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Review

Geochemical Characteristics of Trace Elements and Mineralization Model of the Ediacaran-Early Cambrian Phosphorites, South China

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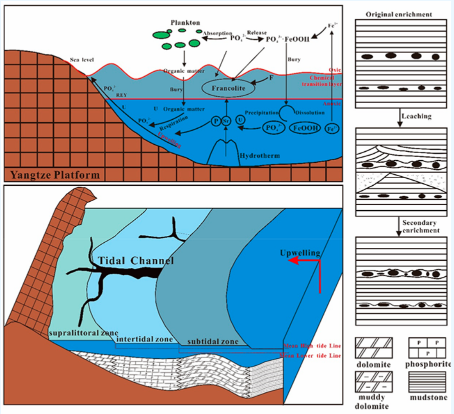
ABSTRACT: As a nonrenewable resource, phosphate rock is an important support for the development and survival of the national economy. The regional distribution and output of phosphate rock in China are extremely uneven, and the amount of high-quality ore resources is relatively poor, which seriously restricts the development and utilization of phosphate rock resources in China. This paper briefly summarizes the distribution characteristics of phosphate rock resources and summarizes the characteristics and research progress of Ediacaran-early Cambrian phosphorus mineralization types, geological characteristics, and deposit genesis of the Yangtze platform in South China. The Ediacaran-early Cambrian sedimentary phosphorite deposits in China are mainly distributed in Yunnan, Guizhou, Hubei, Sichuan and Hunan provinces of the Yangtze platform, in which the early Cambrian phosphate deposits are also rich in rare earth elements, associated with uranium, nickel, molybdenum, vanadium, and other beneficial metal elements. The increase of atmospheric oxygen content at the Ediacaran-Cambrian boundary may have promoted the extensive oxygenation of the late Neoproterozoic oceans, so the Ediacaran-early Cambrian oceans generally showed a reductive environment, and there may be dynamic chemical stratification of the oxidation zone-sulfide zone-iron zone. Up to the early Cambrian, the redox stratified structure of Precambrian seawater may still be inherited, showing that the surface water is an oxidizing environment, changing to a reduction environment, and even wedge-shaped sulfide water is developed at the bottom of the deep basin. The main phosphorus sources are deep phosphorus-rich seawater, continental weathering, and deep hydrothermal activity of Ediacaran-early Cambrian marine sedimentary phosphorite deposits in South China. The genetic mechanisms of phosphorite deposits in the Yangtze platform in South China are mainly biogenic, upwelling phosphorus-forming theory, mechanical mineralization, and syn-sedimentary hot water mixed genesis. In the future, it is still necessary to further explore the internal relationship between phosphorus deposits and major geological events, the in situ analysis of microstructure of phosphate rock ores, and the genetic mechanism of phosphate deposits and the reconstruction of paleo-marine environment.



The main rock types are clastic phosphorite, dolomitic phosphorite, phosphorous dolomite, biological phosphorite, etc.
Phosphorus mineralization goes through three stages:original enrichment-leaching-secondary enrichment.

1. INTRODUCTION

The transitional period of the Ediacaran-early Cambrian witnessed dramatic changes in the marine environment, significant negative carbon isotope excursion of seawater and radiation evolution of metazoan in the early Cambrian,[1−8] leaving abundant geological evidence in several sedimentary sequences. At the Precambrian-Cambrian boundary, it is accompanied by frequent dynamic changes in marine redox conditions,[9−11] the rapid fluctuation of $\delta^{13}C_{carb}$, long-term positive $\delta^{34}S_{sulfate}$ excursion and instantaneous anomaly of $\delta^{95/97}$ Mo all record the frequent changes of marine environment,[12,13] in response to the change of atmospheric-ocean oxygenation after the Snowball Earth event.[14] Many studies on the characteristics of mercury isotopes, molybdenum isotopes and rare earth elements show that there is obvious chemical stratification in the marine water from Ediacaran to early Cambrian, and the increase of atmospheric oxygen content drives the regional oxidation of the shallow sea.[13,15−17] During this period, a large-scale marine phosphorite deposited around the world, including two important metallogenic periods, namely, the Ediacaran (635−541Ma) and the early Cambrian (541−529Ma), which is widely distributed in Asia, Australia, Africa, and other regions.[18] During this period, phosphate mineralization is closely related to the global carbon cycle, two Neoproterozoic oxidation events, and biological evolution, so the geochemical characteristics and paleo-marine environment of marine phosphorites in this period are ideal objects for in-depth analysis of the original

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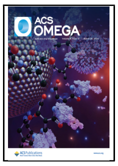

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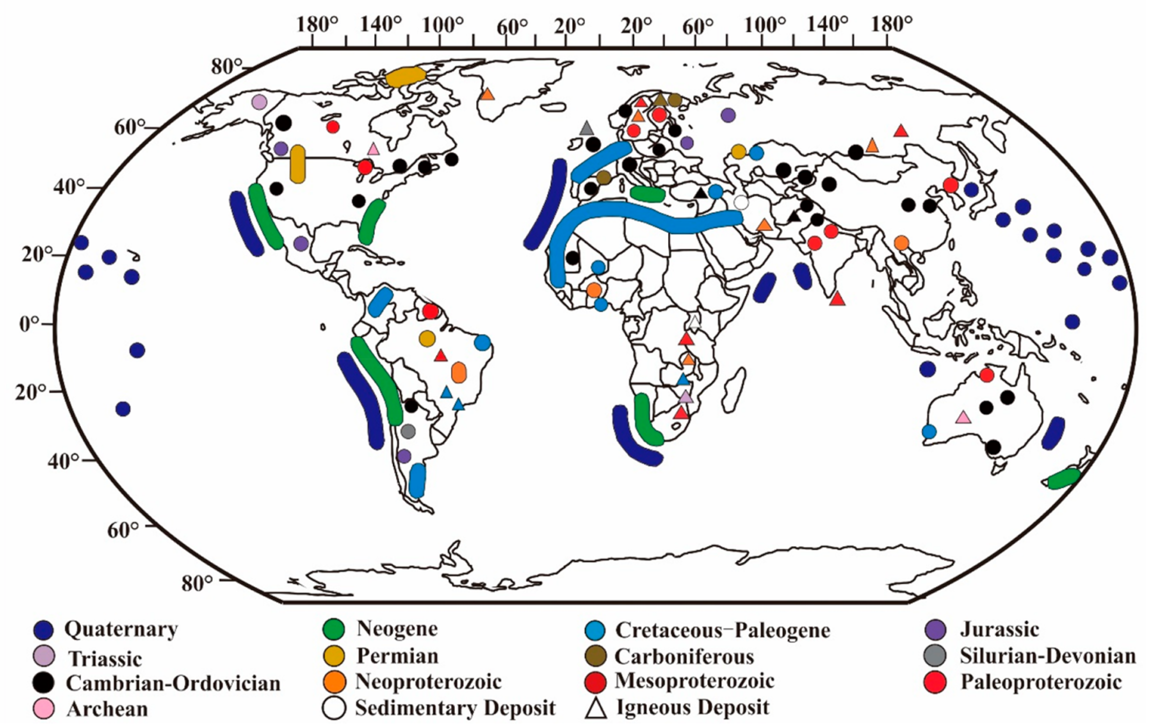

Figure 1. Global distribution map of phosphate resources (modified from Pufahl and Groat[25]).

geochemical information on seawater and the influence of paleo-marine environment on phosphorus mineralization.

The Ediacaran-early Cambrian phosphorus mineralization in China mainly developed in the Yangtze platform and the northern margin of the northwestern Tarim block, especially the Yangtze platform in south China, which is widely distributed in Yunnan, Guizhou, Hubei etc. In the past, many scholars have carried out detailed studies on the geological characteristics, process mineralogy, radioisotope chronology, enrichment mechanism, and mineralization of phosphorite deposits on the Yangtze platform.[19−24] This paper summarizes the geological and geochemical characteristics of the Ediacaran-early Cambrian phosphorus-rich sedimentary series in South China, as well as the evolution characteristics of the paleo-marine environment in South China during the Ediacaran-early Cambrian transition period.

2. DISTRIBUTION OF PHOSPHATE ROCK RESOURCES IN THE WORLD AND CHINA

The world is rich in phosphate rock resources, but the geographical distribution is extremely uneven, mainly concentrated in Morocco/Western Sahara, China, Algeria, Syria, Jordan, Egypt, the United States, and Australia (Figure 1; Table 1). The total amount of phosphate resources in the world is about 300,000Mt, of which sedimentary phosphate rock deposits account for more than 95% of the total resources, which is the main industrial phosphate ore type.[25] According to the geological conditions and genetic mechanism of the formation of phosphorus deposits, phosphorus deposits are divided into two types: primary phosphorus deposits and secondary phosphorus deposits. The primary phosphorus deposits can be divided into three types: endogenous magmatic phosphate deposits, exogenous sedimentary phosphate deposits, and metamorphic phosphorus deposits, while the secondary phosphorus deposits are mainly bird manure accumulation, weathering-leaching residue, and cave accumulation type. The global sedimentary phosphorite deposits are mainly distributed in the United States, China, the Middle East, and North Africa.[25] The main metallogenic periods include late Proterozoic-Cambrian, the phosphate deposits are mainly distributed in Central and South Asia; Permian phosphorus is deposited in North America; Jurassic-early Cretaceous phosphorus is deposited in Eastern Europe; late Cretaceous-Eocene phosphorus deposit is mainly found in North Africa, the Middle East and Central Asia; Cenozoic Miocene phosphorus formation period is in the southeastern United States.[26]

Table 1. Global Distribution of Phosphate Resources[25]

Country	Resources/Mt	Country	Resources/Mt
Sedimentary deposits			
Morocco/W. Sahara	50,000	Tunisia	100
China	3,700	India	65
Senegal	2,200	Senegal	50
Syria	1,800	Togo	30
Jordan	1,300	Mexico	30
Egypt	1,250	Vietnam	30
United States	1,100	Total	65,661
Australia	1,030		
Saudi Arabia	956	Igneous deposits	
Peru	820	Brazil	315
Iraq	430	Russia	1,300
Other Countries	380	South Africa	1,500
Kazakhstan	260	Total	3,115
Israel	130		
		All sources of the world	68,776

Table 2. Distribution of Phosphate Deposits in China

Classification	Types	Distribution	P_2O_5/%	Associated minerals	References
Igneous deposits					
ultramafic-alkalic rock	Fanshan	Northern margin of North China Block	3%∼15%	V, Ti, REE	27
ultramafic rock-carbonatite	Qieganbulake	Northern margin of North China Block, Tarim Block	2%∼10%	Nb, Th, REE	27
alkalic rock		Liaoning, Shanxi	2%∼10%	REE	27
carbonatite	Baiyan Obo	Inner Mongolia, Xinjiang	4%∼10%	Nb, Th, REE	27
ultramafic rock	Kawuliuke Tag	Northern margin of North China Block, Tarim Block	2%∼10%	V, Ti, Co	27
mafic rock	Maying	Northern margin of North China Block, Tarim Block	2%∼10%	V, Ti	27
pegmatite	Yousuopu	Hebei, Inner Mongolia	11%∼29%	REE	27
greenstone belt	Zhaobinggou	ancient continent nucleus of North China, Shandong	3%∼5%	Ti	27
	Wulanwusu	ancient continent nucleus of Liao-Ji	3%∼7%	Ti	27
Metamorphic deposits					
migmatite	Mahsan	Kiamusu Block	2%∼5%	C	27
sedimentary migmatite	Haizhou	Eastern margin of North China Block	12%∼16%	Mn, Ca	27
	Bulongtu	Northern margin of North China Block	5%∼7%	Fe, REE	27
	Luotun	Northern margin of North China Block	5%∼10%	Fe	27
Sedimentary deposits					
Sinian	Kaiyang	Southwestern margin of Yangtze Block	10%∼30%	I	29
	Jingxiang	Southern margin of Yangtze Block	19%∼25%	Ti, Cu, Pb	27
	Shimen	Southern margin of Yangtze Block	8%∼22%	C	27
	Xiangxi		17%∼19%	Ca, Mg	27
Cambrian	Kunyang	Western margin of Yangtze Block	26%∼30%	Ca, Mg	30
	Mabian	Western margin of Yangtze Block	23%∼31%	C, F	24
	Tiantaishan	Western margin of Yangtze Block	12%∼26%	U, Mn	27
	Xinhua	Southern margin of Yangtze Block	10%∼26%	REE	21
	Xinji	Eastern, northwestern margin of Yangtze Block	6%∼20%	Ca	27
	Pingtaishan	Northern margin of Tarim Block	3%∼25%	V	27
	Hanyuan	Eastern, northwestern margin of Yangtze Block	11%∼23%	K	27
	Dongxi	Zhejiang, Jiangxi	5%∼23%	Ni, Pt, V	27
	Damao	passive margin of Sanya	12%∼19%	Mn	27
Devonian	Shifang	foreland thrust belt of Longmenshan	20%∼28%	REE	27
Weathered deposits					
weathering - leaching accumulation	Huangjingping		18%∼28%	Th, U, REE	27
cave accumulation	Tiandeng		-		27
	Ceheng		11%∼33%		31
guano accumulation	Xisha islands	Hainan, south islands	-		

China is not only the main supplier of global phosphate production, but also a large agricultural country, with an average annual demand of 11−12 million tons of phosphate fertilizer. China is rich in phosphate rock resources and various deposit types, but its geographical distribution is uneven. Endogenous magmatic and metamorphic phosphorus deposits are mainly distributed in North China and Tarim blocks, while sedimentary phosphorite deposits are mainly distributed in Yunnan, Sichuan, Guizhou, Hubei, and Hunan provinces around the Yangtze block (Table 2).[27] The phosphogenic stage mainly includes the late Neoproterozoic Ediacaran, early Cambrian Meishucun stage, and early Devonian in China. Among them, the Ediacaran phosphorites are mainly distributed in central Guizhou, western Hunan and western Hubei. The early Cambrian phosphorites are distributed in three metallogenic belts of Sichuan-Yunnan, Sichuan-Shaanxi and central Guizhou, which is rich in rare earth elements and associated with metal elements such as uranium, nickel, molybdenum, and vanadium.[28]

3. PALEO-MARINE ENVIRONMENT OF THE EDIACARAN-EARLY CAMBRIAN IN SOUTH CHINA

The Ediacaran-early Cambrian transition period was an important period of early earth evolution, which recorded the radiation differentiation conditions and evolution of metazoans as well as the drastic changes of marine chemical conditions accompanied by the gradual oxidation of the global atmosphere at that time. Marine phosphorite mineralization is not only closely related to the biogeochemical cycle of phosphorus but also related to paleogeography, paleomarine environment, and biological evolution. The late Neoproterozoic Ediacaran-early Cambrian phosphorite deposits in China are mainly distributed in Guizhou, Hubei and Yunnan, and their geological characteristics are as follows:1) the distribution is controlled by paleogeographic environment; 2) the deposits are distributed along the direction of paleo-plate movement; 3) there are rich fossil records; 4) the deposit is of high grade and associated with REE (rare earth elements) mineralization.

The early Cambrian black rocks of the Yangtze platform in South China are widely distributed, forming a series of Barite, phosphorite and Ni−Mo polymetallic sulfide deposits and rich in biological fossils, which are favorable objects for studying

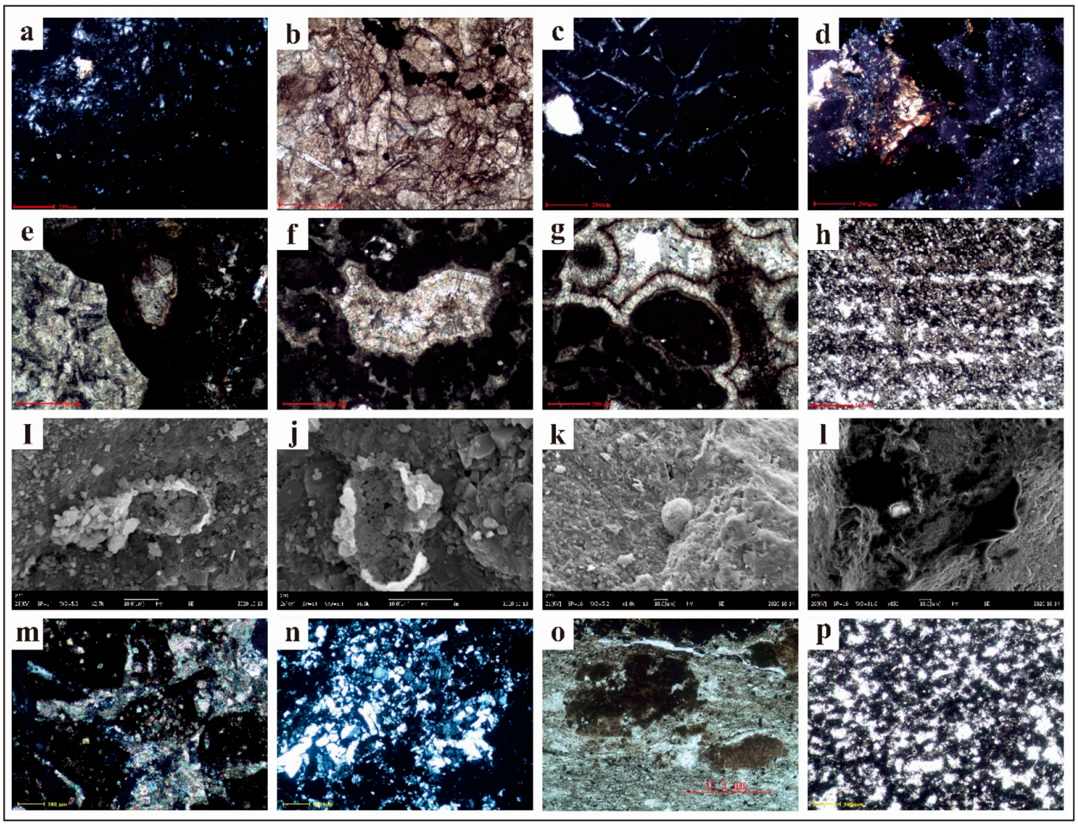

Figure 2. Late Ediacaran-early Cambrian phosphorus-rich sedimentary types in South China. a-phosphorite, Doushantuo Fm, 5 × 10(+); b-detrital phosphorus dolomite, Doushantuo Fm, 5 × 10(−); c-detrital phosphorite, Doushantuo Fm, 5 × 10(+); d-dolomitic phosphorite, Doushantuo Fm, 5 × 10(+); e−g stromatolite phosphorite, Dengying Fm, 5 × 10(+); h-layered phosphorus dolomite, Dengying Fm, 5 × 10(−); i−l-algal pellet of stromatolite phosphorite, Dengying Fm (scanning electron microscope); m-phosphorus dolomitic limestone, Niutitang Fm, 10 × 10(+); n-silicic phosphortie, Niutitang Fm, 10 × 10(+); o-phosphorus nodules, Niutitang Fm, 10 × 10(−); p-dolomitic phosphorite, Niutitang Fm, 10 × 10(−).

the changes of the marine environment in the geological history.[32,33] Previous studies have shown that early Cambrian organic-rich shales were deposited under anoxia caused by global transgression events and were affected by many factors: primary productivity, sedimentary rate, upwelling range and local hydrothermal activity,[34−36] and the gradual expansion process and influence of surface oxygen-containing seawater in the ocean under the background of the increase of oxygen content in the atmosphere during the early Cambrian. In the process of phosphorus enrichment, collophane precipitates directly from seawater or pore water, recording paleo-oceanic environmental information.[37] Therefore, the trace elements, rare earth elements, and isotopic composition characteristics of phosphate rocks can reflect the characteristics of paleo-marine environment, which provide favorable conditions for evaluating the changes of paleo-oceanic redox state, biological mineralization, and marine geochemical vertical changes.

In the early Ediacaran, the southeastern margin of the Yangtze platform can be divided into four sedimentary facies from NW-SE: nearshore tidal flat facies, shallow slope facies with barrier shoals, deep slope facies and deep basin facies.[38] The Ediacaran Doushantuo Formation is composed of clastic rocks, phosphorite rocks and carbonate rocks, integrated or pseudointegrated on the Nantuo Formation tillites, integrated with Dengying Formation carbonate rocks, and the sedimentary time is limited to 635−551Ma.[39,40] The Doushantuo Formation recorded the oxidation of the water column during the late Neoproterozoic Oxidation Event (NOE) and the accompanying phosphate mineralization event.[36,41] The phosphorus-rich deposit of the Dengying Formation was overlying the black shale of the early Cambrian Niutitang Formation, and the sedimentary time is limited to 551−542Ma.[42] The phosphorus deposits are mostly found in the semiconfined lagoon environment of the platform margin shoals.[43]

After the late Neoproterozoic ice age, the Yangtze Platform rapidly transformed from slope facies carbonate to shelf-slope facies deposits dominated by clastic rocks, phosphorite rocks and carbonate rocks,[44] which can be divided into southwest palaeo-continent and eastern coastal tidal flat-shallow slope-deep basin facies and formed early Cambrian phosphorus-rich deposits under the influence of transgression and upwelling. The early Cambrian phosphorite deposits in China were mainly deposited in shelf environment, and the typical sedimentary areas are mainly Gezhongwu Formation and Meishucun Formation, in which Gezhongwu Formation phosphorites in Zhijin, Guizhou Province is offshore deposit, and the Meishucun Formation in eastern Yunnan Province is coastal deposit with relatively shallow water,[37] both of which contain a large number of small shell fossils (SSF).

The Ediacaran Doushantuo Formation in South China are mainly distributed in central Guizhou, western Hubei and western Hunan, and phosphorite and carbonate are widely developed, mainly composed of dolomite phosphorite, clastic phosphorite, granular phosphorite, siliceous phosphorite and phosphate dolomite (Figure 2a−d), with an average P_2O_5

Table 3. Trace Element Characteristics of Ediacaran to Early Cambrian Phosphorite in South China[a]

Area	Strata	Number	Lithology	Co/μg/g	Ni/μg/g	Th/μg/g	U/μg/g	V/μg/g	Cr/μg/g	V/(V+Ni)	δU
Tuanshanpu[b]	Dengying Formation	Z-3	uranium-bearing phosphorite	9.46	375.40	0.96	320.60	1201.50	30.20	0.76	2.00
		Z-4	uanium-bearing phosphorite	8.90	285.60	1.45	330.10	1586.00	256.30	0.85	2.00
		Z-5	uanium-bearing phosphorite	33.28	346.20	1.24	658.40	948.50	18.50	0.73	2.00
Xinchong[c]		XC-2	phosphorite	3.55	103.00	6.85	3.47	1501.00	916.00	0.94	1.21
		XC-2-1	phosphorite	4.61	72.20	0.19	13.60	1368.00	503.00	0.95	1.99
		XC-8	phosphorite	10.30	79.80	0.18	11.70	1232.00	532.00	0.94	1.99
Xia'an[d]	Dengying Formation	WLX-2	sandy phosphorite	0.30	2.20	0.40	30.30	12.00	30.00	0.85	1.99
		WLX-3	phosphorus dolomite	0.30	2.10	0.40	7.40	15.00	13.00	0.88	1.96
		WLX-4	stromatolite phosphorite	0.20	0.50	<0.2	24.30	7.00	10.00	0.93	
		WLX-5	phosphorus dolomite	1.00	4.00	0.60	5.70	8.00	36.00	0.67	1.93
		WLX-6	stromatolite phosphorite	0.20	0.20	<0.2	13.20	6.00	8.00	0.97	
		WLX-7	phosphorus dolomite	0.70	1.60	0.80	6.10	11.00	19.00	0.87	1.92
		WLX-8	phosphorus dolomite	0.80	8.60	0.60	4.10	5.00	25.00	0.37	1.91
Weng'an[e]	Doushantuo Formation	YP-1-A	granular phosphorite	58.60	9.25	2.31	12.50	17.10	10.70	0.65	1.88
		YP-4-A	granular phosphorite	27.50	8.24	2.35	13.30	14.50	9.73	0.64	1.89
		YP-5-A	granular phosphorite	25.80	7.89	2.37	14.40	13.30	5.96	0.63	1.90
		YP-7-A	biotic phosphorite	15.80	12.80	0.53	4.10	13.50	14.00	0.51	1.92
		BD-1-A	biotic phosphorite	18.10	10.00	0.66	11.50	40.40	18.80	0.80	1.96
		BD-2-A	biotic phosphorite	14.00	6.99	0.13	4.15	21.10	5.04	0.75	1.98
		BD-8-B	granular phosphorite	19.60	8.97	7.85	8.42	74.40	44.60	0.89	1.53
		BD-9-A	detrital phosphorite	18.70	19.10	5.44	9.69	57.80	30.90	0.75	1.68
		BD-10-A	detrital phosphorite	21.60	18.80	4.31	8.13	41.10	24.70	0.69	1.70

[a] Notes:$\delta U = 6U/(3U + Th)$. [b,c] From refs 58, 59. [d] From ref 47. [e] From ref 45.

content of 28.96%.[38,45] The REE content in Weng'an phosphorus rocks are (18.59−285.91) × 10^{-6}, Ce/Ce* = 0.56−1.02. The REE distributed pattern is characterized by typical "cap type", showing slight enrichment of MREE (middle rare earth elements), suggesting that organic matter is involved in phosphorus mineralization during Doushantuo period.[46] The stromatolite phosphorite (Figure 2 e−l) of Late Ediacaran Dengying Formation is mainly found in the Weng'an area. The milky white and gray columnar stromatolite and dark gray fine crystalline dolomite are interspersed vertically, and colloidal and granular texture is developed, with average P_2O_5 content is 19.93%.[38,47] The Cambrian Niutitang Formation is mainly phosphate nodules, clastic phosphorite and siliceous phosphorite (Figure 2 m−p), with clastic texture and grain texture, with average P_2O_5 content is 28.58%.[40,43]

The increase of atmospheric oxygen during the late Ediacaran-early Cambrian may have promoted extensive ocean oxygenation at the end of Neoproterozoic, and the atmospheric oxygen content may reach 10%−40%PAL (Present Atmospheric Level),[48] which also caused the evolution of the Ediacaran biota and the subsequent Cambrian metazoans explosion.[49] The exponential increase of oxidation−reduction sensitive elements in marine sediments also indicates that the once widespread anoxic environment is transforming into an oxidizing environment, but intermittent anoxic and ferritic environment may still occur in the deep basin of the Early Cambrian Yangtze Platform.[1,50] Li et al.[4] proposed that the dynamic chemical stratification of oxidation zone-sulfide zone-iron zone was maintained in the Ediacaran to Early Cambrian ocean and believed that the chemical stratification from nearshore to deep sea included oxidation zone, nitrate reduction zone, iron and manganese reduction zone, sulfate reduction zone, methanogenic zone and iron mineralization zone.[51]

During the Early Cambrian, the Yangtze Platform suffered from transgression from southeastern to northeastern, its sedimentary facies gradually transited from shallow carbonate to continental shelf slope and deep basin facies.[43] Among the important mineralization sequences widely distributed in South China, phosphorite is usually deposited on the continental shelf from the coast to the shelf edge. Weng'an and Kaiyang in central Guizhou were shallow platform facies deposits, while Xiangyang in western Hubei belonged to deep basin facies deposits. Therefore, shallow basin and bay tidal flat environment at the margin of paleo-continent or underwater uplift are ideal places for phosphorus mineralization, while shelf and basin in deep area are mostly thin layer, nodule or lenticular phosphorites, which do not have geological conditions for forming large-scale high-grade phosphorite deposits.[36]

In recent years, with the development of metal stable isotope analysis technology, based on C, S isotopes, stable isotopes such as U, Mo and Fe have been gradually applied to paleo-marine environment research, becoming effective indicators for tracing the redox state of marine water.[7,13,52,53] Many studies based on various geochemical indicators such as inorganic carbon isotope, molybdenum isotope and sulfur isotope show that there is a highly stratified redox structure in the Ediacaran to Early Cambrian oceans in the Yangtze region of South China.[54−57] At the Doushantuo Formation, Dengying Formation and Niutitang Formation in Ediacaran to Early Cambrian in South China, synthesizing many discrimination indexes of trace elements and rare earth elements, the average V/(V + Ni) value is 0.70, 0.79, and 0.86 respectively, and the average δU value is 1.83, 1.92, and 1.87, respectively (Table 3); δCe always shows negative anomaly (δCe value is 2.70, 1.74, and 1.57 respectively, Table 4), and the negative anomaly trend gradually weakens with time. It is considered that the Ediacaran to Early Cambrian phosphorus mineralization period in South China is generally a reducing environment, but with the end of the ice age, climate warming promotes the enhancement of continental chemical weathering and promotes the increase of oxygen content, and there are local oxidation events. Due to the influence of transgression, the sea level fluctuates frequently, which makes the Ce negative anomaly weaken.

Table 4. Rare Earth Element Characteristics of Ediacaran to Early Cambrian Phosphorite in South China (with Average Values)[a]

Strata	Niutitang Formation	Dengying Formation	Doushantuo Formation
number of samples/piece	153	45	164
$\sum$REY/μg/g	653.74	63.26	86.51
LREE/HREE	5.84	6.06	6.26
δCe	1.57	1.74	2.70
δEu	0.23	0.24	0.26
Ce_{anom}	0.07	0.13	0.29
$(La)_N/(Yb)_N$	19.11	16.71	11.93
$(La)_N/(Sm)_N$	7.28	6.95	5.56

[a] Note: "N" stands for continental upper crust standardization, standardized data from [60]; $\delta Ce = 2Ce_N/(La_N + Pr_N)$; $\delta Eu = 2Eu_N/(Sm_N + Gd_N)$; $Ce_{anom} = \lg[3Ce_N/(2La_N + Nd_N)]$.

δ^{56}Fe in the lower and upper phosphate layers of Doushantuo Formation in Weng 'an is −0.33‰~0.27‰, −0.32‰~0.21‰ respectively,[38] and the oxidation−reduction sensitive element content in the upper phosphate layer (Mo = 0.23−1.35 μg/g, U = 3.79−7.05 μg/g, V = 13.9−24.5 μg/g) is obviously lower than that in the lower layer (Mo = 1.52−14.00 μg/g, U = 5.53−22.10 μg/g, V = 9.7−52.7 μg/g),[61] the Ce_{anom} = −0.26~−0.29 in upper phosphate layer, and Ce_{anom} = −0.065~−0.077 in lower layer. In addition, Fe-redox pumping is also key for phosphorus enrichment. In shallow oxidation-sub oxidation ocean, iron hydroxide (FeOOH) can adsorb a large amount of phosphorus, forming iron−phosphorus complex ($PO_4^{3-}\cdot FeOOH$) and sinking into bottom sediments. In the anoxic bottom water, these iron−phosphorus complexes deoxidize phosphorus and release it into the water column, and with the strong upwelling action, the deep phosphorus-rich seawater enters the shallow ocean.[23]

All the geochemical evidence mentioned above indicate that the late Neoproterozoic ocean changed from anoxic to oxidizing environment,[45] and the oxidation−reduction interface gradually shifted from shallow ocean to deep ocean with the expansion of seawater oxidation range. Wen et al.[62] analyzed $\delta^{97/95}$ Mo of phosphorite in Meishucun Formation, Yunnan Province, and proposed that the early Cambrian ocean inherited the oxidation−reduction layered structure of Precambrian ocean, and the surface water was in oxidation environment, which changed to reduction environment in depth, and even wedge-shaped sulfide water column may be locally developed at the bottom. Zhu et al.[63] studied Hg abundance and δ^{15}N in slope facies of Niutitang Formation in Songtao, Guizhou Province. It is considered that the enhancement of nitrogen fixation and nitrification of marine organisms in the early Cambrian reduced environment caused obvious negative excursion of δ^{15}N and abnormal enrichment of Hg, and the gradual oxidation of seawater and the decrease of organic matter buried in the later stage led to the decrease of Hg concentration, which showed the dynamic chemical stratification characteristics of the ocean from Ediacaran to Early Cambrian and the frequent changes of marine environment during this period.

4. GENETIC MECHANISM OF PHOSPHORITES

4.1. Phosphorus Sources. The material source of phosphorus is the premise of the study on the genetic mechanism of phosphate deposits. It is considered that the main sources of phosphorus in marine sedimentary phosphate rocks are the following. 1) Seawater, that is, phosphorus-rich bottom water brought by upwelling. After the death of the organism, the body's decomposition may release phosphate, which is absorbed and sunk by pore water. Under the influence of transgression, frequent sea level fluctuations provide a power drive for the exchange of deep bottom water and shallow oxidized seawater, and the upwelling carries the deep phosphorus-rich bottom water, which brings a lot of phosphorus to the shallow field. 2) Terrigenous detrital, under the background of the great oxidation event and the breakup of Rodinia supercontinent, the erosion and chemical weathering of paleo-continent were strengthened, and a large amount of phosphorus-bearing terrigenous debris was imported into the ocean. 3) Deep hydrothermal activity, submarine volcanic eruption brought a large amount of Sr, U, P, Si etc., the global $^{87}Sr/^{86}Sr$ of Ediacaran-Cambrian marine sediments (>0.7090)[64] also indicates that the seafloor hydrothermal activity was frequent during this period, and hydrothermal elements were imported, resulting in Sr isotope fractionation.[25,64]

4.2. Biological Genesis. The discovery of stromatolite phosphorite, microfossil assemblages, and algae fossils in the late Neoproterozoic indicates that microorganisms played an important role in the process of phosphate mineralization. The Doushantuo Formation phosphorite in Weng'an and Kaiyang area of Guizhou are rich in biologically related elements such as Cr, Co, Sr and Pb, also found that the phosphate sediments are mainly composed of calcium phosphate minerals and have fossils,[65] they all indicate that the biological prosperity may have a positive effect on phosphorite deposition of the Doushantuo period. The stromatolite phosphorite and gel phosphate rock of the Ediacaran Dengying formation are characterized by low REE concentrations, with an average REE content of 63.26 μg/g,[47,53] combined with the REE characteristics of modern marine organisms (such as modern fishbone fossils $\sum$ REE < 100 μg/g),[66] indicating that bacteria and algae were involved in phosphate mineralization during the Precambrian period.[67] Stromatolites, microfossils, algae fossils in the phosphorus-rich strata of the Ediacaran Doushantuo Formation and Dengying Formation, and many small shell fossils in the early Cambrian Meishucun Formation (Gezhongwu Formation) indicate that in the two phosphorus mineralization events there is a close relationship between the occurrence of high-quality and high-grade phosphate deposits and biological activities.

Biological participation in phosphorus mineralization is mainly reflected in two aspects: biological organisms absorb phosphorus from seawater and pore water, and after the death of organisms, the degradation of organic matter by bacteria causes phosphorus to decompose. Phosphate is concentrated into pore water. In addition, the life activities of organisms also indirectly change the physical and chemical conditions of the ocean. Ph value of pore water increases due to the decomposition of organic matter, which promotes the crystallization of some phosphate to form authigenic apatite minerals such as fluoroapatite and fine-grained apatite.[68,69] The other phosphorus of the wreckage is directly consolidated under diagenesis to form phosphate nodules, which are accumulated and mineralized.[70]

4.3. Upwelling Genesis. Upwelling is the most possible mechanism to explain the genesis of marine phosphorite deposits, but it is closely related to biological processes. It is considered that during the decomposition of biological remains, some phosphorus is released and enriched in the bottom water, and the upwelling is an important driving force for the migration of deep phosphorus-rich bottom water to shallow coastal areas. For the phosphorus-rich seawater brought to the shallow ocean by the upwelling, due to the decrease of pressure and the increase of temperature, the solubility of phosphate in the water column decreases and directly precipitates to form phosphorus-rich sediments. On the other hand, the nutrient elements reaching the shallow ocean increase the primary productivity and prosper the organisms, which in turn absorb the phosphate in the pore water and enrich the phosphorus. However, with the deepening of the study, it is found that the modern phosphorus mineralization in Peru and Namibia is mainly distributed in the continental shelf and slope environment under the upwelling area.[71] Therefore, it is considered that the upwelling is beneficial to the upward migration of bottom phosphorus-rich seawater, but it is not a necessary condition for the phosphorus mineralization, and the migration-enrichment process of phosphorus-rich bottom water in the shallow ocean is still controversial.

4.4. Mechanical Mineralization. Most of phosphorite deposits are mechanical sedimentation of the Ediacaran-early Cambrian in South China, which is the initial enrichment of phosphorus-rich sediments in the early stages is the product of erosion and redeposition under the influence of geological forces. During the study of phosphorus-rich sedimentary genesis of Kaiyang and Weng'an Doushantuo Formation in central Guizhou, Wang et al.[72] considered that Weng'an phosphorus rock experienced at least two stages of transgression-retrogression cycle, and accordingly, the phosphate mineralization of Doushantuo Formation was divided into three stages: 1) In the early stage, transgression was frequent, carbonate tidal flat deposits were developed in central Guizhou. And the water depth deepened from south to north, the upwelling and biological prosperity cause the deposition of phosphorus-rich organic matter, which degrades the organic matter at the redox interface, releases a large amount of phosphate, and completes the initial enrichment. 2) In the middle stage, with the large-scale retrogression, the carbonate cements were dissolved by the erosion and leaching of the primary phosphorite, and the broken clastic particles were deposited in situ or accumulated after transportation, so as to improve the phosphorus grade. 3) In the late stage, the transgression once again caused the sea level to rise and the microbial activity flourished, and the early clastic phosphorite continued to accept phosphorus deposition and cementation, resulting in the second phosphorus mineralization event. In summary, it is considered that the transgression in the late Neoproterozoic triggered the exchange between the deep phosphorus-rich seawater and the shallow seawater, and the widely distributed shallow ocean was an ideal place for phosphorus accumulation. The rhythmic variation characteristics of the lithology of the Doushantuo Formation and the transgression-retrogression cycles of the two stages also indicate that the intermittent fluctuation of sea level has led to the formation of phosphorite-carbonate deposits with cycle characteristics in central Guizhou.

4.5. Syn-Sedimentary Hydrothermal Genesis. The strong hydrothermal activity can change the chemical composition of seawater and marine environment and provide a habitat for biological communities.[15] The major and microgeochemical indexes of phosphorite in Doushantuo Formation in central Guizhou indicate that hydrothermal activity is accompanied by transgression-retrogression cycle, which is an important contributor to phosphorus source of late Neoproterozoic phosphorus mineralization events, it also plays an important role in phosphorus transport and deposition.[45] Liu et al.[73] found that mineral fluid inclusions (quartz and muscovite) in phosphorite of the Lower Cambrian Gezhongwu Formation in Zhijin, Guizhou, which is direct evidence that hydrothermal activity is involved in phosphorus mineralization. At the same time, the phosphate nodules preserved in the black shale also recorded some information on volcanic and hydrothermal activities of the Lower Cambrian Niutitang Formation in South China. It was found that the volcanic ash and hydrothermal activities carried a large amount of nutrients, which promoted the development of marine primary productivity and produced many phosphate-rich water masses.[41] Silicon isotope measurements of authigenic quartz in the upper phosphate layer of Zhongyicun member in Yunnan (δ^{30}Si = −0.40‰),[64] the δ^{13}C of phosphorite in Zhongyicun member in Laolin area (δ^{13}C = −3.20‰~0‰)[74] also indicate that hydrothermal fluid was added in the process of phosphate mineralization.

Although the earth has experienced extensive weathering and imported many terrigenous materials, the strontium isotopic composition of sediments is still lower than that of terrestrial materials due to strong hydrothermal activities.[12] The geochemical characteristics of the above phosphorite deposits indicate that the seafloor hydrothermal solution can provide some phosphorus and metal-ore-forming elements in the mineralization process. Some scholars associate hydrothermal activities with biological activities and believe that submarine hot water provides energy and rich nutrients for the biota,[75] which indirectly promotes the improvement of marine primary productivity and is beneficial to the accumulation and precipitation of phosphorus.

Marine sedimentary phosphorite deposits have been studied for a long time. Scholars have put forward a variety of genetic mechanisms and models about the phosphorite deposits, but they have also been controversial. For a long time, a large number of detailed studies have been carried out on the temporal and spatial distribution, rock and mineral assemblage,

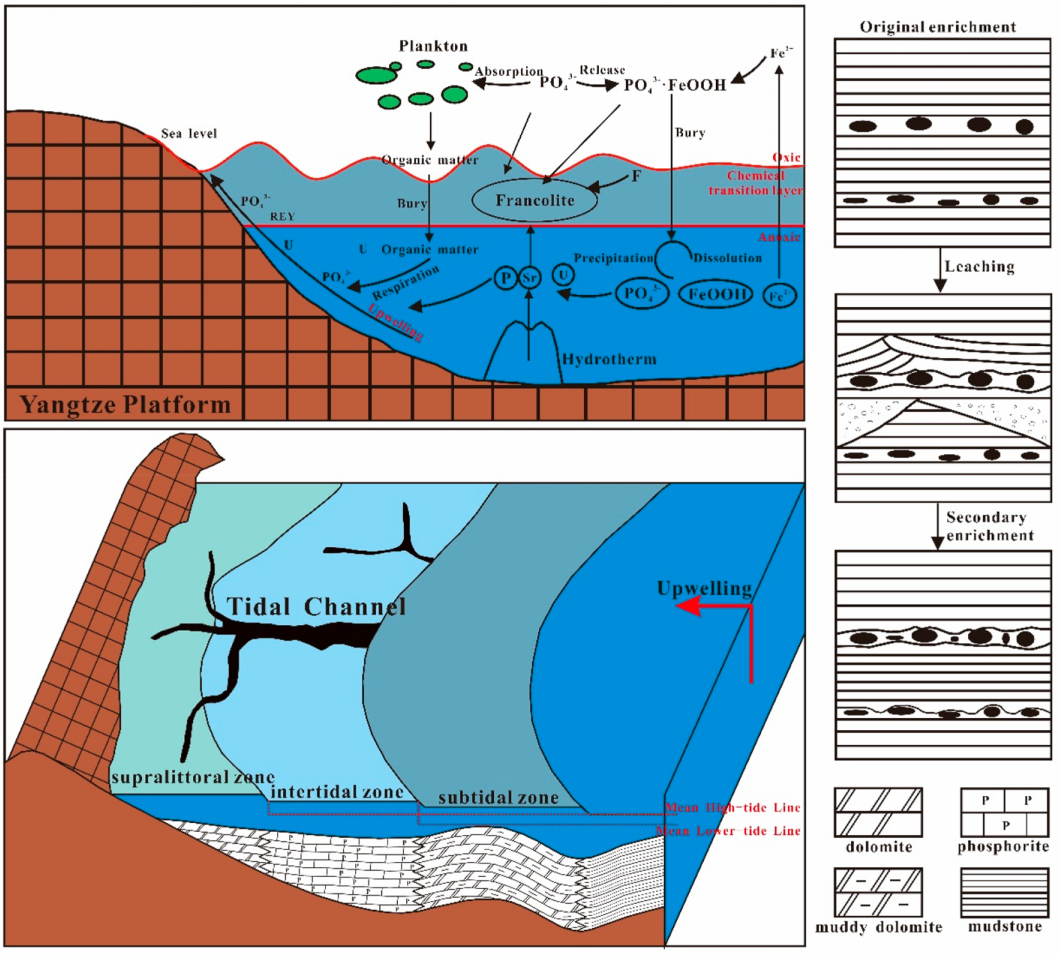

Figure 3. Sedimentary model of the phosphorite deposit.

lithofacies, paleogeography, major and trace elements and isotope geochemistry of phosphorite, it is considered that the direct precipitation of phosphorus-rich seawater, carbonate metasomatism, microbial interaction, or the interaction of the above processes may produce different phosphorus-bearing sedimentary facies (Figure 3).[11] Therefore, the genetic mechanism of phosphate deposits cannot be demonstrated solely from one aspect; we should pay more attention to the internal relationship between phosphorus mineralization and major geological events. And the microfabric analysis of phosphate rocks should be strengthened, comprehensively considering various influencing factors to discuss the process of phosphorus deposition and mineralization.

5. CONCLUSIONS

1) China is very rich in phosphate resources, but there are extreme imbalances of geographical distribution and utilization etc. There are many types of phosphate deposits, and sedimentary phosphate rock deposits are the main industrial phosphate ores. The Ediacaran-early Cambrian sedimentary phosphorite deposits are mainly distributed in Yunnan, Guizhou, Hubei, Sichuan, and Hunan provinces of the Yangtze platform in South China, in which the early Cambrian phosphorite deposits are also rich in rare earth elements, associated with uranium, nickel, molybdenum, vanadium and other beneficial metal elements.

2) The paleo-marine environment from Ediacaran to early Cambrian changed frequently, showing a reductive environment overall, and there may be dynamic chemical stratification of oxidation zone-sulfide zone-iron zone. However, due to the influence of transgression, the sea level fluctuates frequently, and in the early Cambrian, it may still inherit the redox stratified structure of Precambrian ocean, showing that the surface water is an oxidizing environment, changing to a deep reduction environment, and even wedge-shaped sulfide areas are developed at the deep basin.

3) The main phosphorus sources of Ediacaran-early Cambrian marine sedimentary phosphorite deposits in South China are deep phosphorus-rich seawater, terrigenous detritus, and hydrothermal activity. The genetic mechanism and metallogenic model of marine sedimentary phosphorite deposits have been controversial. At present, the established genetic mechanisms mainly include biogenic mechanism, upwelling mechanism, mechanical mineralization, and syn-sedimentary hydrothermal genesis. Various genetic hypotheses are not independent, but interrelated and influence each other, so in the future, it is necessary to further explore the internal relationship between phosphorus deposits and major geological events and deepen the genetic mechanism and the reconstruction of paleo-marine environment.

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Notes

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