ASPECTS OF BIOMINERALIZATION

Edited by
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FOREWORD

This book is the second collection of the latest achievements of a key research project, "The study of biomineralization and its geological background", established and supported by the National Natural Science Foundation of China and Chinese Academy of Sciences during 1992 to 1996. The first book, "Biogenic biomineralization," has already been published in Chinese in 1993 by China Ocean Press. In that book, our achievements on the research project during the first working period (1992-1993)are collected.

The main achievements of the first working period include a great number of first hand data and direct proofs which prove that the biomineralization occurs commonly and plays very important role in the forming processes of many sedimentary and stratabound ore deposits. After one year further work, i.e. the second working period (1994-1995), we have already attained more successful developments not only on studying biomineralization, but also on understanding of types, processes, mechanisms and geological backgrounds of ore formations made by organisms and organic matter. All those achievements indicate that the study on ore forming processes by organisms and organic matter enters into a new period.

As we pointed out two years ago, "the biomineralization is a kind of ore-forming process by organisms and their byproducts--organic matter". The research on biomineralization mainly includes the studies of biochemical mechanism and depositional condition of ore formations and of ore-forming element behavior such as mobile or stable, concentrated or diluted during different ore-forming stages, i.e. leaching, transporting, depositing, and enriching. Studies on absorption and enrichment of ore forming elements by organisms and on goechemical environment influenced by decomposition and thermal degradation of organisms and organic matter, and on sedimentary environment and geological background, in which ore-forming processes by organisms and organic mater can proceed, are well developed. During the past years, we have made many efforts on these aspects.

From 1994 to 1995, we paid great attention and put many funds on the systematical researches of several economically significant phosphorite, manganese, iron, lead and zinc, barite, gold and natron deposits, and on the modelling experiments of transporting and enriching ore-forming elements, such as Mn and Cu by algae, and Pb and Zn by organic matter. Based on many new results of our research, we have gotten better understanding of type, function, process, and mechanism of ore formation made by organisms and organic matter, and of controlling factors of sedimentary environment and geological background related to biomineralization as well. All these achievements provide theoretical base for confirming and classifying ore-forming districts, belts, and provinces to explore sedimentary and stratabound ore deposits. In addition, it is also pointed out that the study on roles of organisms and organic matter in surficial geological processes is very significant.

Based on the studies on phosphorite, manganese, iron, lead and zinc, barite and natron deposits and on related modelling experiments, achieved during the second period of the research project, this book collects our latest research results and reflects many study aspects of the research project, including ore-forming related petrographic facies, sedimentary formations, and paleoclimates; types and associations of ore-forming organisms and organic matter, markers of biomineralization revealed by geological, petrological, mineralogical, geochemical, biogeochemical, trace elements, rare earth elements, and stable isotope evidences. Our wish to publish this book is to try to exchange our research results with geologists and to carry out this research project continuously and more deeply in China.

Academician Ye Lianjun led writing and editing work of this book. An editing group, participated by Professors Chen Qiying, Li Renwei, Wang Dongan, Li Juying, and Wang Zhongcheng, organized, edited and corrected each part. Wang Zhongcheng, as the general editor, completed the technical editing work.

The research project has been supported by the National Natural Science Foundation and the Chinese Academy of Sciences, and by professionals from Universities, Colleges, and Institutes, who attend the project. Many thanks should go to Seismological Press, and to coworkers of drawing group of the Institute of Geology, Chinese Academy of Sciences, their great efforts made publication of this book to be possible.

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Contents

THE NEW ASPECTS OF BIOMINERALIZATION

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Biomineralization is a frontier subject of modern sedimentology. The idea was set up way back to the early 30's of this century. But since then, it wasn't able to attract due attention in the geological cycle. It's booming up, seems no earlier than the middle years of the 80's.

It is one of the three motive processes that related to sedimentary mineralization viz. the biogenic process, the chemical process and the physical dynamic process. When we speak of metallogenic process, we can never overlook the fact process is not just simply an instantaneous reaction; it needs time, it always runs through a definite schedule, that governed by different factors in different aspects. At the same time, we need to make clear what sedimentary environment and what geological background had been acted with it. Therefore, eventually, in the study of biomineralization, we must always hit two targets at the same time, viz., the "process" and "procedure", and the "paleoenvironment" and "geologic background". This is to say, that the real meaning and complete definition of biomineralization must be comprise two federal kernel parts, the "process" and the "background environment". In this sense , we have to understand , that the role of distribution of economic mineral deposits is basically in comply with the orientation of sedimentary facies which enable us possible to predict or locate the temporal and spacial orientation of mineral deposits. This is what I mean by new aspects of biomineralization. In the following paragraphs, I will set up several of the main points, that our working group had accomplished:

(1) The kernel crux set up for the students of biomineralization is firstly to verify whether organisms were really played on the genesis of sedimentary mineralization. Without the clearing up of this point, there is no ground for further discussion. It was with this viewpoint in mind, our working group were spent our main effort upon this during the last three years. As shown in this memoir, our colleagues have been worked from different angles, such as: on-site sedimentological examination, mineralogical and petrological identification, electron-probe analysis, geochemical and organic-geochemical analysis, isotopic geochemical analysis, palaeontological study, and sequence-stratigraphical investigation, mineralization assimilation test, designed after the actual regime of some typical example of mineral deposits. Based upon the collective results of these different disciplinary works as shown in papers of this memoir, we come to realize that organisms are surely able to participate in the formation of mineral deposits.

Planktonic and neptonic organism, during their life time could through photosynthesis metabolism absorb or adsorb mineral forming material on to their hardparts or as nutriments deposited in their soft body. Organic material when deposited and buried under the sea will suffer diagenetic changes such like degradation, fermentation, and heat differentiation; and thus disrupting the local chemical equilibrium, through the changing of Eh and pH, emanation of HCO_3^-, $CO_2^=$, NH_3^+, H_2S etc., microbial oxidation or reduction, and changing of the pore water concentration, and thus resulting an ability of extraction, transportation and precipitation of different ore-forming elements, through the action of water rock reaction.

The final products of biomineralization of the different diagenetic zones would be different from each other, and possesses different sequences of their own.

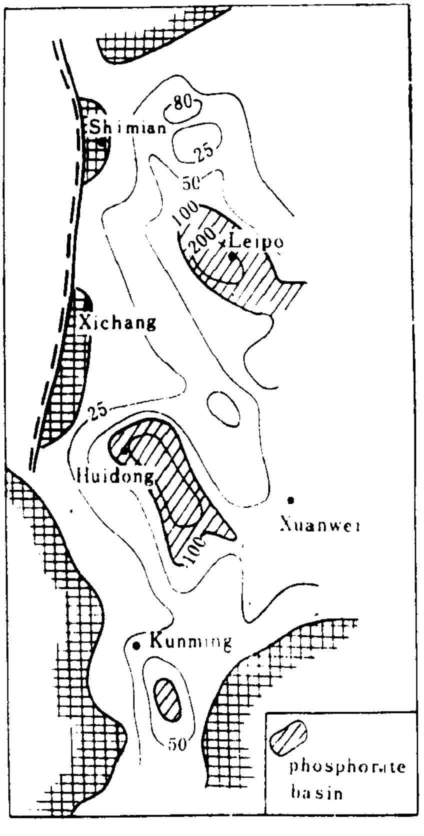


Fig.1 Isopach map of phosphorite-bearing series of Lower Cambrian from Sichuan and Yunnan

(2) The going on of biomineralization processes rely on the inducing effect of relevant sedimentary environment and geological background. This can be viewed in the following two aspects, viz.: (a) The materialistic background. The prosperous growth

of biota rely strictly on the presence of flourish nutrient substances, such as the near shore deeps of estuary areas (Fig.1) and especially the hinge-belt where up-welling current were used to occur (Fig.2, Fig.3).

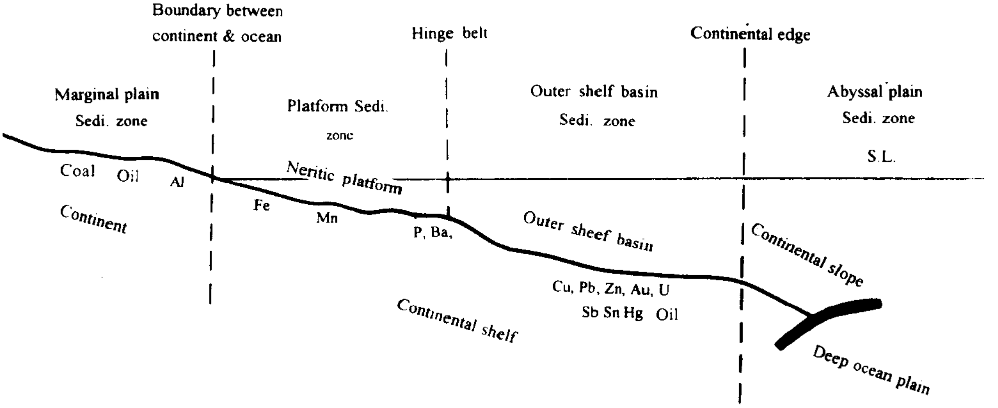


Fig.2 A sketch of continental shelf biomineralization realms

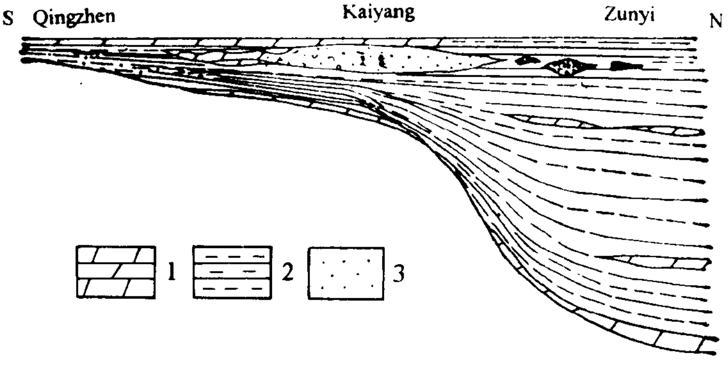


Fig.3 Paleogeographical distribution of the phosphorite deposits in Guizhou Province

1. Dolomite; 2. Black shale; 3. Phosphorite

(b) The environmental and conservational background. The thriving of ore-forming organisms, such as primitive algae, requires not only the prosperity of nutriment, but also a quite steady hydrodynamical regime, rather stable tectonic background, and also desirably a somewhat deep water trapping pool (Figs.1, 3).

(3) Genetic classification and localization of biomineralization versus dynamic sedimentary differentiation:

Sedimentary differentiation is primarily induced from the play of epeiro-eustatic movement, and the distribution of biomineralization zones follows always some of the desirable sedimentary facies or realms, because organisms always clustering around territories where nutrients are booming. The best of these kinds of sedimentary zones belong either to the near-shore estuary deeps (Fig.1) or the near continentalward margin of the outer shelf basin (Figs. 2, 3). These zones coincide strictly with the actual pattern of distribution of most of the industrial mineral deposits of the territory we studied.

Ore-bearing series of mineral deposits ascribed above are predominantly a continuous sequence rich in organic, laminated, fine clastic clayey or silty shales, and overlying no far by a thick carbonate formation.

The ore-bed within the ore-bearing series can be differentiated into two genetic categories, viz., the black argillaceous, organic carbon rich, thin bedded or concretionary ones, and the lighter colored poor in organism carbon and deficient in argillaceous impurities thick bedded ones. We have tried to verify, through both of field evidences and organic geochemical analyses; and the results show that both of these two kinds of ore-beds were all resulted during an eventual episode when the depth of deposition were suffered an abrupt shallowing upward movement, either epeirogenic or eustatic; thus inducing their higher $CO_3^{=}$ or HCO_3^{-} concentrations, and eventually gave rise to the precipitation of carbonate ore minerals. And if this is really the case, then, those of the thin bedded or concretionary ores were simply formed in-situ within its host-sediments, whereas those of the thick bedded ones were formed possibly through the enrichment by capillary penetration of ore rich pore fluid to a neighboring more permeable layer, or even directly added to the overlying sea-bottom water layer during the early stage of diagenesis before their complete lithification. So there are two kinds of biogenic mineral deposits formed during the diagenesis stages, viz., the thick bedded ones, which may be called the capillary invasion type, and the thin-bedded ones, which may be called the autochthonous type. Besides these two types we can still add the strata-bound type which were formed during the later episode of structural-igneous activity.

(4) The role of historical evolution and spacial and temporal orientation of biomineralization. It need not to say how important is to know the process and canon of metallogenic procedure in the prediction of mineral deposits. The purpose of this paragraph is to strengthen the reality of biomineralization, and to find a way of working through a historical view, chiefly follow the line of thinking of sequence stratigraphy and sequence of sedimentary of association. This is surely a rather com-

plex tough job, and obviously short of space to set up any complete narration here within a short space. Therefore, what I could do here will be only a short account. being only to express its importance.

Regarding the spacial and temporal location or orientation of biomineralization for the prediction of sedimentary mineral deposits, it could be set-up some of the basic points as follows:

① Belt of biomineralization, as prescribed above. are almost always coincide with the sedimentary facies or realm belts of dynamic sedimentary differentiation (Figs 2, 3). Among them , the most important ones, are the reef zone and the bathyal black shale deeps that lying beside the hinge belt of the inner continental shelf (Figs. 2. 3) The other desirable belt that worth to mention is the marginal estuary deep oceanic lows of indented coastal regions (Fig. 1).

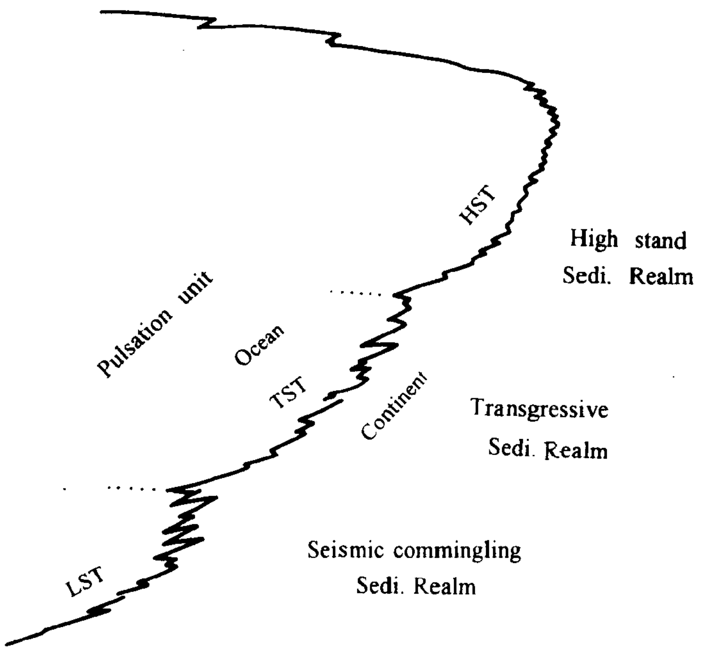


Fig. 4 A sketch showing marine transgression and regression

②Biomineralization is intimately related to certain kind of biocommunities. so that biomineralization is related historically to the stages of organic flourishing episode of different geological periods. Organisms is originated within the hydrosphere since Early Archean. Before the Caladonian movement there were only marine organisms , and continental life appeared only after the Early Devonian. In the

Mesozoic-Cenozoic time there are mostly continental deposits, marine lifes can only find sporadically in some of the border province. Biomineralization between marine and continental environments are quite different indeed both in genetic types and mineral associations.

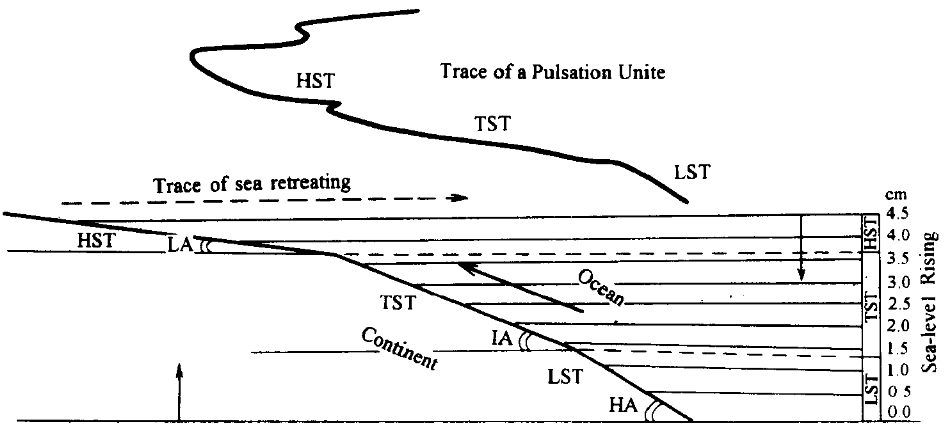


Fig.5 A conceptional model of the dynamic background of pulsation unit
LA: Low angle; IA: Intermediate angle; HA: High angle

③ Within the sequence of the "pulsation unit" of Grabau (Figs. 4, 5, 6), the lower part is the seismic commingling shaly deposit corresponding to the LST of Vail's classification; and it is customarily ore bearing. Above this is generally a huge sequence of carbonate rocks which apparently to the TST and HST members of Vail"s classification. Within these carbonate formations there are not infrequently evaporate salt deposit etc. Grabau's pulsation unit is mostly corresponding to a stratigraphic "system" as he taught us in 1934 in University of Beijing.

As to depict a complete picture of all the ore horizons of the whole span of geological history it is better to run a scrutiny through a complete stratigraphical column from Mesozoic-Cenozoic down to the Archean. This can be shown by the following two figures (Figs. 8, 9). For the Figure 8, the main point is to watch the horizons of the blackish shaly ore bearing layers that lying at the lower part of "system" packages, and their boundary character of the different sedimentary association sequences. For the Figure 9, the importance is to look at the two transgression "climax" and the transgression "low" between them. This "low" is particular significant, because it marks just the time of the first appearance of land organisms, so it marks just a revolution divide of the history of organic lives. Therefore, it is very important to the research of biomineralization. As mentioned above mineralization formed by marine organisms are very much different to those of by continental organisms.

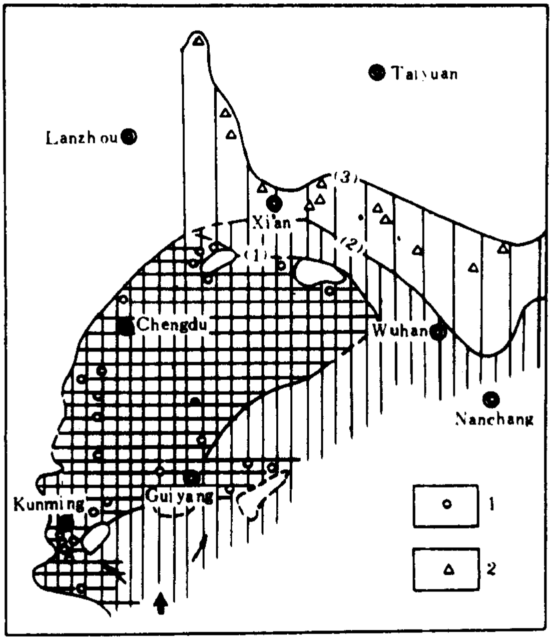


Fig. 6 A sketch of the transgression front of the Early Cambrian of eastern China

(1) Transgression front of the Meishucun stage; (2) Transgression front of the Xinji Stage;

(3) Transgression front during Qiongzhusi Epoch

1. phosphorite occurrence of Meishucun Epoch; 2. phosphorite occurrence of Xinji Epoch

(5) Other than those just described above, climatic factors is also of paramount importance to organic lives, especially to those of continental ones during the Mesozoic and Cenozoic times. The climate at that time are predominantly hot and dry and evaporate deposits including potash salt as well as oil and gas deposits are quite numerous. The same situation seems also had been occurred in some of the Lower Paleozoic times, as shown by some of lab. records. But they don't seem so severe.

From the geological facts described above I am simply intend to present an idea, that the prediction of ore deposit of any kind is no question workable, because there are already so many substancial vestiges right ahead us. The duty of geologists is basically to understand the Earth, to find ways how to use the earth economic mineral deposits and the energy deposits, and how to keep or predict a good living environment. All these, mean progress and efficiency.

Age	Thickness* (m)	Bed thickness	Lithology	Sedi. Asoc.		Sedi. Facies
Q_4			Alluvium		Continental Sedi. Association	Continental Facies
Q_{1-3}	58		Cg.tillite			
E	160		Red ss.	Com. Sedi.		
K	600		Sandy sh., Red bed	Com Sedi.		
J_1	350		Massive ss., sh.			
T_3	400		Grey & blackish ss. & sh	Int. bed.		
T_2	610		Arg. ls. with greenish sh	Com. Sedi.	Epeirogenic Positive Sedi. Association	Commingling Facies
T_1	675		Grey ls. with ss. & sh.	Int. bed.		
P_2	17		Grey chert & arg. ss., Calc. mudstone	Int. bed		
	60		Blackish massive ls. with chert			
	500		Chiefly marine with continental ss. sh. ls. with black sh. & Fe ss.	Int. bed.		
P_1	233		Grey & black massive ls.			
	25		Coal series with one coal seam	Int bed.		
C_3	25		Grey thick bedded ls.			
C_2	15		Thick bedded ls. Feathring-out towards north			
C_1	910		Intermingling marine and continental facies, ss. sh. ls. int. with three coalbeds	Int. Com.		
D_3	240		Ls. with sh.	Int.		
	150		Black ls. with sh.	Int.		
D_2	590		Ls. with sh.	Int.		
S_{1+2+3}	450		ss. sh. ls. ss. sh. sh.	Int Com		
O_2	170		Ls. Calcareous ss. sh.	Com.		
O	396		Ss. calcareous sh. ls. in middle part	Com.		
ϵ_{3+2}	750		Thick-bedded Ps Cab		Eustatic Negative Sedi. Asoc	Marine Facies
ϵ_1	600		Upper part: carbonate; Middle: sh.; Lower: carbon-silicon-mudstone			
Z_2	750		Carbonate Dark purple ss.			

* Not in Scale

Fig. 7 Columnar section of southeastern Guizhou

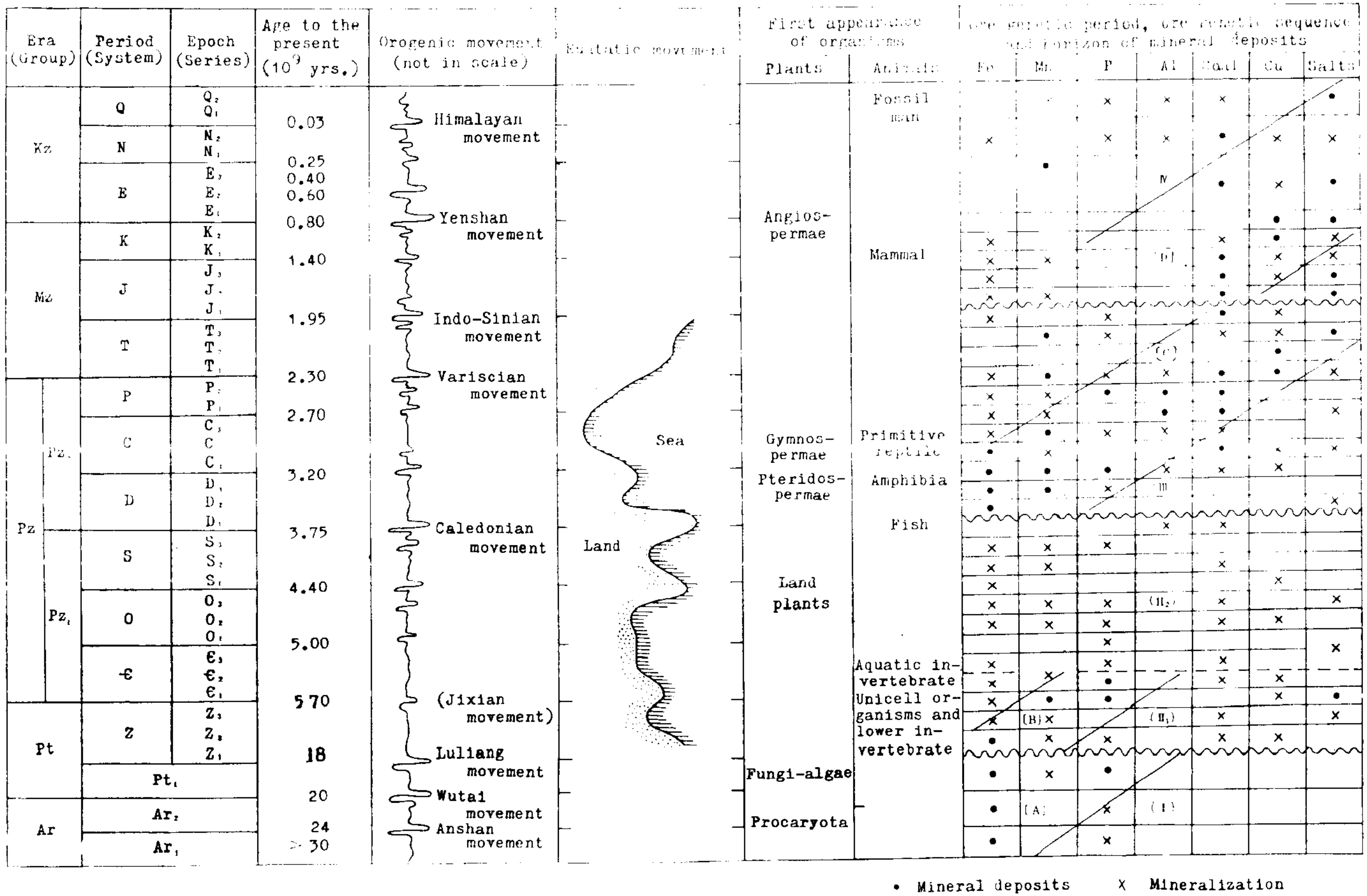
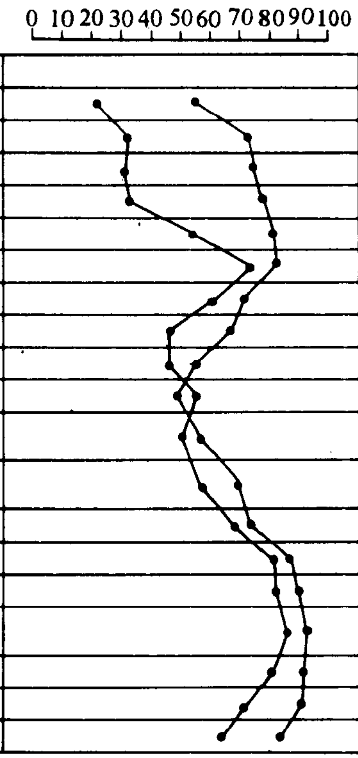


Fig.8 The ore-genetic epoch of the Chinese sedimentary deposits (1976)



Age	(I)	(II)
T_3	21.60	54.00
T_2	32.48	72.60
T_1	30.66	75.97
P_2	32.97	77.37
P_1	53.98	81.23
C_2	73.93	82.33
C_1	61.10	71.33
D_3	46.16	66.67
D_2	46.58	55.07
D_1	55.78	48.73
S_{2+3}	49.39	56.27
S_{1+2}	57.85	69.47
O_3	67.10	73.10
O_2	81.82	86.67
O_1	82.15	88.47
ϵ_{2+3}	84.40	90.80
ϵ_1	81.59	90.60
Z_2	72.00	90.40
Z_1	62.31	83.17

Fig. 9 A eustatic curve through Early Sinian to Late Triassic periods in China and Yangtze Platform (after the Paleogeographic Maps depicted by H.Z. Wang et al)

I . Marine/continental area proportion in China; II . Marine/continental area proportion in the Yangtze Platform

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MICROBIAL CONSTRAINTS ON THE FORMATION OF PHOSPHORITES

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In order to further understand the functions of bacterial and algae microorganisms in the forming process of phosphorite deposits, we recently focus our research work on the phosphorus stromatolite, microfossils, stable isotope, and element geochemistry of the Late Sinian phosphorite deposits in central Guizhou Province. Based on the data obtained, phosphorite concentration patterns and microorganisms which actively involved in phosphorus mineralization are dealt with in this paper.

1 Three models of phosphorus concentration

1.1 P_2O_5 concentrated in biophosphorite

In China, statistical results from a large number of analysis data of phosphorite deposits indicate that the most economically significant phosphorite deposits, having good quality ores, are made up of the bio-phosphorite, containing a great deal of bacteria and algae fossils (Chen Qiying, 1987). This fact can be proved by statistical study on phosphorite formations with different ages (Table 1), on phosphorite mineralization in different areas, and on ore beds within a single phosphorite deposit (Table 2). However, the genesis of phosphorites can be ascribed to the participation of bacterial and algae during the process of the phosphorite mineralization.

Table 1 P_2O_5 Contents in the major type phosphorites of the Sinian and Cambrian

Age	Biophosphorite	Phospholutite	Recrystalline phosphorite	Phospharenite
Cambrian	37.21 (1)	33.38(6)	32.88(1)	28.23(13)
Sinian	35.23(10)	30.17(5)	33.48(5)	29.74(13)

Table 2 Comparitive P_2O_5(%) contents among major types phosphrites from Central Guizhou and Jingxiang

Site	Stromatolitic phosphorite	Recrystalline phosphorite	Phospholutite	Phospharenite
Central Guizhou	35.41(7)		34.41(2)	30.61(5)
Jingxiang	24.11～37.50	28.22～38.00[1)]	26.00～33.00[1)]	15.00～19.00[1)]
Mean	34.43	33.00	29.50	17.00

1) Based on Li Yinhou 1976.

1.2 P_2O_5 concentrated in the stromatolitic pillars of bio-phosphorite

The bio-phosphorites in central Guizhou Province are mainly composed of algae stromatolites. The stromatolite column, resulted from rapid growth of bacteria and algae, concentrated higher organic carbon in the columns than that in intercolumn fillings. Organic carbon content in the column can be two times as high as in the intercolumn, correspondingly, P_2O_5(1% ~ 2%) content is higher than that in the intercolumn. The variation of P_2O_5 content between stromatolite columns and filling material of intercolumns is commonly found in dolomitic stromatolite phosphorites in Jingxiang, Hubei Province, in Shimen, Hunan Province, and other phosphorite deposits (Table 3, 4). In fact, this regularity is not only featured by variation of P_2O_5 content, but also by variations of mineral composition and distribution between stromatolite column and filling material (Table 5).

Table 3 Comparitive organic-carbon (%) between stromatolitic column and intercolumn

Sample	Stromatolitic column	Intercolumn
H156	0.10	0.04
H73	0.07	0.05
H58-1	0.05	0.04
H124	0.03	0.02
K76	0.07	0.06
mean	0.064	0.042

Table 4 Comparitive P_2O_5(%) contents between stromatolitic columuns and filling

Stromatolitic column	Intercolumn	Location
38.68(8)	35.56(8)	Kaiyang
37.13(2)	36.65(2)	Xifeng
31.67(1)	27.60(1)	Weng'an
25.70(1)	12.06(1)	Shimen
32.35(3)	1.35(3)	Jingxiang

Note: Brackets reffering to the number of samples.

Table 5 Mineral components of phosphatic stromatolites in central Guizhou

Mineral component	Column		Intercolumn	
Ore mineral (granular apatite)	francolite calcisilt	93% ~95%	francolite oncolite phosphatic pellet phosphaticinterclast	88% ~90%
Gangue mineral	clay mineral organic matter pyrite (perlimonite) quartz silt micritic dolomite	5% ~7%	clay mineral pyrite (perlimonite) quartz silt dolomite	10% ~12%