



Article Microdistribution and Mode of Rare Earth Element Occurrence in the Zhijin Rare Earth Element-Bearing Phosphate Deposit, Guizhou, China

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Abstract: Rare-earth elements (REEs) are often highly concentrated in sedimentary phosphate deposits, and the microdistribution characteristics and occurrence state of rare earth in these deposits play a crucial role in the overall development and utilization of mineral resources. This study aims to analyze the microdistribution of REEs in REE-bearing phosphate deposits in the Zhijin region of Guizhou at the microstructural level and investigate their occurrence modes. Specifically, rock and mineral identification, X-ray diffraction (XRD), scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS), and laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS) were utilized to analyze the samples. The correlation between the distribution of REEs and phosphorus was examined. In addition, the microdistribution of REEs in specific mineral phases and the locations of their occurrence were investigated. The analysis revealed that no REEs existed independently in the deposit. Instead, the distribution of REEs was highly consistent and significantly positively correlated with that of phosphorus. In the microarea structure, REEs were predominantly found both in particles, such as bioclasts, sand debris, and agglomerates, and in phosphate cement, where the main mineral components were collophane and apatite. Conversely, the content of REEs in dolomitized sand debris edges, sparry dolomitic cement, and siliceous cement was considerably lower. Based on these findings, it is speculated that REEs primarily occur within the lattice defects of apatite or on the surface of collophanite. There is a notable contrast in the REE content between the unaltered sand debris at the periphery and the dolomitized sand debris, indicating that the dolomitization in the diagenetic stage resulted in a depletion of REE abundance in the ore. Obviously, the dominant gangue mineral, dolomite, does not serve as the primary host for REEs. Furthermore, the highest concentration of REEs was inside organisms. This finding suggests that the high content of REEs in biological soft tissue may remain under the influence of waves and tides, and REE-bearing apatite may be preferentially separated and fill the cavities of deceased organisms. The second highest content of REEs was found in the shells of organisms, indicating that small shelly organisms absorb phosphorus materials through their life activities to construct their shells, resulting in REE enrichment. Quantitative analysis through sequential extraction procedures displayed that most REEs were present in the residual state, with a smaller portion combined with organic matter. These results confirm that REEs in the Zhijin phosphate deposits primarily exist as isomorphic substitutions in the lattice defects of apatite, with a secondary occurrence as organic matter-bound REEs.

Keywords: rare-earth elements; microdistribution characteristics; occurrence state; REE-bearing phosphate deposit; Zhijin; Guizhou



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1. Introduction

Rare-earth elements (REEs) consist of 15 lanthanide elements, along with scandium and yttrium. These elements are highly valued for their unique physical and chemical properties, making them essential for various advanced technological applications. As the global demand for rare-earth resources continues to rise, it is crucial to explore new sources of REEs [1,2]. It is noteworthy that current research suggests that REEs found in phosphate deposits offer a potential solution to the global rare-earth crisis [3–6].

One such deposit is the phosphate deposit in Zhijin, Guizhou Province, characterized by its abundant light and heavy REEs, particularly yttrium. This large-scale deposit, with REE reserves of up to 3.5 million tons, offers a significant opportunity for rare-earth mineral extraction [7,8]. The occurrence state and distribution characteristics of REEs play a crucial role in determining the effectiveness of their separation and the comprehensive utilization of rare earth-phosphorus ore resources. This has led to a significant interest among scholars to study this area. Previous studies have primarily focused on analyzing single minerals and whole-rock powder using techniques such as X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), electron probe microanalysis (EPMA), laser ablation-inductively coupled plasma-mass spectrometry (LA-ICP-MS), and chemical beneficiation methods. These studies suggest that REEs predominantly exist in the form of isomorphic substitutions within the apatite lattice [9–14]. Additionally, REEs can also be adsorbed onto mineral surfaces, forming ion-adsorbed REEs [10]. Various independent REE minerals have been identified [15]. However, according to some scholars, the distribution of REEs extends even further. They posit that REEs can be found in abundance in minerals, such as collophanite, dolomite, quartz, chalcedony, feldspar, pyrite, and others. In fact, these scholars suggest that REEs exist as phosphate ultramicroinclusions within these minerals [16].

It is evident that differing views exist regarding the occurrence of REEs. Some propose that isomorphism within the apatite lattice, adsorption onto mineral surfaces, the dispersion distribution of independent mineral forms, and the wide distribution of ultramicroscopic inclusions within various minerals may account for their presence. Most of the research conducted in this field focuses on single minerals or whole-rock powder, mainly considering the distribution of REEs within single minerals [13]. However, the distribution variation in REEs in the microstructural components, the impact of bio-organic matter during the mineralization process, and the influence of dolomite during diagenesis are rarely examined from a comprehensive ore perspective [17].

Similar to the distribution of REEs in Paleocene–Eocene sedimentary phosphorite in northeastern Algeria, where it is closely associated with transported and redeposited glauconite particles in the microstructure, as well as the enrichment of REEs in spherical phosphorized microfossils and the phosphorized detritus of the Ediacaran Doushantuo Formation in Weng' an, Guizhou, it is apparent that the occurrence state and distribution characteristics of REEs in the Early Cambrian rare earth-rich phosphorite in Zhijin need to be determined through more detailed mineralogical, petrological, and geochemical studies [18,19]. Valuable insights into the formation process of marine phosphate deposits can be gleaned from sedimentary structural features [20]. In situ microanalysis techniques allow for the comprehensive examination of elemental behavior within microstructural components [21-23], while stepwise chemical extraction experiments provide the quantitative characterization of element occurrence states [24–27]. Hence, this study primarily employs LA-ICP-MS and sequential chemical extraction experiments. Through the integration of polarized light microscopy, XRD, SEM-EDS, ICP-MS, and other testing methods, the distribution of REEs in different minerals and various structural components of the ore is meticulously distinguished at the microarea level, thus revealing the occurrence state of REEs. This aims to provide a reliable theoretical foundation for the development and utilization of REE-rich phosphorites.

2. Geological Background

The Zhijin REE-bearing phosphate deposit occurs in the southwestern section of the central Guizhou uplift, within the passive marginal fold belt of the southern Yangtze block [28]. In the period of phosphorus formation, the paleogeography of central Guizhou was dominated by submerged platform facies and Zhijin was in the shallow water environment of the submerged platform. The mineral deposit is mainly controlled by the northeast-southwest Guohua anticline, which trends in a northeast-southwest direction. Notably, the northeast segment of this anticline is 4.0 km wide and exhibits a series of faults and wavy folds, while the southwest segment is narrower, measuring only 0.4 km in width [29]. The core strata found within the anticline is mainly composed of the Ediacaran Dengying Formation. However, the southeast wing of the anticline has been destroyed by a strike fault, leading to the absence of early Paleozoic strata, with the exception of some isolated occurrences of the Lower Cambrian Mingxinsi Formation. On the other hand, the northwest wing of the anticline offers a complete exposure of rock layers, including the Lower Cambrian Gezhongwu Formation, Niutitang Formation, Mingxinsi Formation, Carboniferous Datang Formation, and Quaternary sediments. It is within this section that the Zhijin REE-bearing phosphate deposit is located, near the central axis of the northwest wing of the anticline [8]. The REE-bearing phosphate ore body is strata-bound, and the orebearing formation is the Lower Cambrian Gezhongwu Formation (\mathcal{E}_1 gz). The Gezhongwu Formation (\mathcal{E}_1 gz) is conformable with the black shale of the overlying Niutitang Formation (\pounds 1n) and unconformable with the dolomite of the underlying Dengying Formation $(Z_2 dy)$ [9] (Figure 1). The mining area exhibits a significant development of fault structures, primarily characterized by the presence of the northeast-oriented normal fault. These faults have a detrimental effect on the overall integrity of certain ore layers within the region. The ore layers found within the mining area range in thickness from 4 to 28 m, with an average thickness of 12 m.



Figure 1. Geological map of Zhijin REE-bearing phosphate deposit. Modified from [30].

The REE-bearing phosphate deposit in Xinhua, Zhijin, is composed of bioclastic phosphate rocks, phosphatic rocks, and phosphorus-bearing dolomite. These rocks are rich in phosphate minerals, such as apatite and collophanite, while gangue minerals, like dolomite, quartz, calcite, and chalcedony, are also present. The ore usually have a laminar, banded, and massive structure. The common ore texture is a granular texture, which mainly includes biological debris, sand debris, agglomerates, and ooids. Bioclasts mainly consist of small shelly fossils and are composed primarily of collophanite, with a small amount of apatite and dolomite. The cement materials include phosphate minerals, dolomitic minerals, and siliceous minerals. (Figure 2).



Figure 2. Texture and structure characteristics of ore-bearing formations in Xinhua of Zhijin. Apapatite; Clh—collophanite; Dol—dolomite; Qtz—quartz; (**a**) massive structure; (**b**) laminar structure; (**c**) banded structure; (**d**) organic matter structure; (**e**) bioclastic texture; (**f**) sand texture; (**g**) agglomerate texture; (**h**) oolite texture.

3. Materials and Methods

3.1. Sampling

In the study area of Zhijin, a total of 22 bottom-up samples were collected from the surveyed cross-section of the Gezhongwu Formation (Figure 3). These samples represent different mineral compositions. Two of the samples contained dolomite (DY1 and DY1-2), nineteen samples (GZW2-1, GZW5-2, GZW8-3, etc.) were composed of phosphate minerals, and one (NTT9-1) was composed of carbonaceous minerals.



Figure 3. Sedimentary characteristics of the cross-section and the sampling location of the Gezhongwu Formation in Zhijin.

3.2. Test Analysis

After conducting an analysis of the polished thin sections of rocks under a polarizing microscope, a selection of samples with representative mineral compositions and texture were chosen for further analysis. These samples, labeled as GZW2-1, GZW2-3, GZW3-1, GZW4-1, GZW5-1, GZW5-2, GZW6-1, GZW6-2, GZW6-5, GZW7-1, GZW7-2, GZW7-3, and GZW8-3, underwent a series of tests, including a major elements test, a total REEs test, a total organic carbon (TOC) test, an XRD test, an SEM-EDS analysis, an LA-ICP-MS analysis, and sequential chemical extraction.

The representative samples were rinsed with deionized water following the removal of the weathered surface, and subsequently subjected to drying in a 105 °C incubator. The dried samples were broken and ground to a size of less than 200 meshes for the major elements test, total REEs test, and XRD test. For the major elements and total REEs tests, 0.1 g of sample powder was precisely weighed and dissolved in a tube at first. Prior to this, the tube had been heated to 110 $^{\circ}$ C and thoroughly cleaned with 20% HNO₃ for an hour. Then, 1 mL of HF and 0.5 mol of HNO3 were added in the tube, and the sample was allowed to dissolve for 12 h in the tube at a temperature of 190 °C. Subsequently, 0.5 mol of HNO₃ was added, and the solution was heated to 140 °C and dwelled for 3 h. After the solution was cooled, deionized water was added to dilute it to 100 mL for the tests. Finally, the composition of major elements and REEs were determined by an X-ray fluorescence spectrometer (XRF) and ICP-MS analysis, respectively. The average standard deviation of the measured values was found to be less than 10%, while the average relative standard deviation was less than 5%. During the XRD test, a ground powder sample weighing 2 g was measured. The Cu K α X-ray tube was selected with a voltage of 40 kV and a current of 40 mA. The scanning range for the 2 θ angle was set from 5° to 80°, with a step size of 0.0131° and a scanning speed of 0.187575° s⁻¹. The device model was the Empyrean Sharp Shadow.

The specified quantity of the sample was collected, followed by the addition of an excess amount of 4 mol/L HCl, and the reaction was allowed to proceed for a duration of 24 h. The acid was then rinsed with deionized water until neutral, dried in a 60 °C oven to achieve a constant weight, ground into a powder, and finally sieved through a 60-mesh sieve. The sample powder weighing 10 mg was measured in a tin cup measuring 5×9 mm and securely sealed for future use. The Sercon Integra2 elemental analysis–stable isotope ratio mass spectrometry (EA-IRMS) technique was utilized for the determination of the TOC. The analysis revealed a deviation in the test accuracy below 0.5%.

Initially, the bioclastic phosphate rock samples containing different cement materials were made into round thin sections after removing the weathered surface. These sections were then cleaned with alcohol, dried, and gold-sprayed. Subsequently, a scanning electron microscope (SEM) and energy-dispersive spectrometer (EDS) were used for the microscopic observation of the morphology and microchemical analysis. The specific equipment used for this purpose was the COXEM (EM30) model.

Then, a total of 11 samples were subjected to LA-ICP-MS microanalysis, including 8 REE-rich bioclastic phosphate rock samples and 2 REE-rich sand phosphate rock samples, and 1 REE-rich agglomerate sample. Similar to the previous step, the weathered surface was removed from the samples, and laser sheets were created with dimensions of 47 mm \times 25 mm \times 3 mm. These target samples underwent two cycles of ultrasonic cleaning, each lasting 30 min, before being dried. The LA-ICP-MS test instrument used was the Resolution SE-S155, incorporating a laser-ablation system (LA).

The modified Tessier method [27] was employed for sequential chemical extraction to determine the different states of the REEs. These states included a water-soluble state, exchangeable state, carbonate-bound state, ferromanganese oxide-bound state (reducible state), organic matter-bound state (oxidizable state), and residual state. All reagents used were of high purity. The experimental procedure is detailed below (Figure 4).



Figure 4. Flow chart of the sequential chemical extraction.

Step 1: To start the experiment, a 2 g sample powder was accurately weighed and added to 40 mL of deionized water. The sample was fully oscillated at room temperature (25 °C \pm 1 °C) for 2 h. Next, the mixture was centrifuged at 4000 rpm for 20 min to obtain the supernatant. This supernatant was then filtered to obtain filtrate A.

Step 2: The residue left in Step 1 was mixed with 48 mL of 0.5 mol/L MgCl₂, and the pH was adjusted to 7.0 with NaOH. The solution was then oscillated continuously at a temperature of 25 °C \pm 1 °C for 20 min, followed by centrifuging at 4000 rpm for 20 min. The supernatant was separated from the residue, which was then washed with 20 mL of deionized water and centrifuged again for 20 min. The resulting supernatant was combined with the previous supernatant, and the mixture was filtered to yield filtrate B.

Step 3: The residue left in Step 2 was mixed with 48 mL of 1 mol/L NaOAc solution, and the pH value was adjusted to 5.0 using HOAC. The mixture was then continuously oscillated at a temperature of 25 °C \pm 1 °C for 5 h, followed by centrifuging at 4000 rpm for 20 min. The supernatant was separated from the residue, which was then washed with 20 mL of deionized water and centrifuged again for 20 min. The supernatant was then taken. The two supernatants were combined and filtered to give filtrate C.

Step 4: The residue left in Step 3 was mixed with 40 mL of 0.04 mol/L NH₂OH·HCI (dissolved in 25% HOAC (V/V) solution). The solution was then intermittently oscillated in a water bath at a temperature of 96 °C \pm 3 °C for 6 h, followed by centrifuging for 20 min. The supernatant was separated from the residue, which was then washed with 20 mL of deionized water and centrifuged again. The resulting supernatant was combined with the previous supernatant, and the mixture was filtered to obtain filtrate D.

Step 5: The residue left in Step 4 was mixed with 6 mL of 0.02 mol/L HNO₃ and 10 mL of 30% H₂O₂ solution, and the mixture was shaken well. The pH value was adjusted to 2 using HNO₃ and then oscillated for 2 h at a constant temperature of 85 °C \pm 2 °C. After 6 ml of 30% H₂O₂ (pH = 2) was added, the solution was oscillated for 3 h at a constant temperature of 85 °C \pm 2 °C and cooled to 25 °C \pm 1 °C. Subsequently, 10 mL of 3.2 mol/L NH₄OAC (dissolved in 20% HNO₃ solution) was added, and the solution was washed with deionized water. The resulting mixture was diluted to 40 mL, and then continuously oscillated for 30 min before centrifuging for 20 min. The supernatant was taken and filtered to obtain filtrate E.

Step 6: The remaining solid substance from Step 5 was dried in an oven. After adequate mixing, 1 g of the substance was taken and placed into a digestion tube. Then, 3 m of LHF and 1 mL of concentrated HNO₃ was added in the tube. The mixture was allowed to react at a high temperature and high pressure for 10 h. After the digestion tube was taken out and cooled, and 1 ml of HClO₄ was added. The tube was then heated in an electric heating plate for sample digestion for 2 h. The digestion was continued by adding more nitric

acid until it completed, and the resulting solution was processed by extracting with 1 mL of concentrated nitric acid. The extract was then transferred to a 50 mL volumetric flask and diluted with water to the scale to obtain solution F. Finally, the REEs in the obtained solutions (A–F) were detected and analyzed with ICP-MS.

4. Results and Discussion

4.1. Correlation Analysis of the REEs and Major Ore Components

The analytical results of the major elements and TOC in the ore-bearing rock series of the Xinhua Gezhongwu Formation in Zhijin are presented in Table 1. The data reveal that phosphate ores exhibit high concentrations of P_2O_5 , CaO, and SiO₂, with MgO being the subsequent element in abundance. This is consistent with the observation under the microscope that the main minerals of phosphorite are apatite and collophanite, while the gangue minerals are mainly dolomite, quartz, and calcite. The TOC content in the phosphate rock samples ranges from 0.01% to 0.12%, with an average value of 0.04%, indicating the presence of a certain amount of organic matter in the phosphate rock. According to the results of the content test for the REEs (Table 2), it is evident that phosphate ore exhibits significant enrichment characteristics in REEs, with a total amount ranging from 187.99×10^{-6} to 1952.23×10^{-6} , and an average value of 1084.27×10^{-6} . It is 40 times higher than that of the bottom Dengying Formation (\sum REY: 26.86 \times 10⁻⁶), and nearly 6 times higher than that of the top Niutitang Formation (193.14 \times 10⁻⁶). The heavy rare-earth element yttrium (Y) exhibits extensive enrichment, with a content ranging from 66.70×10^{-6} to 669.00×10^{-6} , and an average value of 378.57×10^{-6} , which is 13 times higher than the average content found in the Earth's crust. This indicates that the ore-bearing rock series of the Gezhongwu Formation is rich in REEs, especially yttrium (Y).

Table 1. The composition of major elements and TOC in the ore-bearing rock series of the Zhijin Gezhongwu Formation (%).

Sample No.	Lithology	P_2O_5	SiO ₂	Al_2O_3	Fe ₂ O ₃	FeO	MgO	CaO	Na_2O	K ₂ O	MnO	TiO ₂	LOL	TOC
NTT-9-1	Carbonaceous shale	0.12	62.43	15.75	3.76	0.76	1.59	0.22	0.04	4.88	0.01	0.75	9.49	1.77
GZW-8-3	Phosphorite-bearing rock	2.99	11.00	0.69	3.05	1.22	16.39	28.14	0.01	0.22	0.34	0.04	37.15	0.01
GZW-8-2	Siliceous phosphorous rock	22.14	29.94	0.98	0.12	0.10	0.32	33.14	0.07	0.36	0.01	0.05	1.77	0.09
GZW-8-1	Siliceous phosphorous rock	12.01	64.06	0.62	< 0.010	0.10	0.15	16.48	0.02	0.16	0.01	0.04	1.46	0.03
GZW-7-4	Siliceous phosphorous rock	17.59	44.53	2.81	0.05	0.10	0.38	23.74	0.02	0.81	0.01	0.15	1.91	0.04
GZW-7-3	Phosphorous rock	37.38	2.21	0.43	0.42	0.35	0.19	50.65	0.10	0.16	0.04	0.04	2.37	0.05
GZW-7-2	Phosphatic rock	14.46	2.86	0.39	1.02	0.60	12.69	37.73	0.02	0.13	0.16	0.03	28.66	0.01
GZW-7-1	Phosphorous rock	21.51	2.57	0.48	0.43	0.35	8.30	41.48	0.11	0.18	0.09	0.04	19.78	0.01
GZW-6-6	Siliceous phosphorous rock	26.84	25.21	1.29	0.50	0.40	0.44	36.57	0.06	0.44	0.03	0.08	2.55	0.12
GZW-6-5	Siliceous phosphorous rock	14.03	58.23	1.51	0.24	0.20	0.23	18.83	0.02	0.45	0.00	0.08	1.39	0.11
GZW-6-2	Phosphorous rock	32.68	3.11	0.43	0.12	0.10	2.68	47.99	0.09	0.14	0.03	0.10	7.63	0.02
GZW-6-1	Phosphatic rock	17.27	4.54	0.43	0.21	0.15	10.96	39.06	0.03	0.15	0.07	0.04	24.82	0.01
GZW-5-1	Silica-containing phosphorous rock	12.77	11.66	0.35	2.51	1.41	11.15	33.90	0.02	0.12	0.31	0.03	26.19	0.04
GZW-4-2	Phosphatic rock	9.33	5.92	0.38	0.93	0.67	14.79	34.49	0.01	0.13	0.14	0.02	33.01	0.02
GZW-4-1	Phosphorous rock	32.68	1.98	0.80	0.03	0.10	2.27	48.13	0.10	0.27	0.02	0.07	7.18	0.01
GZW-3-2	Phosphatic rock	11.30	6.51	0.26	0.51	0.42	13.59	35.08	0.01	0.09	0.09	0.02	30.69	0.01
GZW-3-1	Phosphorous rock	22.40	5.91	0.40	0.17	0.10	7.35	41.11	0.06	0.14	0.05	0.05	17.46	0.03
GZW-2-3	Phosphorous rock	32.41	3.82	0.50	0.04	0.10	1.83	47.06	0.11	0.18	0.01	0.20	6.37	0.09
GZW-2-2	Phosphorite-bearing rock	5.05	13.02	0.48	0.14	0.10	13.96	31.67	0.01	0.16	0.08	0.06	34.57	0.01
GZW-2-1	Phosphorous rock	31.57	8.26	1.05	0.09	0.10	0.31	44.67	0.11	0.40	0.01	0.07	2.46	0.06
DY-1-2	Siliceous rock	1.09	92.20	1.44	0.01	0.10	0.23	1.67	0.01	0.40	0.00	0.06	0.90	0.01
DY-1-1	Dolomite rock	0.28	2.60	0.14	0.16	0.10	21.71	30.03	0.01	0.05	0.08	0.01	44.94	0.01

Based on the correlation analysis between the REEs and major components of the phosphate ore samples, it can be observed from Table 3 that there is a significant and evident positive correlation between the average \sum REY and P₂O₅, as well as CaO, which are characterized by higher concentrations of major elements, with correlation coefficients reaching 0.98 and 0.66, respectively, while the correlation coefficient between P₂O₅ and CaO is 0.75, indicating a strong positive correlation. It is worth noting that both CaO and P₂O₅ are the primary components of apatite. This observation suggests a close association between REEs and apatite, leading to the speculation that REEs predominantly exist within this mineral. The \sum REY is also positively correlated with Na₂O, TiO₂, K₂O, and Al₂O₃, which contain less in the main elements, and the correlation coefficients are 0.88, 0.55,

0.23, and 0.15, respectively. And Na₂O, TiO₂, K₂O, and Al₂O₃ are the main components of clay minerals. This is related to the phosphate ore minerals in addition to part of the fine crystal apatite, and more for collophanite, because collophanite is formed by amorphous apatite mixed with clay minerals, and clay minerals have a strong ability to adsorb REEs. The correlation coefficient between \sum REY and TOC is 0.46, indicating a moderate positive correlation, suggesting that organic matter also exhibits a certain adsorption effect on REEs.

Table 2. Content of REEs in the ore-bearing rock series of the Zhijin Gezhongwu Formation (%).

Sample No.	Lithology	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y	ΣREY
NTT-9-1	Carbonaceous shale	41.30	76.90	8.01	25.80	4.02	0.73	3.25	0.57	3.70	0.82	2.51	0.42	2.79	0.43	21.90	193.14
GZW-8-3	Phosphorite-bearing rock	37.80	25.30	6.13	26.20	4.79	1.06	5.92	0.85	5.31	1.21	3.35	0.46	2.56	0.35	66.70	187.99
GZW-8-2	Siliceous phosphorous rock	280.15	204.00	49.40	220.00	41.80	12.70	50.00	6.56	37.10	7.66	18.70	2.14	9.70	1.18	471.00	1412.09
GZW-8-1	Siliceous phosphorous rock	138.00	98.00	26.20	117.00	22.70	7.48	27.00	3.55	20.00	4.17	10.20	1.18	5.32	0.65	237.00	718.45
GZW-7-4	Siliceous phosphorous rock	208.00	172.00	38.30	173.00	33.60	11.00	40.70	5.45	31.50	6.65	16.50	1.91	8.76	1.07	402.00	1150.44
GZW-7-3	Phosphorous rock	398.50	234.00	59.80	254.00	45.30	10.40	55.00	7.63	45.60	9.93	25.30	3.04	14.20	1.77	654	1818.47
GZW-7-2	Phosphatic rock	138.00	94.70	25.30	111.00	20.60	6.18	25.40	3.40	19.70	4.21	10.70	1.29	6.05	0.77	263.00	730.30
GZW-7-1	Phosphorous rock	240.00	152.00	37.20	160.00	29.00	8.37	35.40	4.85	28.40	6.12	15.50	1.85	8.62	1.08	399.00	1127.39
GZW-6-6	Siliceous phosphorous rock	336.00	225.00	54.30	235.00	43.00	11.60	51.60	7.06	41.40	8.94	22.80	2.75	13.20	1.65	556.00	1610.30
GZW-6-5	Siliceous phosphorous rock	159.00	101.00	27.20	119.00	22.20	6.57	26.70	3.63	21.20	4.54	11.50	1.40	6.71	0.84	281.00	792.49
GZW-6-2	Phosphorous rock	365.00	228.00	57.80	247.00	44.30	11.60	53.30	7.34	43.30	9.32	23.60	2.80	13.10	1.63	590.00	1698.09
GZW-6-1	Phosphatic rock	190.00	111.00	30.90	133.00	24.10	6.67	29.10	4.00	23.50	5.05	12.80	1.53	7.18	0.91	316.00	895.74
GZW-5-1	Silica-containing phosphorous rock	136.00	93.30	24.50	106.00	19.90	5.47	23.80	3.21	18.60	3.98	10.10	1.23	6.05	0.78	231.00	683.92
GZW-4-2	Phosphatic rock	93.60	54.30	15.30	65.70	12.00	2.68	14.50	2.05	12.40	2.73	7.19	0.92	4.66	0.61	163.00	451.64
GZW-4-1	Phosphorous rock	380.14	218.00	56.10	238.00	42.20	9.63	50.80	7.09	42.50	9.40	24.3	2.98	14.40	1.83	614.00	1711.37
GZW-3-2	Phosphatic rock	121.00	68.60	19.50	83.80	15.20	3.35	18.30	2.55	15.30	3.37	8.77	1.10	5.50	0.72	201.00	568.06
GZW-3-1	Phosphorous rock	265.00	159.00	41.00	174.00	31.30	7.05	37.00	5.14	30.40	6.61	17.00	2.07	9.86	1.24	424.00	1210.67
GZW-2-3	Phosphorous rock	405.30	269.00	68.70	294.00	53.40	12.50	62.40	8.60	50.50	10.80	27.30	3.29	15.50	1.94	669.00	1952.23
GZW-2-2	Phosphorite-bearing rock	54.30	33.70	9.28	39.80	7.36	1.67	8.69	1.22	7.25	1.59	4.19	0.54	2.74	0.36	88.20	260.89
GZW-2-1	Phosphorous rock	338.20	223.00	55.20	236.00	42.70	10.50	50.80	6.94	41.00	8.90	22.80	2.76	13.20	1.66	567.00	1620.66
DY-1-2	Siliceous rock	6.57	7.33	1.37	6.08	1.23	0.30	1.31	0.18	1.00	0.21	0.57	0.08	0.51	0.07	9.24	36.05
DY-1-1	Dolomite rock	3.52	3.30	0.65	2.74	0.52	0.13	0.58	0.08	0.47	0.10	0.28	0.04	0.20	0.03	5.02	17.66

Table 3. Correlation analysis of total REEs and major components.

	ΣREY	P_2O_5	SiO ₂	Al_2O_3	Fe ₂ O ₃	FeO	MgO	CaO	Na ₂ O	K ₂ O	MnO	TiO ₂	TOC
ΣREY	1.00												
P_2O_5	0.98	1.00											
SiO_2	-0.18	-0.29	1.00										
Al_2O_3	0.15	0.04	0.61	1.00									
Fe ₂ O ₃	-0.52	-0.50	-0.19	-0.22	1.00								
FeO	-0.50	-0.47	-0.20	-0.26	0.97	1.00							
MgO	-0.77	-0.71	-0.46	-0.51	0.60	0.59	1.00						
CaO	0.66	0.75	-0.85	-0.43	-0.17	-0.14	-0.07	1.00					
Na ₂ O	0.88	0.90	-0.38	-0.08	-0.41	-0.41	-0.57	0.76	1.00				
K ₂ O	0.23	0.12	0.55	0.99	-0.24	-0.27	-0.55	-0.35	0.01	1.00			
MnO	-0.62	-0.58	-0.30	-0.34	0.97	0.95	0.76	-0.14	-0.47	-0.37	1.00		
TiO ₂	0.55	0.43	0.15	0.50	-0.37	-0.42	-0.53	0.12	0.37	0.50	-0.45	1.00	
TOC	0.46	0.35	0.44	0.42	-0.22	-0.19	-0.66	-0.12	0.24	0.48	-0.40	0.45	1.00

The correlation coefficients between \sum REY and MgO, MnO, Fe₂O₃, and FeO are -0.77, -0.62, -0.52, and -0.50, respectively, indicating a clear to moderate negative correlation, while any two of MgO, FeO, Fe₂O₃, and MnO are an obvious to significant positive correlation. This is consistent with the phenomenon that Fe²⁺ and Mn²⁺ isomorphism replaces Mg²⁺ in dolomite. It can be seen that, when the content of dolomitic cement in phosphate rock increases, the content of rare earth decreases. This indicates that REEs do not occur in dolomite. The siliceous components in the ore, on the one hand, contribute to the formation of clay minerals, and, on the other hand, exist as ore cements. The \sum REY has a weak negative correlation with SiO₂, and the correlation coefficient is -0.18, indicating that, when the siliceous cement increases, the rare earth decreases, indicating that REEs do not occur in gangue mineral quartz.

The aforementioned analysis indicates that REEs predominantly occur in apatite and are absorbed by collophanite and organic matter. Their host minerals exhibit no correlation with gangue minerals, such as dolomite and quartz.

4.2. Microdistribution and Occurrence of REEs Based on SEM-EDS and XRD

The SEM analysis, combined with the polarized light microscopy (PLM) observation, reveals that the REE-bearing phosphate sedimentary ore has a distinct bioclastic structure (Figure 5). These bioclasts, visually indicated by yellow dashed lines, exhibit an elongated shape and are arranged in a specific direction. Through EDS point analysis, several interesting observations can be made regarding the composition of these bioclasts. Positions G1, G3, G6, and G7 within the bioclasts show a relatively high phosphorus (P) content, while the magnesium (Mg) content is low. After performing calculations, it has been determined that the primary minerals found in G1, G3, G6, and G7 are collophanite (Clh) (apatite + illite). Additionally, a minor presence of finely grained apatite (Ap) has been detected in the vicinity of G6. In contrast, at positions G4, G5, and G8, a high Mg content is observed, accompanied by a low P content. The calculation results show that the main mineral is dolomite. As cement, the dolomite crystals in this region are intact and rhombus-shaped. Analysis of the G2 sample revealed a relatively high silicon (Si) content. Further calculations identified it as a short columnar quartz crystal (Qtz) with a sporadic distribution, indicating the presence of siliceous cement. However, no independent rareearth minerals, such as monazite, allanite, bastnaesite, or phosphyttrite, were found in either bioclasts or cement. This finding suggests that the REEs in the phosphate deposit in Zhijin do not exist independently or in easily detectable concentrations using the SEM-EDS analysis. However, it is important to note that these results do not rule out the possibility of REEs being present in the form of extremely fine-grained particles that fall below the detection limits of the SEM-EDS technique. This conclusion is in line with the finding that the dominant minerals observed in the XRD pattern of the powder are apatite and dolomite, while no rare earth independent minerals were detected (Figure 6).



Figure 5. The SEM-EDS analysis and oxide percentages (%) of dolomitic phosphate rocks.

The surface scanning diagram in Figure 7 provides a clear depiction of the distribution range of collophane and apatite biological debris, which primarily consist of the chemical element phosphorus (P). Interestingly, this distribution range is found to be in perfect complementarity with that of dolomite and siliceous cement, which predominantly consist of the elements magnesium (Mg) and silicon (Si). The overlay image further confirms this observation, as the distribution range of P elements corresponds closely with that of Y, a characteristic rare-earth element found in the dolomitic phosphate deposit in Zhijin. The areas marked in yellow, representing the distribution of P, overlap with the areas in red, indicating the distribution of Y, resulting in a vibrant orange color. This overlap illustrates a positive correlation between the distributions of P and Y elements. Conversely, the

distributions of Mg and Si elements are distinctly separated from the distributions of P and Y elements. This signifies that REEs are predominantly present in bioclasts, particularly in apatite or collophanite, with minimal occurrence in the cement materials. Veinstone minerals, such as dolomite and quartz, do not serve as hosts for REEs. Based on previous studies, it has been found that apatite, which has a hexagonal columnar structure, can incorporate REEs by substituting calcium ions (Ca²⁺) within its crystal structure [9]. This means that REEs can exist in apatite through a process called solid–solution exchange. On the other hand, collophanite, being a conglomeration of fine-grained minerals, such as nanoscale apatite, also contains various other minerals, like micro- or nanosized clay minerals, iron oxides, pyrite, and quartz [5,31]. As a result, collophanite possesses a strong capability to adsorb REEs.



Figure 6. The XRD pattern of phosphorite.

Based on the analyses conducted using polarizing microscopy, SEM-EDS, and XRD, it can be inferred that the examined samples do not harbor distinct rare-earth minerals. Nevertheless, it was noted that regions with significant concentrations of yttrium (Y) and phosphorus (P) exhibit a high degree of overlap, especially within the small shelly fossil bioclasts. This observation leads us to speculate that REEs, with Y as the primary constituent, may undergo an isomorphic substitution with calcium ions (Ca²⁺) within the crystal structure of apatite. As a result, these elements could potentially be present within the apatite lattice or adsorbed onto collophane.



Figure 7. Cont.



Figure 7. SEM elemental mapping of dolomitic phosphorite. (a) Distribution of Mg elements; (b) Distribution of P elements; (c) Distribution of Y elements; (d) Distribution of Si elements; (e) Overlay of elemental distributions.

4.3. Microdistribution and Occurrence Modes of REEs Based on LA-ICP-MS

In this study, we utilized in situ LA-ICP-MS to investigate the content of REEs and phosphorus in various components of phosphate rocks, including particles such as bioclasts and sand debris, as well as cement materials. A total of 11 samples were analyzed, with a selection of 64 points for examination. Among these points, 24 were from bioclast samples, 8 were from sand debris samples, 5 were from agglomerate samples, and 27 were from cement material samples. The spatial distribution of certain sampling points is presented in Figure 8, whereas the statistical results of the analysis can be found in Table 4.

A one-way analysis of variance was performed on the test point data (Table 5). The results indicated that the P element and \sum REY element showed significant differences across different test positions. The F values, which represent the ratio of the mean square between groups to the mean square within groups, were found to be 10.619 and 22.901 for the P element and \sum REY element, respectively. Furthermore, the *p* values, which indicate the level of difference between the control group and the experimental group, were both lower than 0.05 and 0.01, respectively. These findings suggest that the content of the P element and \sum REY element varied significantly at different test positions.

Figure 9, which displays the histogram of the average content of the P element and \sum REY element at different positions, reveals a notable similarity in the trend of the phospho-

rus and REE content among various types of particles and cement materials with different compositions. The average content of \sum REY elements, ranked from highest to lowest, was as follows: the interior of bioclasts (2325.33 ppm), biological shell walls (2270.13 ppm), the interior of sand debris (1811.99 ppm), nondolomitization sand debris edges (1695.15 ppm), phosphate agglomerates (1521.45 ppm), phosphate cement (1456.29 ppm), bright crystalline dolomitic cement (308.15 ppm), siliceous cement (48.59 ppm), dolomitization sand debris edges (41.42 ppm). This sequence highlights the distribution patterns of \sum REY elements in the different materials. In addition, there is a strong consistency between the distributions of REEs and phosphorus, as indicated by a high correlation coefficient (R) of 0.92 (Figure 10).



Figure 8. Typical in situ test locations for the REE-bearing phosphate ore in Zhijin. The yellow blank shows the in-situ test area; (**a**) Interior of bioclasts and biological shell walls, interior and edges of sand debris, phosphate agglomerates, and phosphate cement; (**b**) Interior and edges of sand debris and dolomitic cement; (**c**) Phosphate cement; (**d**) Siliceous cement; (**a**'-**d**') The location of the in-situ test points.

Sample No.	Test Position	Р	P (Avg)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Y	∑REY	∑REY (Avg)
GZW-2-1	phosphate agglomerates	304,323.17 299,898.52 123,584.77 125,287.36 114,251.47	193,469.06	454.29 428.05 174.09 284.89 336.92	293.00 278.57 103.64 173.59 200.43	79.98 73.89 27.57 47.14 51.81	335.93 308.51 116.69 196.22 214.98	60.84 54.74 20.81 34.06 36.22	15.44 14.21 5.04 9.04 8.94	74.64 65.46 24.00 43.18 44.03	9.72 8.59 3.15 5.61 5.67	60.98 54.57 19.34 35.96 36.38	13.02 11.54 4.16 7.73 7.90	35.23 31.06 11.31 20.81 21.30	3.89 3.54 1.25 2.43 2.40	19.78 18.58 6.59 12.58 13.05	2.40 2.31 0.80 1.59 1.58	706.81 623.46 233.36 420.33 435.66	2165.94 1977.08 751.82 1295.15 1417.28	1521.45
GZW-5-1 GZW-3-1 GZW-6-1 GZW-6-2 GZW-6-5 GZW-7-1 GZW-7-3	interior of bioclasts	203,510.74 205,590.03 172,549.65 297,242.94 208,288.38 218,632.79 215,972.39 235,223.76 334,237.58 327,423.26 367,203.36 370,768.53	263,053.62	447.84 473.25 392.14 442.44 557.18 512.79 519.05 452.19 529.99 615.96 543.62 533.42	307.72 322.18 226.83 253.63 311.50 328.35 320.67 290.75 291.17 336.53 306.45 304.70	83.16 88.03 65.35 72.62 85.58 86.98 85.10 82.93 82.55 90.13 86.18 87.48	361.62 380.76 275.94 303.86 365.36 363.65 364.74 365.30 339.95 368.76 365.32 370.47	$\begin{array}{c} 67.75\\72.06\\48.85\\54.66\\61.61\\64.96\\64.18\\68.76\\60.28\\64.43\\66.91\\65.83\end{array}$	$18.81 \\ 19.81 \\ 11.86 \\ 12.91 \\ 14.62 \\ 18.10 \\ 17.90 \\ 19.46 \\ 13.61 \\ 14.06 \\ 15.38 \\ 15.39 \\ 15.39$	86.47 90.17 63.70 70.00 77.81 80.21 82.68 88.97 77.90 81.36 84.28 85.83	$11.31 \\ 11.61 \\ 8.56 \\ 9.38 \\ 10.22 \\ 10.06 \\ 10.73 \\ 11.20 \\ 10.46 \\ 10.55 \\ 10.87 \\ 11.08 \\$	$\begin{array}{c} 68.64 \\ 72.28 \\ 54.58 \\ 58.75 \\ 64.36 \\ 63.85 \\ 66.57 \\ 70.52 \\ 66.15 \\ 69.00 \\ 69.66 \\ 68.93 \end{array}$	$\begin{array}{c} 14.25\\ 15.06\\ 11.53\\ 12.73\\ 14.31\\ 13.53\\ 14.43\\ 14.17\\ 14.69\\ 14.98\\ 14.96\\ 14.84 \end{array}$	37.53 39.02 30.99 34.38 38.60 36.55 37.80 36.13 39.34 40.78 39.82 39.72	$\begin{array}{c} 4.09\\ 4.10\\ 3.35\\ 3.73\\ 4.30\\ 4.15\\ 4.10\\ 3.82\\ 4.35\\ 4.63\\ 4.34\\ 4.32\end{array}$	$19.04 \\ 19.89 \\ 16.67 \\ 18.42 \\ 21.01 \\ 19.65 \\ 19.32 \\ 16.67 \\ 21.85 \\ 22.75 \\ 20.75 \\ 20.57 \\ $	2.33 2.35 2.02 2.23 2.56 2.47 2.37 2.02 2.74 2.90 2.60 2.55	752.42 792.99 636.88 701.14 809.47 721.00 785.23 762.99 827.21 841.45 834.85 830.15	2283.00 2403.56 1849.26 2050.87 2428.49 2326.30 2394.87 2385.88 2382.24 2578.26 2465.99 2455.28	2325.33
GZW-3-1 GZW-6-2 GZW-6-5 GZW-7-1 GZW-7-2 GZW-7-3	biological shell walls	$\begin{array}{c} 147,448.20\\ 219,451.47\\ 220,438.86\\ 111,517.25\\ 58,303.98\\ 426,778.54\\ 202,821.84\\ 214,149.22\\ 250,125.48\\ 298,303.57\\ 318,726.59\\ 330,428.29\\ \end{array}$	233,207.77	428.36 560.63 600.22 328.58 173.50 608.09 528.55 498.35 543.48 584.71 600.97 657.55	$\begin{array}{c} 239.08\\ 310.74\\ 332.90\\ 196.69\\ 105.81\\ 362.99\\ 323.08\\ 316.03\\ 305.81\\ 328.09\\ 327.31\\ 358.92 \end{array}$	67.61 86.86 93.97 50.34 26.77 105.55 92.31 88.25 84.67 88.85 88.70 98.49	$\begin{array}{c} 283.45\\ 359.71\\ 388.63\\ 207.17\\ 109.33\\ 439.34\\ 389.39\\ 384.35\\ 350.79\\ 370.04\\ 367.07\\ 408.65\\ \end{array}$	$50.35 \\ 64.98 \\ 69.63 \\ 36.75 \\ 19.69 \\ 78.20 \\ 69.07 \\ 70.00 \\ 63.75 \\ 66.64 \\ 64.45 \\ 72.68 \\$	$11.31 \\ 15.13 \\ 16.08 \\ 9.45 \\ 5.83 \\ 18.79 \\ 17.20 \\ 18.78 \\ 14.57 \\ 14.84 \\ 14.40 \\ 15.61 \\$	63.18 79.30 84.84 44.33 24.02 96.44 88.02 89.76 77.84 81.72 81.31 89.45	$\begin{array}{c} 8.54 \\ 10.30 \\ 11.11 \\ 5.97 \\ 3.25 \\ 12.63 \\ 11.42 \\ 11.24 \\ 10.44 \\ 10.86 \\ 10.83 \\ 11.61 \end{array}$	54.57 66.20 70.56 38.26 19.79 79.80 71.75 70.90 66.32 71.21 69.52 76.41	$\begin{array}{c} 12.25\\ 14.41\\ 15.13\\ 8.16\\ 4.39\\ 16.58\\ 15.02\\ 14.53\\ 14.90\\ 15.26\\ 15.03\\ 16.44 \end{array}$	$\begin{array}{c} 31.40\\ 38.90\\ 41.02\\ 22.89\\ 11.80\\ 42.04\\ 39.32\\ 37.40\\ 38.46\\ 41.28\\ 41.42\\ 44.27\end{array}$	$\begin{array}{c} 3.45 \\ 4.27 \\ 4.52 \\ 2.60 \\ 1.39 \\ 4.53 \\ 4.41 \\ 3.92 \\ 4.37 \\ 4.73 \\ 4.64 \\ 5.25 \end{array}$	$\begin{array}{c} 17.03\\ 21.76\\ 22.96\\ 13.44\\ 7.12\\ 20.93\\ 20.55\\ 18.65\\ 21.34\\ 23.30\\ 21.81\\ 24.77 \end{array}$	2.09 2.65 2.80 1.75 0.83 2.52 2.62 2.26 2.64 2.94 2.86 3.18	660.97 825.75 863.38 464.50 246.16 882.45 824.19 798.21 802.56 862.77 847.55 937.16	1933.64 2461.59 2617.73 1430.89 759.67 2770.87 2497.00 2422.62 2401.95 2567.23 2557.87 2820.45	2270.13
GZW-3-1 GZW-5-1 GZW-7-1 GZW-8-3	interior of sand debris	276,426.52 163,127.15 331,929.57 86,431.63	214,478.72	383.64 361.47 507.22 203.81	254.26 275.34 305.01 134.62	75.79 80.93 80.42 32.08	331.78 369.15 332.04 133.90	59.60 74.87 58.37 25.06	17.18 25.40 16.60 5.41	73.27 91.96 72.81 29.82	9.44 11.46 9.50 4.02	57.87 68.45 61.55 25.43	12.11 13.84 13.06 5.63	30.87 34.54 35.07 15.06	3.23 3.55 3.90 1.67	15.22 15.33 18.12 8.57	1.81 1.81 2.39 1.05	630.01 689.61 731.11 300.86	1956.10 2117.71 2247.15 926.99	1811.99
GZW-3-1 GZW-5-1	dolomitization sand debris edges	1422.21 4651.76	3036.99	7.49 7.99	4.15 6.52	1.07 1.57	3.96 7.70	0.75 1.44	0.17 0.40	0.93 1.98	0.13 0.24	1.08 1.38	0.32 0.28	1.00 0.80	0.12 0.09	0.85 0.55	0.15 0.07	14.54 15.10	36.73 46.12	41.43

Table 4. In situ microarea phosphorus and REE content (ppm) of Zhijin REE-bearing phosphate rock.

Table 4. Cont.

Sample No.	Test Position	Р	P (Avg)	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Ŷ	∑REY	∑REY (Avg)
GZW-7-1 GZW-8-3	ondolomitization and debris edges	42,0900.80 56,128.66	238,514.73	606.65 193.98	340.32 127.12	88.62 30.54	354.48 131.39	61.03 23.75	16.00 5.28	76.76 29.02	9.90 3.85	64.73 25.70	14.15 5.55	37.09 14.54	4.29 1.60	20.75 7.61	2.76 0.89	803.14 288.83	2500.66 889.64	1695.15
GZW-2-1	s n	69,238.05 80,105.51 61,407.58 85,372.64		75.04 167.91 140.78 167.80	45.73 109.26 91.37 107.87	12.65 28.73 23.91 28.00	52.67 125.95 103.79 119.92	9.55 22.32 18.08 20.91	2.59 6.08 4.93 5.32	10.58 25.68 20.75 24.65	1.34 3.36 2.85 3.18	8.61 21.44 16.62 20.30	1.72 4.57 3.63 4.32	5.03 12.21 9.76 11.85	0.52 1.49 1.11 1.39	2.92 8.78 5.79 8.13	0.37 1.22 0.73 1.05	96.33 248.10 197.14 238.81	325.64 787.10 641.22 763.50	
GZW-6-2 GZW-7-1	cement	205,433.86 353,636.01 77,620.73	177,192.69	379.44 319.43 178.33	213.59 187.86 105.27	58.72 54.64 31.28	243.63 230.72 131.48	43.76 42.02 24.19	11.27 10.09 5.58	52.72 52.66 30.06	6.94 6.79 4.18	43.19 44.06 26.61	9.26 9.04 5.75	25.21 24.69 15.27	2.94 2.56 1.71	14.13 12.81 8.80	1.73 1.55 1.12	514.73 486.68 296.72	1621.26 1485.59 866.33	1456.29
GZW-7-3	Н	233,151.85 270,891.10 286,020.50		525.13 489.34 503.71 573.39	291.02 283.64 296.33 325.37	79.84 81.40 84.87 92.78	342.60 356.92 394.47	64.76 64.80 72.67	12.88 14.94 15.05 16.60	80.34 83.14 91.02	9.40 10.50 10.75 11.66	67.78 69.28 75.64	13.48 14.32 14.57 15.71	37.06 38.84 42.29	4.05 4.06 4.09 4.70	20.01 19.45 19.72 22.95	2.43 2.35 2.48 2.76	740.71 775.99 795.62 875.06	2282.80 2288.51 2360.15 2617.09	
GZW-5-1	stalline cement	5074.21 46,630.75		13.10 139.78	11.44 89.82	2.39 25.27	10.14 108.98	2.20 20.75	0.59 5.55	2.38 24.31	0.31 3.19	2.12 19.84	0.44 4.18	1.41 11.04	0.17 1.32	1.35 6.63	0.22 0.92	23.56 217.79	71.82 679.36	
GZW-6-5	ght cry omitic	29,280.88	20,893.81	87.94	58.60	15.10	64.39	11.65	3.49	14.25	1.68	11.28	2.50	6.44	0.71	3.67	0.44	132.77	414.91	308.15
GZW-7-2	bri dol	2589.38		12.71	7.16	1.69	7.82	1.23	0.40	1.86	0.27	2.18	0.54	1.82	0.31	1.84	0.31	26.35	66.49	
GZW-3-1 GZW-5-2 GZW-6-5 GZW-7-1 GZW-8-3	siliceous cement	$\begin{array}{c} 132.78\\ 43.31\\ 238.92\\ 10,447.88\\ 55.59\\ 478.71\\ 147.36\\ 258.95\\ 87.95\\ 0.00\\ 19.03\\ 74.94\end{array}$	998.74	$14.66 \\ 29.47 \\ 3.22 \\ 32.23 \\ 11.49 \\ 5.04 \\ 3.43 \\ 2.65 \\ 1.98 \\ 3.26 \\ 6.35 \\ 2.72 \\ 2.72 \\ 1.92 \\ 3.26 \\ 3.26 \\ 3.26 \\ 3.26 \\ 3.27 \\ 3.26 \\ 3.26 \\ 3.27 \\ 3.26 \\ 3.27 \\ 3.2$	7.09 11.35 4.13 21.66 5.51 2.19 2.00 1.52 1.02 2.07 3.09	$\begin{array}{c} 1.79\\ 3.31\\ 0.45\\ 5.48\\ 1.36\\ 0.41\\ 0.39\\ 0.32\\ 0.23\\ 0.33\\ 0.57\\ 0.22\end{array}$	$\begin{array}{c} 7.00 \\ 12.99 \\ 2.31 \\ 23.02 \\ 5.60 \\ 1.69 \\ 1.46 \\ 1.20 \\ 0.78 \\ 1.22 \\ 1.89 \\ 2.96 \end{array}$	1.22 1.90 0.44 4.10 0.81 0.36 0.20 0.19 0.12 0.30 0.19	$\begin{array}{c} 0.28 \\ 0.43 \\ 0.13 \\ 1.17 \\ 0.26 \\ 0.09 \\ 0.05 \\ 0.03 \\ 0.07 \\ 0.06 \\ 0.22 \end{array}$	$\begin{array}{c} 1.50\\ 2.95\\ 0.49\\ 4.95\\ 1.27\\ 0.30\\ 0.26\\ 0.16\\ 0.39\\ 0.40\\ 0.16\end{array}$	0.25 0.46 0.07 0.67 0.25 0.13 0.07 0.05 0.03 0.08 0.09	$ \begin{array}{r} 1.99\\ 2.98\\ 0.59\\ 4.05\\ 1.89\\ 1.20\\ 0.78\\ 0.36\\ 0.49\\ 0.72\\ 0.84\\ 2.42 \end{array} $	0.56 0.83 0.15 0.86 0.51 0.47 0.26 0.13 0.13 0.27 0.31	$1.95 \\ 2.70 \\ 0.64 \\ 2.30 \\ 1.66 \\ 2.14 \\ 1.13 \\ 0.54 \\ 0.89 \\ 1.04 \\ 1.45 \\ 2.65 \\ 0.55 \\ $	0.28 0.40 0.10 0.23 0.24 0.45 0.25 0.10 0.13 0.19 0.31	2.00 2.20 0.74 1.28 1.53 4.30 1.94 0.80 1.05 1.26 2.44 1.26	0.27 0.35 0.14 0.19 0.22 0.72 0.30 0.13 0.17 0.22 0.41	$\begin{array}{c} 27.59\\ 53.20\\ 6.93\\ 47.34\\ 25.88\\ 17.87\\ 10.46\\ 6.07\\ 6.92\\ 11.47\\ 13.85\\ 7.52\end{array}$	68.44 125.50 20.54 149.52 58.48 37.55 23.04 14.36 14.15 22.88 32.24	48.59

Analysis Item	Dolomitic Cement (n = 4)	Interior of Bioclasts (n = 12)	Biological Shell Walls (n = 12)	Dolomitization Sand Debris Edges (n = 2)	Interior of Sand Debris (n = 4)	Siliceous Cement (<i>n</i> = 12)	Phosphate Agglomer- ates (n = 5)	Phosphate Cement (<i>n</i> = 11)	Nondolomitization Sand Debris Edges (n = 2)	Difference	Quadratic Sum	Freedom	Mean Square	F Value	p Value
	20,893.81	263,053.62	233,207.77	3036 99	214,478.72	998 74	193,469.06	177,192.69	238.514.73	among	654,787,425,461.879	8	81,848,428,182.735	10.619	0.000
Р	± 20,960.64	± 71,242.96	$^{\pm}_{101,422.63}$	\pm 2283.64	± 110,552.06	± 2978.71	± 99,277.20	± 105,319.39	± 257,932.85	intragroup total	423,944,291,676.237 1,078,731,717,138.115	55 63	7,708,078,030.477		
	308 15	2325.33	2270 13	41 42	1811 99	48.59	1521 45	1456 29	1695 15	among	50,652,366.216	8	6,331,545.777	22.901	0.000
∑REY	± 296.34	± 197.90	± 608.52	± 6.64	± 601.89	± 45.21	± 565.10	± 821.83	± 1139.16	intragroup total	215,206,001.072 65,858,367.288	55 63	276,472.747		

Table 5. Statistical table of one-way ANOVA of test location (mean \pm standard deviation).



Figure 9. P- \sum REY content histogram.



Figure 10. P-∑REY correlation plot.

This shows that particles, such as bioclasts, sand debris, phosphate agglomerates, and phosphate cement, are found to contain elevated levels of REEs, primarily in the form of apatite and collophanite. However, a significant decrease in the REE content is observed at the edges of certain sand debris, which can be attributed to the dolomitization processes. The replacement of apatite by dolomite at the peripheries of these sand debris is confirmed through microscopic observations using a polarizing microscope. Notably, the peripheral regions of nondolomitized sand debris still exhibit high concentrations of phosphorus and REEs. Yet, dolomite cement and silicate cement display a low REE content, indicating that the main veinstone minerals, such as dolomite and quartz, do not exhibit a significant enrichment of REEs.

In summary, there is a close relationship between REEs and phosphorus in the REEbearing phosphate ore in Zhijin. These elements are likely to be present in the form of isomorphic substitutions in the apatite lattice or to be adsorbed onto phosphate rocks. The enrichment of both REEs and phosphorus is particularly notable in bioclasts, with a higher concentration observed in the interior of these organic fragments compared to their outer shells. This phenomenon may be attributed to the decomposition of biological death software and the high presence of REEs in the original soft tissue [32]. And the preferential filling occurs as a result of wave and tide activities, which causes the phosphorus-rich rocks to separate and deposit within the voids left by decomposed soft tissues. Moreover, REEs are found widely distributed in particles, such as sand debris, the edges of nondolomitized sand debris and agglomerates, and in phosphate cement, while the dolomite cement and siliceous cement are scarcely distributed. Additionally, dolomitization during diagenesis also leads to extremely low levels of rare-earth content in certain areas of sand debris.

4.4. Sequential Extraction of REEs

To further clarify the occurrence modes of REEs, a six-step chemical extraction experiment was meticulously designed. The measured value of the whole rock closely aligned with the total REE content calculated in each step (Table 6), validating the effectiveness of the experimental design. Upon analyzing the test results (Table 7), it became evident that different samples exhibited distinct distribution patterns of various REE states. Although the proportions of different REE states varied, they remained consistent among the different samples. The average content of each form of rare-earth mineral, ranked from highest to lowest in the total rare-earth composition, is as follows: residual REEs (78.07%) account for the largest proportion of the total REE content on average, followed by REEs bound to organic matters (18.75%), REEs bound to ferromanganese oxides (1.47%), exchangeable REEs (0.89%), REEs bound to carbonates (0.72%), and water-soluble REEs (0.10%), successively.

				1				0	1									
Sample No.	Extraction Steps	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu	Ŷ	∑REY	Each Step Percentage of Total
-		338.200	223.000	55.200	236.000	42.700	10.500	50.800	6.940	41.000	8.900	22.800	2.760	13.200	1.660	567.000	1620.660	
	water-soluble form	0.796	0.587	0.139	0.501	0.072	0.017	0.078	0.014	0.072	0.018	0.044	0.006	0.030	0.004	1.187	3.562	0.23%
	exchangeable ion form	6.670	4.141	0.916	2.897	0.493	0.177	0.570	0.122	0.536	0.163	0.323	0.071	0.255	0.051	12.362	29.747	1.92%
	carbonate-bound form	5.847	3.927	0.893	2.672	0.527	0.320	0.502	0.136	0.434	0.163	0.298	0.071	0.204	0.061	9.965	26.019	1.68%
GZW2-1	iron-manganese	7 705	4.446	1.004	1.016	0 (24	0.451	0.040	0 1 4 2	0.00	0.104	0.404	0.07	0.200	0.054	12 092	24.000	2 200/
	oxide-bound form	7.705	4.446	1.004	4.016	0.624	0.451	0.848	0.142	0.692	0.194	0.494	0.067	0.380	0.054	12.982	34.096	2.20%
	organic matter-bound form	47.431	35.039	8.559	33.135	4.440	1.102	6.335	1.002	5.050	1.416	3.613	0.396	2.082	0.276	61.827	211.702	13.68%
	residual form	280.505	171.816	45.584	173.940	34.135	8.820	40.248	6.408	30.323	7.386	18.493	1.998	11.496	1.347	409.395	1241.892	80.28%
	sum	348.953	219.955	57.094	217.161	40.291	10.886	48.579	7.824	37.105	9.341	23.263	2.609	14.447	1.793	507.718	1547.018	100.00%
		405.300	269.000	68.700	294.000	53.400	12.500	62.400	8.600	50.500	10.800	27.300	3.290	15.500	1.940	669.000	1952.230	
	water-soluble form	0.768	0.564	0.148	0.576	0.097	0.042	0.125	0.012	0.087	0.019	0.040	0.007	0.025	0.004	0.970	3.484	0.19%
	exchangeable ion form	2.577	1.340	0.272	1.074	0.231	0.908	0.265	0.037	0.224	0.054	0.102	0.027	0.071	0.015	4.250	11.449	0.61%
	carbonate-bound form	3.335	2.047	0.490	2.218	0.381	1.020	0.401	0.065	0.340	0.102	0.158	0.048	0.092	0.031	6.875	17.601	0.94%
GZW2-3	iron-manganese oxide-bound form	13.398	7.076	2.021	8.879	1.632	0.954	2.108	0.211	1.609	0.340	0.809	0.104	0.466	0.058	20.983	60.649	3.24%
	organic matter-bound form	74.625	55.854	13.692	63.504	9.594	2.471	13.572	1.323	9.870	2.184	5.009	0.576	2.232	0.288	83.784	338.577	18.08%
	residual form	317.693	172.574	47.014	206.072	45.696	9.914	48.912	5.719	44.544	9.124	20.961	2.640	11.325	1.365	497.436	1440.989	76.95%
	sum	412.396	239.455	63.636	282.323	57.631	15.307	65.384	7.368	56.674	11.823	27.079	3.402	14.212	1.760	614.298	1872.748	100.00%
		380,140	218.000	56.100	238.000	42.200	9.630	50.800	7.090	42,500	9.400	24.300	2.980	14,400	1.830	614.000	1711.370	
	water-soluble form	0.131	0.070	0.019	0.074	0.014	0.009	0.012	0.003	0.014	0.003	0.006	0.001	0.004	0.001	0.254	0.616	0.04%
	exchangeable ion form	3.034	1.537	0.360	1.258	0.299	0.643	0.224	0.055	0.292	0.075	0.122	0.034	0.082	0.020	6.112	14.148	0.81%
	carbonate-bound form	1.519	0.585	0.163	0.530	0.129	0.597	0.107	0.034	0.116	0.048	0.051	0.027	0.041	0.020	3.018	6.985	0.40%
GZW4-1	iron-manganese oxide-bound form	2.500	1.093	0.277	1.182	0.235	0.451	0.229	0.040	0.239	0.052	0.120	0.018	0.073	0.014	5.168	11.690	0.67%
	organic matter-bound form	77.353	48.678	12.498	58.650	8.706	2.025	10.269	1.556	9.726	2.244	5.049	0.582	2.295	0.402	114.953	354.986	20.22%
	residual form	292.451	149.616	39.480	167.914	36.776	6.944	34.910	5.814	37.304	7.864	18.393	2.380	10.437	1.676	555.473	1367.430	77.88%
	sum	376.989	201.579	52.798	229.609	46.160	10.668	45.751	7.502	47.690	10.285	23.741	3.042	12.931	2.134	684.975	1755.854	100.00%
		398 500	234 000	59 800	254 000	45,300	10 400	55 000	7 630	45 600	9 930	25,300	3 040	14 200	1 770	654 000	1818 470	
	water-soluble form	0.118	0.071	0.018	0.076	0.011	0.004	0.013	0.002	0.011	0.002	0.007	0.001	0.004	0.001	0.195	0.536	0.03%
	exchangeable ion form	2.935	1.845	0.417	1.488	0.272	0.153	0.306	0.061	0.245	0.068	0.150	0.043	0.095	0.020	5.194	13.290	0.73%
	carbonate-bound form	1.073	0.663	0.270	0.468	0.129	0.133	0.109	0.036	0.088	0.034	0.068	0.026	0.041	0.020	2.091	5.247	0.29%
GZW7-3	iron-manganese oxide-bound form	1.803	0.930	0.240	1.019	0.162	0.230	0.218	0.033	0.157	0.037	0.112	0.017	0.066	0.010	3.029	8.062	0.44%
	organic matter-bound form	57.523	36.665	9.893	43.988	5.256	1.220	8.220	1.175	5.718	1.278	3.882	0.405	1.788	0.216	78.848	256.072	14.12%
	residual form	338.844	185.418	50.158	215.128	37.470	6.962	46.768	7.236	38.132	7.890	24.528	2.930	13.144	1.572	554.715	1530.493	84.39%
	sum	402.295	225.591	60.995	262.165	43.300	8.701	55.634	8.543	44.352	9.310	28.746	3.421	15.138	1.839	644.070	1813.700	100.00%
		280 150	204.000	49 400	220.000	41 800	12 700	50.000	6 560	37 100	7 660	18 700	2 140	9 700	1 180	471 000	1412 090	
	water-soluble form	0.082	0.063	0.016	0.059	0.010	0.012	0.011	0.002	0.009	0.002	0.004	0.001	0.002	0.001	0 154	0 427	0.03%
	exchangeable ion form	1 149	0.876	0.196	0.629	0.116	0.122	0.129	0.036	0.102	0.034	0.051	0.020	0.031	0.001	2 550	6.054	0.42%
GZW8-2	carbonate-bound form	0.978	0 794	0.196	0.604	0.122	0.136	0.129	0.036	0.102	0.041	0.021	0.020	0.026	0.011	1 904	5127	0.36%
92110-2	iron-manganese oxide-bound form	1 729	1.082	0.291	1.383	0.122	0.130	0.129	0.043	0.212	0.047	0.106	0.020	0.020	0.014	3 515	9 200	0.64%
	organic matter-bound form	79.604	75.343	18.030	83.978	10.392	3.462	15.294	2.075	9.918	2.112	4.811	0.486	2.061	0.312	110.723	418,599	29.09%
	residual form	191.226	136.355	35.025	156.100	29.554	9.414	34.558	5.334	26.584	5.326	12.278	1.440	6.287	0.956	349.153	999.589	69.46%

Table 6. The statistical table presents the REE content in each stage of the stepwise extraction.

Extraction			REI	Es Content (p	pm)			The Average
Steps	Occurrence Forms of REEs	GZW2-1	GZW2-3	GZW4-1	GZW7-3	GZW8-2	Average Value	Proportion of REEs in Each Form (%)
1	water-soluble form	3.56	3.48	0.62	0.54	0.43	1.73	0.10
2	exchangeable ion form	29.75	11.45	14.15	13.29	6.05	14.94	0.89
3	carbonate-bound form	26.02	17.60	6.98	5.25	5.13	12.20	0.72
4	iron-manganese oxide-bound form	34.10	60.65	11.69	8.06	9.20	24.74	1.47
5	organic matter-bound form	211.70	338.8	354.9	256.7	418.60	315.99	18.75
6	residual form	1241.89	1440.99	1367.42	1530.49	999.59	1316.08	78.07
	Sum	1547.02	1872.75	1755.85	1813.70	1439.00	1685.68	100.00

Table 7. The content and proportion of REEs in the sequential extraction.

4.4.1. Water-Soluble State and Exchangeable State

Water-soluble and exchangeable REEs can be adsorbed onto soil and sediment surfaces through diffusion. They are sensitive to environmental changes and easily migrate. In neutral solutions, they can be desorbed by ion-exchange processes [33]. According to Table 2, the content of water-soluble and exchangeable REEs in the phosphate ore in Xinhua, Zhijin, ranges from 0.43 ppm to 29.75 ppm, with an average of 8.33 ppm. However, these two sates only account for 0.03% to 1.92% (average: 0.99%) of the total REE content. This finding indicates that the content of water-soluble and exchangeable REEs is extremely low, so it is difficult to extract them with neutral solutions. Therefore, water-soluble and exchangeable states are not the main modes of REE occurrence.

4.4.2. Carbonate-Bound State

REEs bound to carbonates occur in the form of precipitates or coprecipitates in carbonate minerals. They are sensitive to changes in pH and can be easily released in acidic conditions [34]. To specifically target these carbonate-bound REEs, an extraction experiment was conducted using acetic acid—a weak acid that does not react with ferromanganese oxides and has no impact on organic matter. According to the data in Table 2, the content of REEs bound to carbonates ranges from 5.13 ppm to 26.02 ppm, with an average of 12.20 ppm. REEs bound to carbonates account for an extremely low proportion (range: 0.29% to 1.68%; average: 0.72%) of the total REE content. This suggests that the content of REEs in metal carbonates is low, and it is difficult to extract them from phosphate rocks with weak acids. Therefore, the carbonate-bound state is not the main mode of REE occurrence.

4.4.3. Ferromanganese Oxide-Bound State

REEs are commonly found bound to ferromanganese oxides, either enclosed within the oxides or forming coprecipitates. The binding between REEs and ferromanganese oxides is primarily through strong ionic bonds [35]. However, when the conditions become reducing, the stability of metal ions in water is compromised. To release the bound REEs, hydroxylamine hydrochloride can be used to reduce the iron and manganese in the sample to soluble low-valent states.

After sample extraction with a hydroxylamine hydrochloride solution, the content of REEs bound to ferromanganese oxides in the sample ranges from 9.20 ppm to 34.10 ppm, with an average of 24.74 ppm. REEs bound to ferromanganese oxides account for a relatively low proportion (range: 0.44% to 3.24%; average: 1.47%) of the total REE content. This indicates that the reducible metal content in the sample is low, and only a small proportion of REEs bound to ferromanganese oxides can be released during the reduction in iron and manganese to soluble low-valent states. Hence, the ferromanganese-bound form is not the primary mode of REE occurrence.

4.4.4. Organic Matter-Bound Form

REEs bound to organic matters are generated when REEs and other heavy metals entering or encapsulated by organic particles in different forms chelate with organic matters to produce sulfides [36]. These REEs can only be released under strong oxidizing conditions.

Data in Table 2 show that the content of REEs bound to organic matters ranges from 211.70 ppm to 418.60 ppm, with an average of 315.99 ppm. This state of REEs accounts for 13.68% to 29.09% (average: 18.75%) of the total REE content. The proportion of REEs bound to organic matters far surpasses that of each of the abovementioned three states of REEs. In strong oxidizing conditions, a certain number of REEs can be released. Most of the bound REEs are bound to organic matters. Thus, the organic matter-bound state is an important mode of REE occurrence in the REE-bearing phosphate ore in Xinhua, and it may be related to the presence of a certain quantity of organic matters in this phosphate ore [37].

4.4.5. Residual State

Residual REEs refer to the solid material that remains after each of the six steps in a chemical reaction. Typically, residual REEs are found in stable minerals, both primary and secondary, which exhibit limited reactivity with other substances [35,36].

In the REE-bearing phosphate ore in Xinhua, the content of residual REEs ranges from 999.59 ppm to 1530.49 ppm, with an average of 1316.08 ppm. Residual REEs account for 69.46% to 84.39% (average: 78.07%) of the total REE content. The residual state is considered the most important mode of REE occurrence.

In the polarizing microscope and electron microscope examination, no independent REEs were found, highlighting the strong connection between REEs and phosphorus, as indicated by the SEM-EDS and LA-ICP-MS analyses. This leads us to speculate that residual REEs mainly exist in the form of isomorphic substitutions within the crystal lattice of apatite.

Given the above, the stepwise chemical extraction experiment for quantitative analysis reveals that the majority of REEs occur in the residual state, with only a small portion being bound to organic matter. Therefore, it can be inferred that, in the phosphate rocks in Xinhua, REEs exist primarily in the form of isomorphic substitutions in the lattice defects of apatite, and the organic matter-bound state is the second important mode of REE occurrence.

5. Conclusions

(1) The primary occurrence of REEs in the Zhijin REE-bearing phosphate deposit is predominantly in the form of isomorphism, wherein they replace Ca^{2+} ions within the crystal structure of apatite and then occur in the apatite lattice defects. Additionally, a significant portion of REEs is bound to organic matter, which represents the second important mode of occurrence for these elements.

(2) At the microscale, there is a considerable overlap between the distributions of REEs and phosphorus in the ore. Primarily, these elements are concentrated within bioclasts, sand debris, agglomerates, and phosphate cement, which consist of collophanite and apatite. Additionally, they can be found along the edges of nondolomitized sand debris. However, the abundance of REEs in sparry dolomitic cement, siliceous cement, and the edges of dolomitized sand debris experiences a sharp decrease.

(3) The content of rare earth is greatly different between the edge of sand debris without dolomite and the edge of dolomite sand debris, indicating that dolomite is not conducive to rare-earth enrichment during diagenesis.

(4) Bioclasts, particularly within organisms, exhibit a notable enrichment of REEs and phosphorus. Speculation suggests that the reason behind this phenomenon may be linked to the decomposition of biological death software, as well as the high content of REEs in the original soft tissue. It is believed that the apatite, which carries a high concentration of REEs, undergoes preferential differentiation and fills the biological cavities due to the washing and winnowing action of waves and tides. Furthermore, the enrichment of REEs

in shell walls can be attributed to small shelly organisms actively absorbing phosphorus during life activities to build shell walls.

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