in shallow waters.

ILLING (1954) gives a detailed description of the fecal pellets contained in Bahaman calcareous sands. He noted different colors in the pellets varying from light gray to almost black. The difference was referred to changes in diet of the animal producing an increase or decrease in the quantity of the ground-up chitinous fragments which constituted the black part of the digested material. ILLING identified in the fecal pellets small skeletal remains, especially of foraminifera and sponges. In regard to their hardness and thus to the possibility of preservation of those organic structure, ILLING wrote:

> When first excreted fecal pellets are soft and friable aggregates of silt particles, bound together by a certain amount of organic mucus . . . some samples . . . contain all transitions from those that disintegrate at a pin prick, to completely cemented forms, . . . The scarceness of friable pellets indicates that their cementation is rapid. It is probably aided by bacteriological precipitation of aragonite within the pellet (p. 25).

KORNICKER and PURDY (1957, p. 126) explain the reasons why fecal pellets despite their fragility are so abundant in Bimini lagoon (Bahama Islands). One of the reasons adduced by the two authors is the possible bacteriological precipitation of aragonite in the pellets as had been previously suggested by ILLING (1954).

NEWELL and RIGBY (1957, p. 53) describe the fecal pellets of the Great Bahama Bank in the following way:

> When fresh the pellets are friable aggregates of fine detritus held together by mucus. They very soon become firmly bound together by aragonite cement, deposited perhaps through bacterial agencies (ILLING, op. cit.). Eventually they become nearly amorphous as a result of recrystallization of the finest constituents. They always contain a few relatively unaltered chitinous, siliceous, and calcite skeletal inclusions. The animals responsible for the huge quantities of faecal pellets have not been identified.

HOUBOLT (1957) found in the surface sediment of the Persian Gulf large numbers of dark-bluish, almost black particles which he compared for shape and dimensions to the most common form of fecal pellets described by MOORE (1939). The chemical composition of the pellets of the Qatar Gulf differs however from that of Scottish waters, the former consisting mainly of calcium carbonate and the latter of silica.

The difference in composition is explained by HOUBOLT as due to chemical difference of the sediments in which the pellets occur. White fecal pellets were found regularly in the area before mentioned, but in small quantity. HOUBOLT tentatively explains as coprolites of bigger animals also a group of pellets, which are lighter, bigger and coarser in grain size.

According to GINSBURG (1957) almost any animal, whether detritus or filter feeder can produce preservable fecal pellets. Surface carbonate muds in Florida have as much as 50 per cent of pellets, that, however, lo~~o~~se their individuality few feet below the surface. In regard to the most easily preservable pellets GINSBURG writes : " More permanent fecal material occurs as subspherical to ellipsoidal and rod-shaped pellets in a variety of sizes. They consist of mineral grains bound by organic matter. Similar pellets are abundant in the fossil record, and form the major component of some calcarenites" (p.81).

3. BRIEF REVIEW OF THE COMPOSITION OF COPROLITES AS COMPARED WITH THE COMPOSITION OF THE HOST ROCK

As it has been mentioned at the beginning of the section on definitions, there is no defined distinction between the terms fecal pellet and coprolite. In the following pages on composition~~s~~ of fossil excreta these terms have, as before, been used in the same sense as that assigned by the quoted authors.

One of the first quantitative analyses of coprolites was made by DANA (1845) who analyzed a specimen collected by HITCHCOCK in the New Red Sandstone formation of New England. The data are as follows:

Water, organic matter, urate, and volatile salts of ammonia	10.30
Chloride of sodium	.51
Sulphates of lime and magnesia	1.75
Phosphate of lime and magnesia	39.60
Carbonate of lime	34.77
Silicates	13.07
	100.00

This analysis having been made in order to ascertain the presence of urates in the specimen and, consequently, to prove its true excremental nature, DANA remarked: "When we reflect that some specimens of guano contain less than one per cent of uric acid, we may well suppose that excrements deposited, ages perhaps, before the oldest guano was evacuated, have undergone changes by which their urates have disappeared."

TAKAHASHI and YAGI (1929) in a discussion on the origin of the glauconite, tentatively call "coprolite" the mud grains not yet completely glauconitized and state that these grains are frequently found in Japan in rocks of later Tertiary age. They also assume a coprolitic origin for many fossil glauconites, especially in the sediments of the littoral facies.

An example of fossil fecal pellets is given by GALLIHER (1931) who found in the Miocene brown shales of California certain collophane bodies that he called "sporbo" (local name of the oolites) and of which only in a later paper (1932) he recognized the fecal nature. Sporbo are described by GALLIHER as ovoidal or spheroidal bodies, with linear dimensions well under the size of a millimeter. Many of them show a different degree of pyritization increasing toward the center. Two flattened, partly pyritized "sporbo" represented in Figure 2 of the paper in question, are explained as due either to a molding when soft or to interference for secondary growth. The average chemical composition of the pellets was calculated by GALLIHER who analyzed 85 milligrams of grains with the following results:

Insoluble (quartz, feldspar, and clay)	9.8
Fe_2O_3	2.1
CaO	41.2
MgO	trace
P_2O_5	30.7
CO_2	3.7
S	1.4
H_2O	11.1

The grains are mainly contained in a matrix of clay or of very fine quartz and feldspar sand. No tuffaceous material is reported to be present.

GALLIHER summarizes the process of formation of the phosphatic grains as "decomposition of organic remains and possibly the presence of ammoniacal salts and albuminoid matter" (p. 267). In a successive paper (1932, p. 47) the same author writes: "Their phosphatization may probably be accounted for on the basis of their [of the fecal pellets]

action as centers of actraction for phosphates. Such a process is not thoroughly understood, but is profusely covered by the term diagenesis." GALLIHER (1931, p. 267) also writes: "The evidence available fails to show at exactly what stage or stages in the history of the rock the process of disulphide formation occurred. This study had suggested pyritization at a time after the oolites assumed their present form, that is, after they became somewhat hardened."
GALLIHER, although doubting the exact time of pyritization of the pellets, considerd them clearly syngenetic.

Pellets excreted by termites were found by ROGERS (1938) in fossil silicified wood in the Pliocene of Santa Maria, California. The pellets present hexagonal cross-sections about 0.3 - 0.5 mm. suggesting opal pseudomorphs after quartz. This first interpretation is discarded by ROGERS because of the highly improbable change from a stable crystalline form to an unstable amorphous mineral. The termite pellets have, according to ROGERS, about the same composition as the original wood, and are thus easily replaced by the same generation of silica as the wood itself.

The samples studied by ROGERS are somewhat similar to the ones obtained from Eureka and described in the second chapter, section 5 of this thesis. The similarities are striking and include composition and location inside a stem or trunk. The similarity also includes to a certain extent the shape. However, in the samples studied for this thesis (and to the knowledge of the writer, described here for the first time), the cross-sections of the crystals are always hexagonal and usually quite perfectly so, as shown in Figures 4, 5, 6, and 7. In ROGERS' samples the shapes are usually irregularly spheroidal and approach or reach distinctly hexagonal shapes only in some cases(10 out of 40 "pellets" pictured in ROGERS' Figure 2). The similarity of the composition and the occurrence inside wood is so striking that the question arises, whether the evidence of the samples from Eureka does not offer evidence against a pellet-origin of ROGERS' However, in the sample from Eureka the hexagonal shapes are intergrown, zoned and occasionally terminated at neighboring crystal faces. This speaks clearly for crystal growth. ROGERS' pictures do not show any features, at least not between the approximately forty individual "pellets" pictured by him. A more definite conclusion would require a careful detailed study of both samples and localities.

BRADLEY (1946) describes some remarkably well preserved coprolites from the Bridger formation, Wyoming. The coprolites are referred to many reptiles, turtles, and mammalians, either carnivores or omnivores. The coprolite analyzed was studied extensively because of its content of silicified microorganisms. BRADLEY wrote:

> ". . . the protecting sediment was volcanic ash whose small particles of metastable glass soon gave up silica to form the siliceous waters that converted the microorganisms to opaline and chalcedonic silica. Just how the fecal matter was converted to the phosphate mineral francolite it is not known but it is certain that the conversion must have happened before the overlaying sediment was thick enough to flatten the coprolite. If the original fecal matter was as thick in calcium phosphate as certain modern dog feces no great chemical changes occurred during the process" (p. 230).

A chemical analysis of one of the coprolites gave the following result:

	Whole sample (percent)	Insoluble portion (percent)
SiO_2	1.20	5.46
Al_2O_3	1.00	
Fe_2O_3	.86	
FeO	.81	
MgO		
CaO	34.24	
H_2O_{-}	1.55	
H_2O	2.77	
TiO_2	.04	
CO_2	3.46	
P_2O_5	22.78	
MnO	.09	
BaO	none	8.59
SrO	none	none
Cl	none	
F	2.47	
B	none	
SO_3	none	5.94
Ce_2O_3	.28	
Th_2O	trace	
La_2O_3, etc.	.38	
V_2O_5	.01	
Cr_2O_3	none	
As_2O_3	trace	
Organic matter		.68
		7.99
Insoluble	28.66	28.66
	100.60	

According to the analysis the coprolite has a phosphatic composition, not a siliceous as AMSTUTZ (1958) mentions, very close to that of the mineral francolite. The soluble silica is reported as opal contained in microorganisms.

DIETRICH (1951, ref. AMSTUTZ, 1958) described phosphatic coprolites of carnivorous mammals.

BROTZEN (1951, ref. AMSTUTZ, 1958) determined phosphoritic concretions of the Mesozoic as anellid coprolites.

AMSTUTZ (1958c) gives a list of occurrences of coprolites in the literature and describes some specimens from Southern Washington. Those coprolites were collected in the bed and on the bank of Salmon Creek, but they are mentioned in place in the Wilkes formation (ROBERTS, 1958, p. 35). This formation consists mainly of semiconsolidated siltstone and sandstone, the grains of which are of volcanic origin. Quartz, feldspar, hornblende, chlorite, magnetite, muscovite, augite, volcanic glass, biotite and zircon are very frequent. The composition of the coprolites, as shown by a semiquantitative spectrographic analysis is:

Major constituents (probably over 10%)	Fe
Minor constituents (probably 1-10%)	--
Strong traces (probably 0.1-1.0%)	As, Si
Weak traces (probably 0.01-0.1)	Cu.Ca
Very weak traces (probably less than 0.01%)	Sb, Pb

The microscopic study showed only the presence of siderite and limonite in the samples. In regard to the origin of the replacement AMSTUTZ writes:

> "It is reasonable to assume that this replacement was pre-diagenetic. It thus took place before consolidation, which means that the solutions could move around freely, the mobility of the material involved was great and it is not necessary to think in terms of diffusion along intergranular films or diffusion in a solid state" (p. 506).

4. THE COPROLITES IN MISSOURI

Dr. E. L. CLARK, former state Geologist of Missouri in a personal communication to Dr. G. C. AMSTUTZ, mentioned some occurrences of coprolites in the Sylamore sandstones of Southwestern Missouri. In the literature(GROHSKOPF et. al., 1941-42, 62d Bienn. Rep. State Geol.) no mention is made of coprolites, but phosphatic nodules are described in the Sylamore sandstone.

Dr. MEHL of the University of Missouri, at Columbia, kindly provided the location of outcrops in Boone and Callaway Counties, where the phosphatic nodules are very abundant; but Dr. MEHL said that he could not see any reason why these nodules should be coprolites, and an examination of the locality and the nodules for this thesis did not disclose any criteria for an excremental nature either.

Problematic fossils of the Geology Department of the Missouri School of Mines and Metallurgy collection have been indicated as possible coprolites by Dr. A. SPRENG. The elongated, cylindrical bodies form a very irregular pattern on the surface of some specimens of Davis shale~~s~~. The length varies proportionally to the diameter. In some of them the cylindrical external surface presents a certain segmentation which might be considered to correspond to the great gut~~ter~~ of an animal. This is, however, not enough proof for the fecal nature of the fossils.

CHAPTER IV

CONCLUSIONS

In conclusion it may be said that the literature dealing with sedimentation and fossilization processes, including many papers on coal, proposes unanimously a pre- and syn-diagenetic origin of fillings and replacements in fossils.

On the other hand papers dealing with the economic and mining aspects of deposits, such as for example the red bed and sandstone type uranium deposits, propose an epigenetic origin of "mineralized" fossils. It may be said, however, that criteria for epigenetic processes of mineralization, replacements (e.g. silicification, pyritization, sericitization, dolomitization, etc.), are generally not given, and the many assumptions involved in such later metasomatic processes are apparently not realized.

The samples studied for this thesis, including sulphides in fossil animals, appear to corroborate a pre- or syn-diagenetic "mineralization".

BIBLIOGRAPHY

ABELSON, P. H. (1957) : Organic Constituents of Fossils. Geol. Soc. Am., Memoir 67, pp. 87-92.

ALLEN, R. T. and DAY, A. L. (1935) : Hot springs of the Yellowstone National Park. Carnegie Inst. Washington, Publ. 466, 525 p.

AMSTUTZ, G. C. (1948) : Pflanzenreste in Verrucano des Glarner Freiberges. Verh. Schweiz. Naturf. Ges., 2 p.

AMSTUTZ, G. C. (1952) : Replaced fluorite crystals. Schweiz. Min. Petr. Mitt. 32, p. 334-337.

AMSTUTZ, G. C. (1954) : Versteinerte Wälder. Leben und Umvelt 10/11, p. 224-225.

AMSTUTZ, G. C. (1956a) : A note on a peculiar association of copper with fossil plants in Central Peru. Bol. Soc. Geol. Peru 30 (Anal. Primer Congr. Nac. Geol.), p. 5-11.

AMSTUTZ, G. C. (1956b) : Cerro de Pasco's famous fossil plants. El Serrano, August, 1 p.

AMSTUTZ, G. C. (1958a) : The genesis of the Mississippi Valley type deposits, U. S. A. Experientia XIV, p. 235-237.

AMSTUTZ, G. C. (1958b) : Epigenetic and syngenetic theories on formation of rocks and mineral deposits. Geol. Soc. Am., 1958 Annual Meeting, Program, p. 25.

AMSTUTZ, G. C. (1958c) : Coprolites: A review of the literature and a study of specimens from Southern Washington. Jour. Sedimentary Petrology 28, p. 498-508.

AMSTUTZ, G. C. (1959a) : Sedimentary petrology and ore genesis. Annual Meeting Am. Assoc. Petrol. Geol., 1959 Dallas (abstract).

AMSTUTZ, G. C. (1959b) : Syngenese und Epigenese in Petrographie und Lagerstättenkunde. Schweiz. Min. Petr. Mitt. 39, 84 p.

ANDREWS, H. N. (1946) : Coal balls - A key to the past. Scientific Monthly 62, p. 327-334.

ANDREWS, H. N. JR. (1951) : American coal ball Floras. The Botan. Rev. 17, p. 430-469.

ANDREWS, H. N. JR. and MAMAY, S. H. (1950) : A brief conspectus of american coal ball studies. The Palaeobotanist I, pp. 66-72.

BARGHOORN, E. S. (1949) : Degradation of plant remains in organic sediments. Botanical Museum Leaflets, Harvard Univ., Vol. 14, No. 1, p. 1-20.

BARKSDALE, J. D. (1939) : Silicified wood in dolomite. Am. Mineralogist 24, p. 699-704.

BATEMAN, A. M. (1950) : Economic mineral deposits. John Wiley & Sons, New York, 2nd Ed., 916 p.

BERTRAND, C. Eg. (1903) : Les coprolithes des Bernissart. Mém. Musée Roy. d'Hist. Nat. Belgique, 1, p. 10-154.

BISSEL, H. J. (1959) : Silica in Sediments of the Upper Paleozoic of the Cordilleran Area. In: IRELAND, H. A. (ed.) Silica in Sediments. Soc. Ec. Paleont. Mineral. Spec. Publ. 7, 150-185.

BLACKWELDER, E. (1916) : The geologic role of phosphorus. Am. Jour. Sci., Ser. 4, 42, 285-298.

BRADLEY, W. H. (1946) : Coprolites from the Bridger formation of Wyoming: their composition and microorganisms. Am. Jour. Sci. 244, p. 215-239.

BRAMLETTE, M. N. (1946) : The Monterey formation of California and the origin of its siliceous rocks. U. S. Geol. Survey Prof. Paper 212, p. 1-55.

BRANNER, J. C. and NEWSON, J. F. (1902) : The phosphate rocks of Arkansas. Arkansas Agr. Exp. Sta. Bull. 74.

BUCHANAN, J. Y. (1890) : On the occurrence of sulphur in marine muds and nodules and its bearing on their mode of formation. Roy. Soc. Edinburgh, Trans. 18, p. 17-39.

BUCHER, W. H. (1953) : Fossils in metamorphic rocks: a review. Bull. Geol. Soc. Am. 64, p. 275-300.

BURGER, K. (1956) : Mikropetrographische Beobachtungen zur Genese der Graupen-und Kristalltonsteine, in Kohlenflözen. Chemie der Erde 18, p. 19-26.

BURT, F. A. (1932) : Formative processes in concretions formed about fossils as nuclei. Jour. Sedimentary Petrology 2, p. 38-45.

BUTLER, R. D. (1938) : A "Red Beds" type copper occurrence, Wyoming Co., Pennsylvania. Ec. Geol. 33, p. 625-634.

CADY, W. M. (1950) : Fossil cup corals from the metamorphic rocks of central Vermont. Am Jour. Sci. 248, p. 488-497.

CALVINO, F. (1956) : Fossili anfibolizzati in arenaria metamorfica. La Ricerca Scientifica 26, p. 2390-2399.

CAYEUX, L. (1916) : Introduction a l'ètude pètrographique des roches sèdimentaires. Mèm. Carte Geol. France, p. 270.

CAYEUX, L. (1939) : Les phosphates de chaux sedimentaire de France. France Metropolitaine et d'outre Mer Paris, Imprimerie Nationale.

CAYEUX, L. (1940) : Conclusions drawn from comparison of the phosphate concretions of the sea today with the nodules of old sedimentary formations. Compt. Rendu 211, p. 496-499.

CLARKE, F. W. and WHEELER, W. C. (1922) : The inorganic constituents of marine invertebrates. U. S. Geol. Survey Prof. Paper 124, II Ed., p. 1-62.

CLOUD, P. E. (1941) : Color-patterns in Devonian terebratuloids. Am. Jour. Sci. 239, p. 905-907.

CONDIT, C. and MILLER, A. K. (1951) : Concretions from Iowa like those of Mazon Creek, Illinois. Jour. Geol. 59, p. 395-396.

CORRENS, C. W. (1926) : Beiträge zur Petrographie und Genesis der Lydite (Kieselschiefer). Preuss. Geol. Landesandstalt, Mitt. d. Abt. f. Gesteins-, Erz-, Kohle-und Salz-Untersuchungen, Heft 1, p. 18-38.

CORRENS, C. W. (1949) : Einführung in die Mineralogie. Springer Verlag, Berlin, 414 p.

CRESSMAN, E. R. (1955) : Physical stratigraphy of the Phosphoria formation in part of southwestern Montana. U. S. Geol. Survey Bull. 1027a, 1-31.

DAMAS, D. (1935) : Le role des organismes dans la formation des vases marines. Soc. Geol. de Belgique Annales 58, p. B143-B151.

DANA, S. L. (1845) : Analysis of Coprolites from the New Red Sandstone formation of New England, with remarks by Prof. Hitchcock. Am. Jour. Sci. XLVIII, p. 46-60.

DAPPLES, E. C. (1942) : The effect of the macro-organisms upon near-shore marine sediments. Jour. Sedimentary Petrology 12, p. 118-126.

DARRAH, W. C. (1939) : Textbook of Paleobotany. Appleton-Century Co., New York, p. 3-18.

DARRAH, W. C. (1941) : Studies of American coal balls. Am. Jour. Sci. 239, p. 33-53.

DEAN, L. A. (1957) : Plant nutrition and soil fertility. Soil, the yearbook of agriculture, U. S. G. P. O. 80.

DEUL, M. (1958) : Biochemical and geochemical origins of ash-forming ingredients in coal. Paper presented before the Div. of Gas and Fuel Chem., Am. Chem. Soc., Chicago Meeting, Sept. 1958.

DIETZ, R. S., K. O. EMERY, and F. P. SHEPARD (1942) : Phosphorite deposits of the sea floor off Southern California. Geol. Soc. Am. Bull. 53, p. 815-848.

DOLL, C. G. (1943) : A brachiopod from micaschist, South Strafford, Vermont. Am. Jour. Sci. 241, p. 676-679.

DOSS, B. (1912) : Melnikovit ein neues Eisenbisulphid, und seine Bedeutung für die Genesis der Kieslagerstätten. Zeitschr. prakt. Geologie, Jahrg. 20, p. 453-483.

EAGAR, R. M. (1952) : The succession above the Soft Bed and Bassey Mine in the pennine region. Liverpool & Manchester Geol. Jour. 1, p. 23-56.

EAMES, A. J. (1930) : Report on ground-sloth coprolite from Dana Ana County, New Mexico. Am. Jour. Sci. 5th ser., 20, p. 353-356.

EARDLEY, A. J. (1938) : Sediments of the Great Salt Lake, Utah. Bull. Am. Assoc. Petrol. Geol. 22, p. 1305-1411.

EARLAND, A. (1932) : The resistant nature of the Faecal Pallets. Micropaleontology Bull. III, p. 96.

EDGE, F. R. (1934) : Faecal pellets of some marine invertebrates. Am. Midland Nat. 15, p. 78-84.

EITEL, W. (1954) : Physical chemistry of silicates. Univ. Chicago Press, p. 450.

EMIGH, G. D. (1958) : Petrography, Mineralogy and Origin of Phosphate Pellets in the Phosphoria Formation. Idaho Bureau of Mines and Geology, Pamphlet No. 114, 60 p.

EMMONS, W. H. (1940) : The principles of economic geology. McGraw-Hill, New York, p. 78-79.

FINNEL, T. L. (1957) : Structural Control of Uranium Ore at the Monument no. 2 Mine, Apache County, Arizona. Ec. Geol. 52, pp. 25-35.

FISCHER, A. G. (1949) : Petrology of Eocene limestones in and around the Citrus-Levy County area, Florida. Florida Geol. Survey, Rep. of Inv. 9, p. 43-70.

GALLIHER, E. W. (1931) : Collophane from Miocene brown shales of California. Bull. Am. Assoc. Petrol. Geol. 15, p. 257-269.

GALLIHER, E. W. (1932) : Organic structures in sediments. Jour. Sedimentary Petrology 2, p. 46-47.

GINSBURG, R. N. (1957) : Early diagenesis and lithification of shallow-water carbonate sediments in South Florida. In: R. J. Le BLANC and J. G. BREEDING (ed.): Regional aspects of carbonate deposition Soc. Ec. Paleont. Mineral., Special Publ. 5, p. 80-100.

GOLDSTEIN, A. JR. (1959) : Cherts and Novaculites of Ouachita Facies. In: IRELAND, H. A. (ed.) Silica in Sediments, Soc. Ec. Paleont. Mineral. Special Publ. 7, 135-149.

GREENSMITH, J. T. (1958) : In: Discussion on: Micro-organisms and the presence of syngenetic pyrite, by L. G. LOVE. Quarterly Jour. Geol. Soc. London CXIII, p. 439.

GROSS, E. B. (1956) : Mineralogy and paragenesis of the uranium ore, MiVida Mine, San Juan County, Utah. Ec. Geol. 51, p. 632-648.

HÄNTZSCHEL, W. (1939) : Tidal flat deposits (Wattenschlick). In: Trask, P. D. (ed.) Recent Marine Sediments, Soc. Ec. Paleont. Mineral. Special Publ. 4, p. 195-206.

HARDER, E. C. (1919) : Iron-Depositing bacteria and their geologic relations. U. S. Geol. Survey, Prof. Paper 113, 89 pp.

HARRIS, T. M. (1956) : The fossil plant cuticule. Endeavour XV, p. 210-214.

HAYES, C. W., and E. O ULRICH (1903) : U. S. Geol. Survey Geol. Atlas, Columbia Folio (no. 95).

HOLSER, W. T. (1947) : Metasomatic processes. Ec. Geol. 42, p. 384-395.

HOUBOLT, J. J. H. C. (1957) : Surface sediments of the Persian Gulf near the Qatar Peninsula. Mouton & Co., The Hague Netherlands, 113p.

HOWE, W. B. (1956) : Statigraphy of Pre-Marmaton Desmoinesian (Cherokee) rocks in Southeastern Kansas. State Geol. Survey Kansas Bull. 123, p. 76, p. 80.

ILLING, L. V. (1954) : Bahaman Calcareous Sands. Bull. Am. Assoc. Petrol. Geol. 38, p. 1-95.

KAUTZSCH (1958) : Die Sedimentären Erzlagerstätten des unteren Zechstein. In: Kolloquium über "Sedimentäre Erzlagerstätten des Schwefelkreislaufes". Akademie Verlag, Berlin, 48 p.

KAZAKOV, A. V. (1937) : The phosphorite facies and the genesis of phosphorites. Moscoq. Naufhnyi Institut Po Udohreniiam I Insektofungisidan, 142, 95-113.

KAZAKOV, A. V. (1938) : The phosphorite facies and the genesis of natural phosphates. Sovetskaia Geologiia, tome 8, no. 6, 33-47.

KEILIN, D. (1953) : Stability of biological material and its bearing upon the problem of anabiosis. Science Progress XLI, 164, p. 577-592.

KELLER, W. D. (1947) : Sulfide replacement of a Trigonocarpus fossil fern fruit. Am. Mineralogist 32, p. 468-470.

KNIGHT, C. L. (1957) : Ore genesis-the source bed concept. Ec. Geol. 52, p. 808-817.

KORNICKER, L. S. and E. G. PURDY (1957) : A Bahamian faecal-pellet sediment. Jour. Sedimentary Petrology 27, p. 126-128.

KRAUSKOPF, K. B. (1955) : Sedimentary deposits of rare metals. Ec. Geol. Fiftieth Ann. Vol., p. 411-463.

KRAUSKOPF, K. B. (1959) : The Geochemistry of Silica in Sedimentary Environments. In: IRELAND, H. A. (ed.) Silica in Sediments, Soc. Ec. Paleont. Mineral. Special Publ. 7, p. 4-19.

KUENEN, Ph. H. (1939) : Sediments of the East Indian Archipelago. In: Trask, P. D. (ed.) Recent marine sediments. Soc. Ec. Paleont. Mineral. Special Publ. 4, p. 348-355.

KUENEN, Ph. H. (1950) : Marine Geology. J. Wiley & Sons, New York, 568 p.

LEYDIG, F. (1896) : Koprolithen und Urolithen. N. Jb. Min., Geol. u. Pal. Jahrg. 1896 II, p. 139-140.

LIPMAN, C. B. and E. McLEES (1940) : A new species of sulphur-oxidizing bacteria from a coprolite. Soil Sci. 50, p. 429-432.

LOMBARD and MOUSSU (1958) : Sedimentäre Kupferlagerstätten vom Typ Kupferschiefer in Marokko. In: Kolloquium über "Sedimentäre Erzlagerstätten des Schwefelkreislaufes" Akademie Verlag, Berlin, 48 p.

LOVE, L. G. (1958) : Micro-organisms and the presence of syngenetic pyrite. The Quarterly Jour. Geol. Soc. London, CXIII, p. 429-440.

LOVERING, T. S. (1927) : Organic precipitation of metallic copper. U. S. Geol. Survey Bull. 795, p. 47-52.

MAMAY, S. H. and E. L. YOCHELSON (1953) : Floral-Faunal Associations in American Coal Balls. Science 118, p. 240-241.

MASON, B. (1952) : Principles of Geochemistry. John Wiley & Sons, New York, 276 p.

MATHIAS, H. E. (1928) : Syngenetic origin of pyrite concretions in the Pennsylvanian shales of North-Central Missouri. Jour. Geol., 36, p. 440-450.

MATLEY, C. A. (1939) : On some coprolites from the Maleri beds of India. India Geol. Survey Records, 74, Pt. 4, p. 530-534.

MATLEY, C. A. (1939) : The coprolites of Pijdura, Central provinces. India Geol. Survey Records, 74, Pt. 4, p. 535-547.

MITCHELL, R. L. and Geo. J. RITTER (1934) : Composition of three fossil woods mined from the Miocene auriferous gravels of California. Jour. Am. Chem. Soc., vol. LVI, p. 1603-1605.

MONAGHAN, P. H. and M. L. LYTLE (1956) : The origin of Calcareous Olith. Jour. Sedimentary Petrology 26, p. 11-118.

MOORE, H. B. (1931) : Muds of the Clyde Sea area. III. Chemical and Physical conditions; rates and nature of sedimentation; and fauna. Jour. Mar. Biol. Assoc. 17, p. 325-366.

MOORE, H. B. (1939) : Faecal Pellets in relation to Marine Deposits. In: Trask, P. D. (ed.) Recent Marine Sediments, Soc. Ec. Paleont. Mineral. Special Publ. 4, p. 516-524.

MOORE, R. C. (1957) : Mississippian carbonate deposits of the Ozark region. In: LE BLANC, R. J. and J. G. BREEDING, (ed.) Regional aspects of carbonate deposition. Soc. Ec. Paleont. Mineral., special publ. 5, p. 101-124.

MORET, L. (1948) : Manuel de palèontologie animale. Masson & Co. Editeurs, 2nd ed., 745 p.

MURATA, K. J. (1940) : Volcanic ash as a source of silica for the silification of wood. Am. Jour. Sci., 238, p. 586-596.

NEUMANN, W. (1958) : Beitrag zur Kenntnis der Phosphatlagerstätten Nordvietnams. Geologie (Berlin), Jahrg. 7, H. 3-6, p. 702-719.

NEWELL, N. D. and J. K. RIGBY (1957) : Geological studies on the Great Bahama bank. In: R. J. LeBlanc and J. G. Breeding (ed.) Regional aspects of carbonate deposition. Soc. Ec. Paleont. Mineral., special publ. 5, p. 15-79.

NICHOLSON, H. A. (1889) : A Manual of Paleontology. H. Blackwood, London, Vol. I, 2nd ed., p. 21.

NIGGLI, P. (1954) : Rocks and mineral deposits. W. H. Freeman 5 Co., San Francisco, 559 p.

PALMER, W. S. (1935) : Gold in petrified wood. Min. and Met., 16, p. 335.

PANTIN, H. M. (1958) : Rate of formation of a diagenetic calcareous concretion. Jour. Sedimentary Petrology 28, 366-371.

PARÉJAS, E. (1948) : Sur quelque coprolithes de crustacès. Arch. Sci. 1, f. 3, p. 512-520.

PETTIJOHN, F. J. (1949) : Sedimentary rocks. Harper and Brothers, New York, 718 p.

PIVETEAU, J. (1952) : Traitè de Palèontologie. Masson et C. Editeurs, Paris, Tome I, 782 p.

RANKAMA, K. and Th. G. SAHAMA (1950) : Geochemistry. The University of Chicago Press, 912 p.

ROBERTS, A. E. (1958) : Geology and coal resources of the Toledo-Castle Rock District, Cowlitz and Lewis Counties, Washington. U. S. Geol. Survey Bull. 1062, 71 p.

ROGER, J. (1952) : La Fossilisation. In: J. PIVETEAU: Traitè de Paléontologie, Tome I: Masson et C. Editeurs, Paris, p. 13-40.

ROGERS, A. F. (1938) : Fossil Termite Pellets in Opalized Wood from Santa Maria, California. Am. Jour. Sci. 5th ser., 36, p. 389-392.

ROSS, C. S., H. D. MISER and L. W. STEPHENSON (1929) : Water-laid volcanic rocks of early Upper Cretaceous age in South-Western Arkansas, South-Western Oklahoma, and Northeastern Texas. U. S. Geol. Survey Prof. Paper 154, p. 175-204.

SABBATONI, L. (1920) : Saggi di fossilizzazione sperimentale Bull. Soc. Geol. Ital. XXXIX, p. 317-323.

SANDBERGER, F. (1885) : Untersuchungen über Erzgänge. 2. Heft Wiesbaden, S. 15 p.

SCHNEIDERHÖHN, H. (1923) : Chalkographische Untersuchung des Mansfelder Kupferschiefers. N. Jahrb. f. Min. B 47, p. 1-38.

SCHWARTZ (1958) : Die Bakterien des Schwefelkreislaufes und ihre Lebensbedingungen. In: Kolloquium über: Sedimentare Erzlagerstätten des Schwefelkreislaufes. Akademie Verlag, Berlin, 48 p.

SMITH, R. C. and G. I. WHTTLATCH (1940) : The phosphate resources of Tennessee. Tennessee Div. of Geol., Bull. 48, 444 p.

SHROCK, R. R. (1948) : Sequence in layered rocks. McGraw-Hill Book Co., New York, 507 p.

SOSMAN, R. B. (1950) : Centripetal genesis of magmatic ore deposits. Bull. Geol. Soc. Am. 61, p. 1505.

STARK, J. T. and E. C. DAPPLES (1941) : Near shore coral lagoon sediments from Raiatea, Society Islands. Jour. Sedimentary Petrology, Vol. 11, No. 1, p. 21-27.

STOPES, M. C. and D. M. WATSON (1908) : On the present distribution and origin of the calcareous concretions in coal seams known as coal balls. Phil. Trans. Roy. Soc. London, B, 200, p. 167-218.

ST. JOHN, R. N. (1927) : Replacement vs. impregnation in petrified wood. Ec. Geol. 22, p. 729-739.

STRINGHAM, B. (1940) : Occurrence of feldspar replacing fossils. Am. Mineralogist 25, p. 139-144.

STRØM, K. M. (1939) : Land-locked waters and the deposition of black muds. In: Trask, P. D. (ed.) Recent marine sediments, Soc. Ec. Paleont. Mineral. Special Publ. 4, p. 356-372.

SUJKOWSKI, Zb. L. (1958) : Diagenesis. Bull. Am. Assoc. Petrol. Geol. 42, p. 2692-2717.

SVERDRUP, H. U., M. W. JOHNSON and R. H. FLEMING (1942) : The Oceans. Their physic, chemistry and general biology. Prentice Hall, New York, 1087 p.

SWINEFORD, A. and P. C. FRANKS (1959) : Opal in the Ogallala Formation in Kansas. In: IRELAND, H. A. (ed.) Silica in Sediments, Soc. Ec. Paleont. Mineral. Special Publ. 7, p. 111-120.

TAKAHASHI, J. I. and T. YAGI (1929) : Peculiar mud-grains and their relation to the origin of glauconite. Ec. Geol. 24, p. 838-853.

TAKAHASHI, J. I. (1939) : Synopsis of Glauconitization. In: Trask, P. D. (ed.) Recent Marine Sediments, Soc. Ec. Paleont. Mineral. Special Publ. 4, p. 503-512.

TARR, W. A. (1928) : Syngenetic pyritization in local reducing areas of Pennsylvanian shales in Missouri. Journ, Geol., 36, p. 434-439.

THORP, E. M. (1931) : Descriptions of deep-sea bottom samples from the western North Atlantic and Caribbean Sea. Scripps Inst. Ocean. Bull., tech. Ser., 3, p. 1-31.

THORP, E. M. (1936) : Calcareous shallow-Water Marine Deposits of Florida and the Bahamas. Pap. Tortugas Lab. XXIX, Publ. 452, p. 37-120.

THORP, E. M. (1939) : Florida and Bahama marine calcareous deposits. In: Trask, P. D. (ed.) Recent Marine Sediments. Soc. Ec. Paleont. Mineral. Special Publ. 4, p. 283-297.

TOMKEIEFF, S. I. (1954) : Coal and Bitumens and related fossil carbonaceous substances. Pergamon Press, London, 122 p.

TWENHOFEL, W. H. (1932) : Treatise on sedimentation. The Williams and Wilkins Co., Baltimore.

TWENHOFEL, W. H. (1950) : Principles of sedimentation. McGraw-Hill, New York, 2nd ed., 673 p.

TWENHOFEL, W. H. and R. R. SHROCK (1935) : Invertebrate paleontology. McGraw-Hill, New York, 511 p.

VAN HISE (1904) : A treatise on metamorphism. U. S. Geol. Survey, Mon. 47, p. 828.

VAN TUYL (1918) : The origin of chert. Am. Jour. Sci. XLV, fourth series, p. 449-456.

VAUGHAN, T. W. (1924) : Oceanography in its relations to other earth sciences. Jour. Washington Ac. Sci. 14, p. 307-333.

WALTHER, J. (1893/1895) : Einführung in die Geologie als historische Wissenschaft. Jena.

WEEKS, L. G. (1957) : Origin of carbonate concretions in shales, Magdalena Valley, Colombia. Geol. Soc. Am. Bull. 68, p. 95-102.

WESTOLL, P. H. (1955) : In: Discussion on: Concentration in Sediments, by J. H. Taylor. III inter-University Geological Congress. Durham Colleges in the University of Durham. Publ. 124, p. 19-20.

WETZEL, W. (1957) : Selektive Verkieselung. Neues Jb. Geol. u. Paläont., Abh., 105, 1, p. 1-10.

WHERRY, E. T. (1912) : Silicified wood from the triassic of Pennsylvania. Proceedings of the Acad. Nat. Sci. of Philadelphia, Vol. LXIV, p. 366-372.

WHITTINGTON, H. B. (1950) : Two silicified middle Ordovician Trilobites. Geol. Soc. Am. Bull. 61, p. 1514-1515 (abstract).

WIESE, R. G. (1957) : An occurrence of Mineralized Organic Material in Nova Scotia. Ec. Geol. 52, p. 76-82.

APPENDIX

After the completion of the body of this thesis a few additional references were received from specialists to whom letters had been written, and from Dr. Proctor of the Geology Department of this School. The pertinent information contained in these additional references is presented in the Appendix and is also used for the final tabulation. In addition, the conclusions are amplified.

<u>OXIDES</u>: The Clinton Iron Ore deposits contain numerous fossil fragments, which are, according to BATEMAN (1950, p. 569), "coated and partly replaced by hematite and enclosed in amorphous and oolitic hematite". These deposits are accepted by practically all workers in the field of ore genesis to have originated from precipitation of iron oxide in shallow marine waters. Changes in the physico-chemical conditions are explained to have produced the alternating zoning in the inorganic oolites and around fossil fragments as described by TAYLOR[1] (1951, p. 79-80) in the Northampton sand ironstone of England. The same origin is assigned to the huge oolitic deposits of Alsace-Lorraine. Numerous other examples of oxide deposits were found but are not mentioned here because of the reasons mentioned before. Either the information was insufficient to quote or evaluate the time criteria, or they were merely a duplication of the example mentioned here. It is not the aim of this thesis to compile literature but rather to

---

[1] TAYLOR, J. H. (1951) Sedimentation problems of the Northampton Sand Ironstone. Yorkshire Geol. Soc. Proc. XXVIII, p. 74-85.

carefully select and evaluate available information with regard to the time of deposition.

SULPHIDES: A very rich marcasitic fauna was described by STEWART[2] (1927) in the Silica shales of Ohio without any mention of the possible origin of the sulphides and without reference to the time of replacement. Three samples of this material were obtained from the MSM collection. They show a perfect minetic replacement by iron sulphide.

Another marcasitic fauna, of about the same age, is described in detail by D.W. FISHER[3] (1951). In this paper the presence of dwarfed forms is related to the high concentration of H_2S or Fe in the sedimentary environment that created conditions apparently analogous to those existing at present in the Black Sea (see P. NIGGLI, 1954) and in the Persian Gulf (see Houbolt, 1957). If dwarfed forms can be considered to be proof for an exceptionally acid environment, their absence does not, on the other hand, constitute proof against such an environment. Not all the organisms found as fossils in a sediment were living in it; they can as well have fallen into it from more surficial waters or have been transported by currents. The hypothesis of such a displacement of fossils involves, however, additional assumptions.
BUTLER[4] et al. (1920) described and illustrated examples of

---

[2] STEWART, G.A.,(1927) Fauna of the Silica shale of Lucas County. Geol. Surv. of Ohio Bull. 32, p. 5-76.

[3] FISHER, D.W. (1951) Marcasite fauna in the Ludlowville formation of western New York. Journ. Paleont. 25, p.365-371.

[4] BUTLER, B.S. et al. (1920) The ore deposits of Utah. U.S. Geol. Survey Prof. Pap. 111, p. 153-154.

plant structures almost always perfectly preserved by sulphide mineralization. The plants were not botanically identified. These authors noticed that the ore minerals are associated with the carbonized plants, whereas the silicified plants contain very little or no metallic minerals. The "replacement" of the cells by sulphides is said to have occurred before the carbonization. The evidence offered by the authors is the excellent preservation in size and shape of the vegetable structure. The carbonized cells are reported by BUTLER to be perfectly preserved with regard to shape, but smaller than those "replaced" by copper sulphides. They thus assume that shrinkage occurred during carbonization, and that the wood that was"replaced" by sulphides was preserved from shrinkage. The terms "replacement" or "replaced" are put in the quotation marks because the photographs show that most of the sulphides are only filled into the cells and do not replace the cell walls. If the sulphides replaced anything, it was the plasma inside the cells and there is hardly any justification to call this process replacement since most of the plasma consists of water.

The evidence provided by these additional references supports the conclusion reached before: the well-preserved nature of the original structure of the fossil is evidence for a contemporaneous or syngenetic origin of the filling or replacement. This process is often called mineralization by workers interested in the ore minerals, because of the presence of ore minerals. A careful examination of their arguments shows that, with very few exceptions, the term mineralization is used in an epigenetic sense. It is one of the conclusions of this thesis that the term mineralization should be avoided in cases where contemporaneous filling and replacement took place. Instead terms like fossilization, filling, contemporaneous or diagenetic replacement, etc. should be used.

Besides the additional references a tabulation of the data collected during the study of the papers mentioned in the thesis is offered in this appendix. Data such as the lithology of the formation and its age were considered of little importance for the purposes of the thesis and were therefore usually not mentioned in the body of the thesis. These are now included together with all the details that could be collected.

In all sections of this thesis it has become obvious that the information which is needed for the establishment of criteria for the time of deposition of the ore minerals (the so called mineralization), has to be extracted from generally separated fields of geology, namely that of paleontology on one side and ore deposition on the other side. The review of the literature took thus a long time and only a part of what was read and reviewed could be used in this thesis. Many papers were read in which the presence of unusual minerals in fossils was mentioned but without any reference to the geometric or to the mineralogical details which could have permitted conclusions on the time of mineralization. On the other hand many papers mention mode and time of mineralization, or the time can be inferred, but the nature and age of the fossil and its stratigraphic position and lithologic environment are neglected.

In general it is correct that paleontological papers give details about the classification of the organism, its stratigraphic position, and its ecology, but do not mention or discuss the mineralogical composition. In one of those papers marcasite is referred to as iron oxide: "The iron oxide, marcasite, commonly replaces the shell material, and has been referred to as pyrite in various places in this paper" (STEWART, 1927, p. 10). On the other hand papers on ore genesis or some other phases of economic geology or mineral deposits very rarely pay attention to detailed determinations of the fossils encountered. They are, at the most, classified with a group or class term. The authors emphasize only the mineralogic composition and texture, the intergrowth relationship between different ore minerals or gangue and ore minerals, the paragenetic sequence, etc.

It is interesting in this connection to note that the blank spaces in the tables at the end of this appendix are prevalently on the left side for papers on mineral deposits such as those by EMMONS, BUTLER, FINNELL, while for the paleontological papers such as those by ROGER, MAMAY. and YOCHELSON, STEWART, HOWE, etc. the right side usually shows empty fields. This fact would be even more evident, if all the papers read and reviewed would have been included in the table. It was, however, not the intention of this thesis, to set up a bibliography, but rather to critically select and to "map" pertinent data and opinions and to offer an integrated picture of them, as well as to draw the conclusions for o~~n~~re genesis and exploration. It probably should be mentioned

that of all the papers which describe replaced or mineralized fossils only about one third was used for this thesis and listed in the bibliography.Likewise of all the samples available only a part could be used because of the lack of criteria allowing the determination of the time of mineralization.Silicified wood,silicified corals (in hand specimen and thin section), carbonized wood,carbonatized wood,coal balls,pyritized fossils (in hand specimens and polished sections),calamine in a brachiopod (MSM Geology Museum),to mention only afew,could not be used because it was impossible to find any indication or evidence of use as time criteria of mineralization.
When selecting the actual samples for this thesis two criteria of selection were applied.First,among those which appeared to offer time criteria,the one with the largest number of details was selected.Secondly,the selection was also made in such a way as to have a typical sample for each main compositional group.

The scope and the conclusions of this thesis may be emphasized again in this appendix. It was not considered to be necessary to describe the present state of the theories on genesis of mineral deposits at the beginning because this information is readily available in recent papers (NIGGLI,1954, AMSTUTZ,1959a,etc.).The genetic interpretation of layered mineral deposits,particularly those associated with fossil matter,varies greatly between epigenetic and syngenetic extremes.Fossil matter as one criteria for or against one of the two theories had been used in the literature only scarcely and unsystematically.It therefore appeared to be of value to collect and to build up on the best of the available information. In order to be able to evaluate the details better, both with regard to geometry as well as to geochemistry, actual samples were included in this study. An extensive correspondence and many personal discussions made it possible to select samples of outstanding value for time criteria studies. To mention only one instance, none of the papers on sulphides in fossil wood and none of the samples mentioned in the literature describes or contains such a large number of different sulphides as the sample from Mitterberg described on p. 65 and pictured on Figures 9 and 10.

Although it was not repeated after every single chapter, the criteria used for the determination of the time of deposition by papers on stratigraphy or paleontology are always almost identical whereas those on economic geology are usually contrary. It is considered of scientific value to establish similarity or identity, not only between actual samples but also between observations of previous workers, EMMONS, 1940; GROSS, 1950; FINNELL, 1957, and criteria or evidences used. Such an identity establishes proof of the existence, and adds probability to the value of the time criteria described. The statement has been made that science had advanced as much or more from re-interpretations of previous data as from first hand observations.

In summary, these criteria are again the preservation of original textures and thus of the microscopic shape as well as the size. The coincidence of environment and composition of the mineralized fossils is shown by the analysis of the literature. It could not exist if epigenesis would play a role. To mention one example again (see page 62 of this thesis), WESTOLL (1955) describes ammonites form the Yorkshire Lias shales which "often have their gas chambers filled to some extent with blende, galena, etc. and the consolidated rock we know it today must be a serious barrier to mineralising solutions. Therefore these infillings were probably formed during the process of consolidation and lithification." As mentioned at various occasions throughout this thesis, depositional conditions observed today support fully the geometric evidence offered by the perfect preservation, whereas contact metamorphic deposits show crosscutting relationships and offer therefore proof of epigenesis.

It became obvious during the present work that many interesting special problems are of course open to further investigation and it would be most interesting to enter into some of them. For example HARVEY (1955, ref. RICHARDS[5], 1957, p. 88) mentions three mechanisms by which minor elements are concentrated by marine organisms: "(a) by absorption of ions at cell-water or intercellular interfaces; (b) by the combination of ions in solution into organic matter within plant or animal cells; and (c) the attachment of colloidal nicelles to the mucus of plants and animals." However, no experimental data are available in the references checked. It would also be a most interesting experiment to see which fossil absorbs or concentrates which elements, and also which pH and Eh is

---

[5] RICHARDS, F.A. (1957) Some current aspects of chemical oceanography. In: L.H. AHRENS, A.H. et al. (ed.) (1957) Physics and chemistry of the earth. Pergamon Press London, p. 77-128.

necessary to produce certain types of mineralization observed in nature. To the knowledge of the writer SABBATONI (1920) is the only one who has conducted fossilization and replacement or filling experiments. Reports on mineralized objects in mines are numerous. No indication was found, however, of the actual exact physico-chemical conditions.

The conclusions reached on page 85 of this thesis are thus corroborated again by both the geochemical and geometric evidence and it is hoped that this thesis will help in closing the gap mentioned in the introduction.

CARBONATES

FOSSIL	SEDIMENT		ENVIRONMENT	MINERAL	MODE OF MINERALIZATION	TIME OF MINERALIZATION	AUTHOR
	Lithology	Age					
Plants	Sandstone	Triassic	---	Malachite or Azurite	---	---	ROGER, J., 1952
Pelecypods	---	Triassic	---	Smithsonite	---	---	ROGER, J., 1952
Crinoids	---	Jurassic	---	Cerussite	---	---	ROGER, J., 1952
Mold of Foraminifera Valvulinidae	Massive Dolomite	Avon Park Limestone (Eocene)	---	Dolomite	Secondary dolomitization of limestone sediments	Possibly penecontemporaneous	FISHER, A.G., 1953
Fish Elopidae Fam.	Black calcareous Shales with many calcareous concretions	Early Albian (Cretaceous)	Stagnant water	Calcium Carbonate	Concentration of NH_4 from anaerobic decomposition. Increasing of pH till the precipitation of the $CaCO_3$ from the bicarbonate as incrustation	Soon after death of the fish	WEEKS, L.G., 1957
Brachiopods	Coarse grained crinoidal cherty limestone	Burlington Formation (Mississippian)	Large epicontinental sea with clear warm water rich in benthonic organisms	Calcium Carbonate	Calcium Carbonate is the mineral of the original shell	(*)	MOORE, R.C., 1957
Coprolites	Massive tuffaceous clay	Wilkes Formation (Upper Miocene)	Shallow basin containing lakes and swamps	Siderite	Replacement	Prior to the consolidation of the rock	AMSTUTZ, G.C., ROBERTS, 1958
Many organic remains	Cherty Dolomite	Mississippian(?)	---	Calcium Carbonate	Calcium Carbonate is the mineral of the original shell	(**)	This Thesis 1959

(*), (**) The Calcium Carbonate being the original shell forming mineral, no time of mineralization is given for these fossils. Their relationship with the enclosing rock (Chert-carbonate rock) has been used to determine the time of deposition of the chert, which appears to be syngenetic with the carbonate rock.

OXIDES

FOSSIL	SEDIMENT		ENVIRONMENT	MINERAL	MODE OF MINERALIZATION	TIME OF MINERALIZATION	AUTHOR
	Lithology	Age					
Pelecypods	---	Liassic	---	Hematite	---	---	ROGER, J., 1952
Many organic remnants	---	Clinton Age (Silurian)	---	Hematite	Incrustation and replacement	Contemporaneous to deposition or diagenetic	BATEMAN, A.M., 1950
Plants	Sandstone	Chinle Formation (Triassic)	Reducing environment	Uraninite	Replacement	Epigenetic after the formation	GROSS, E.B., 1956

SILICA

Corals	Limestone and cherty Dolomite	Paleozoic	---	Silica	Replacement	Possibly contemporaneously with the deposition of the Limestone	VAN TUYL, F.M., 1918
Plants	---	---	---	Silica, Sulphides	Replacement and filling	---	ST. JOHN, R.N., 1927
Plants	Dolomite	Upper Triassic	Shallow waters	Silica	Filling	---	BARKSDALE, J.D., 1939
Termite pellets	---	Fernando Formation (Pliocene)	---	Silica	Replacement	---	ROGERS, A.F., 1938
Corals	Phyllite with sericite and minor quartz, chlorite, ilmenite	Waits River Formation (Ordovician)	---	Silica	Replacement	During metamorphism	CADY, W.M., 1950
Plants	---	---	---	Silica	Replacement and filling	Growth of the crystals before silicification of the wood	This Thesis, 1959

PHOSPHATES

FOSSIL	SEDIMENT		ENVIRONMENT	MINERAL	MODE OF MINERALIZATION	TIME OF MINERALIZATION	AUTHOR
	Lithology	Age					
Fecal Pellets	Brown Shales	Miocene	---	Phosphate	Replacement	Syngenetic	GALLIHER,E.W., 1931
Many organic remnants	Phosphorite	---	---	Calcium Phosphate	Replacement	In unconsolidated sediments	SMITH,R.W.,and WHITLATCH,G.I., 1940
Foraminifera	Phosphorite	---	Corrent-swept ocean bottom	Calcium Phosphate	Replacement and incrustation	In situ on the ocean floor	DIETZ,R.S.,et al., 1942
Coprolites	Mudstone and volcanic ash	Bridger Formation (Upper Miocene)	Swampy flood plane	Phosphate	Original mineral	---	BRADLEY,W.H., 1946
Many organic remnants	Cherty carbonate rocks,phosphorites,carbonaceous mudstone	Phosphoria Formation (Permian)	Corrent-swept ocean bottom	Calcium Phosphate	Replacement	While still on the bottom of the oceans	EMIGH,G.D., 1958

SULPHIDES

Plants	---	---	---	Sulphides	Replacement	Before carbonization of the wood	BUTLER,et al., 1920
Plants,Corals, Worms,Crinoids, Bryozoa,Brachiopods,Pelecypods etc.	Calcareous Shale rich in marcasite	Hamilton Group (Devonian)	---	Marcasite	Replacement	---	STEWART,G.A., 1927
Brachipods,Gastropods,Bryozoa, Plants	Black Shale over coal	Pennsylvanian	Shallow reducing waters	Pyrite	Replacement	Soon after the death of the organisms	MATHIAS,H.S., 1928

SULPHIDES (continued)

FOSSIL	SEDIMENT		ENVIRONMENT	MINERAL	MODE OF MINERALIZATION	TIME OF MINERALIZATION	AUTHOR
	Lithology	Age					
Pelecypods, Brachipods, Gastropods	Black Shale over coal	Pennsylvanian	Shallow reducing waters	Pyrite	Replacement	Right after the death of the organisms	TARR, W.A., 1928
Plants	---	---	---	Chalcocite	Replacement	Epigenetic	EMMONS, W.H., 1940
Plants in coal balls	Coal with associated marine Limestone	Pennsylvanian	Shallow stagnant waters	Pyrite, Calcite	Filling cells and Replacement	---	DARRAH, W.C., 1941
Plants in coal balls	Coal	---	Very shallow swampy waters	Pyrite, Marcasite, Calcite	Mineralized waters seeping through the swamp	---	ANDREWS, H.N., 1946
Brachiopods, Blastoids, Crinoids, Bryozoa, Gastropods, Pelecypods, Cephalopods, Pteropods, Trilobites, Ostracods, Plants	Soft argillaceous Shale	Ludlowville Formation (Devonian)	Stagnant waters with high content of H_2S and Fe	Marcasite	Whole or part replacement	Syngenetic	FISHER, D.W., 1951
Endocrania of Fishes	Shales	----	Shallow waters with high marine organic content	Galena, Sphalerite and other Sulphides	Replacement	Before advanced diagenesis	WESTOLL, P.H., 1955
Ammonites	Shales	Liassic	---	Sphalerite Galena	Filling of the gas chambers	During consolidation of the sediments	WESTOLL, P.H., 1955
Pelecypods, Foraminifera, Gastropods, Ostracods, in coal balls	Coal	Pennsylvanian	Shallow stagnant waters	Pyrite, Silica, Calcite	---	---	MAMAY, S.H., YOCHELSON, E.L., 1953

SULPHIDES (continued)

FOSSIL	SEDIMENT		ENVIRONMENT	MINERAL	MODE OF MINERALIZATION	TIME OF MINERALIZATION	AUTHOR
	Lithology	Age					
Plants	Sandstone partially of volcanic origin	Mitu Formation (Permo-Carboniferous)	Reducing environment for C action	Chalcocite, Bornite, Covellite	Filling	Syngenetic submarine hydrothermal origin	AMSTUTZ,G.C., 1956
Plants	Sandstone	Chuila Formation(Triassic)	Reducing environment resulting from the production of H_2S and H_2SO_3 in the decomposition of the organic debris	Pyrite, Galena	Replacement	Epigenetic after deformation	GROSS,E.B., 1956
Marginifera muricatina	Limestone and Shale	Lagonda Formation(Pennsylvanian)	Swamp	Pyrite	---	---	HOWE,W.B., 1956
Plants	Coarse grained Sandstone with abundant silicified logs and carbonized wood fragments	Shinarump Formation (Late Triassic Age)	---	Pyrite, Uranium Minerals	Replacement	Late Cretaceous or early Tertiary thus epigenetic	FINNELL,T.L., 1957
Trigonocarpus Fruit	Coal	Pennsylvanian	---	Galena, Sphalerite, Pyrite	Replacement	---	KELLER,W.D., 1957
Plants	Shaly and limy Sandstone with blue and green Cu staining	Ardness Formation(Upper Mississippian	Reducing environment created by decaying of organic matter	Sulphides	Replacement by introduction of Sulphides	---	WIESE,R.G., 1957
Pelecypods, Brachiopods	Limestone	Reabourn Shale (Lower Carboniferous)	Shallow agitated waters	Pyrite	Replacement	Early diagenetic origin	GREENSMITH,J.T., 1958

SULPHIDES (continued)

FOSSIL	SEDIMENT		ENVIRONMENT	MINERAL	MODE OF MINERALIZATION	TIME OF MINERALIZATION	AUTHOR
	Lithology	Age					
Pyritosphaera barbarica, *Pyritella polygonalis*	Limestone and Shale	Oil Shale Group (Lower Carboniferous)	Bottom water in euxinic condition	Pyrite	H_2S produced by the two living organisms and precipitated on them and around them	During lifetime of the organisms	LOVE, L.G., 1958
Plants	---	---	---	Pyrite, Chalcopyrite, Sphalerite, Arsenopyrite	Replacement	Before decaying of the wood	This thesis, 1959

VITA

Giovanna Reggiori Ligasacchi was born in Milano, Italy, on March 28, 1934.

She attended Elementary School in Locate Varesino, Junior High School in Saronno, Senior High School in Milano, from 1939 to 1952.

She entered the University of Milano in 1952 and obtained the degree of Dottore in Scienze Geologiche in November 1956.

She came to the United States September 1957 and enrolled in the Missouri School of Mines and Metallurgy, Geology Department as a graduate student at that time.